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DETERGENT COMPOSITION

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11 Claims. (Cl. 252-117)

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This invention relates to a method of producing improved detergents and detergent mixtures, particularly of the type adapted for use in the presence of hard water or other aqueous media containing polyvalent metal ions such as calcium and magnesium ions which react with soluble soaps to precipitate insoluble soaps. More particularly it is concerned with detergents including a reagent possessing superior sudsing and purging properties to ordinary soaps and adapted to inhibit insoluble soap precipitation in aqueous media when combined with various known detergents and detergent mixtures. Typical examples of detergents contemplated by the invention are various types of ordinary bar soaps, soap powders, cleansers, rinse waters, and special laundering agents.

The usual soluble detergent soaps such as the sodium or potassium soaps of fatty acids are known to react with various metal salts present in hard water, particularly calcium and magnesium salts, to produce insoluble soaps which precipitate and form scum upon the surface of the water. While calcium and magnesium salts are most often present in hard water, salts of other metals such as barium, cadmium, copper, zinc, and the like, also form such insoluble precipitates. These reactions not only decompose a substantial amount of the detergent soap thus destroying its useful properties, but also suppress the foaming or production of suds by the remaining alkali metal or other detergent soap. Relatively large amounts of soluble soaps still present after reaction with the polyvalent metal salts tend to maintain the precipitated insoluble soap in suspension, but upon dilution of the soap solution, for example in rinsing fabrics, the insoluble soaps deposit upon and adhere to the fabrics. Furthermore, rinsing of fabrics, impregnated with a soluble soap solution, in hard water causes insoluble soaps to be formed and deposited within the interstices of the fabric frequently along with the absorption or inclusion of dirt.

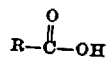
In accordance with the present invention acylated dialkylolamines, which prevent the deposition of the characteristic insoluble soap curd or the formation of scum due to such curd and definitely inhibit the precipitation of the insoluble soap are incorporated in soluble soaps and

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render the calcium and magnesium or other polyvalent metal salts relatively innocuous when present in a washing mixture containing soluble soap. The agents of the present invention effectively prevent the deposition of such insoluble soaps even during rinsing with hard water of fabrics impregnated with soluble soap solutions. Furthermore, by virtue of their sudsing and purging properties, the agents are particularly useful as substitutes for soap constituents ordinarily employed in special detergents, for example, cleansers, wherein they function effectively in the presence of hard water salts whereas the usual soap is inactivated by precipitation. The preferred soap product of the present invention contains a reaction product obtained by reacting secondary alkylolamines with certain carboxylic acids under conditions controlled to cause the carboxylic acid to replace a single reactive acylatable hydrogen atom such as an amino hydrogen or an alcoholic hydroxyl hydrogen.

Heretofore, various methods have been proposed for the manufacture of condensation products of alkylolamines and carboxylic acids and it has been recognized that such products have utility as dispersing and emulsifying agents. Examples of such prior practice are found in the Wolf Kritchevsky Patent 2,089,212 of August 10, 1937, and Reissue Patent 21,530 of August 13, 1940. The known processes for condensing alkylolamines with carboxylic acid, as exemplified in the Kritchevsky patents, result in reaction products predominating in multi-acylated derivatives of the particular alkylolamine employed. It has been found, however, that such prior methods form products which are substantially without activity for purposes of the present invention.

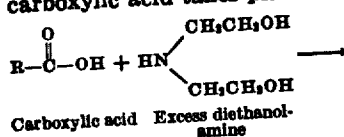
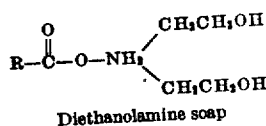
We have found that a number of reaction products are produced on heating the initial soap at high temperature which is formed by the reaction of carboxylic acids and dialkylolamine; for example, the following equilibrium of reaction products results from the reaction of a carboxylic acid having the general formula of



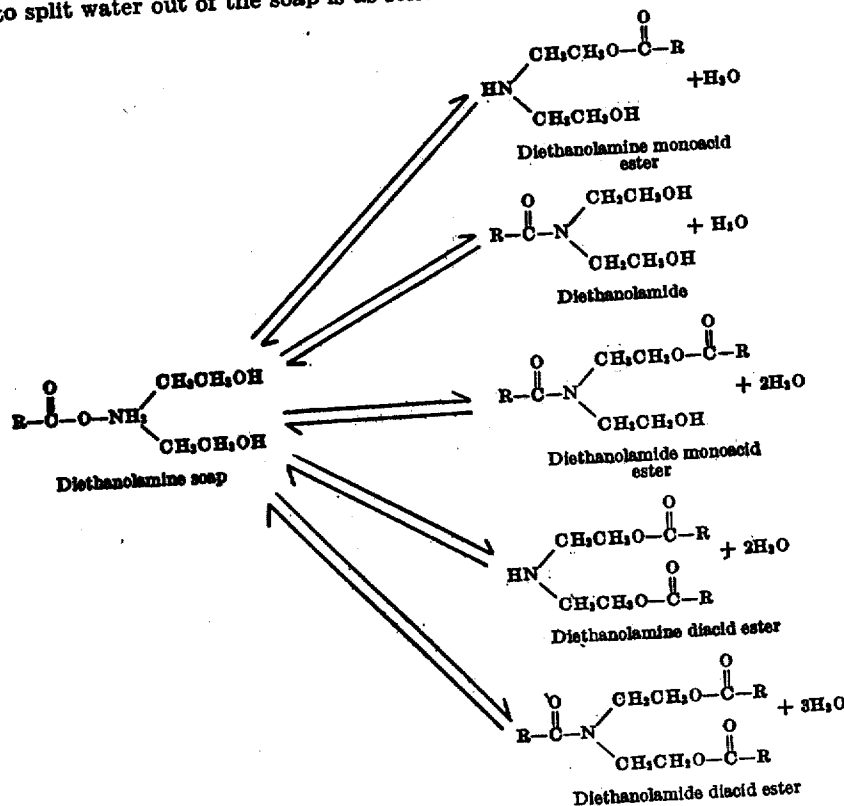
where R is preferably an alkyl group having from

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7 to 13 carbon atoms to the molecule, and diethanolamine:

The neutralization of the diethanolamine with carboxylic acid takes place upon mixing



The equilibrium which occurs on heating this product at temperatures of from 120° C. to 250° C. to split water out of the soap is as follows:



The rate at which the condensation reaction proceeds is a function of the temperature employed and when the reaction conditions are maintained for a sufficient time period with the removal of water of condensation, the soap addition product of dialkylolamine and carboxylic acid is substantially eliminated from the reaction mixture. For purposes of the present invention, condensation is considered to be substantially complete when the dialkylolamine soap content is reduced to about 10% or less by weight of the reaction mixture but ordinarily, is reduced to below 2% thereof. When a triglyceride fat or other compound involving a substitution reaction is employed as the source of the acylating material, the dialkylolamine soap is not formed but an equilibrium mixture of the acylated dialkylolamine compounds likewise occurs containing substantial amounts of the multi-acylated derivatives. The equilibrium mixture, however, resulting from initial condensation at elevated temperatures, is not found to impart any improvement to detergent action in the presence of the

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polyvalent metal ions of hard water. We have discovered that a decided change in inhibiting action occurs when the product resulting from initial condensation of a dialkylolamine and an acylating material is heat treated or aged at a lower temperature producing a reaction mixture having remarkable properties when combined with detergents in enhancing detergent action and preventing precipitation of insoluble soaps in the presence of the polyvalent metal ions of hard water. Moreover, it has been found that the prolonged heat treatment at lower temperatures in the presence of an excess of the dialkylolamine apparently shifts the equilibrium in the reaction mixture to the formation of a predominating quantity of dialkylolamine compounds having one acylatable hydrogen replaced by a carboxyl group; i. e., the dialkylolamide and dialkylol-

amine monoacid ester. These materials have been found to have remarkable inhibiting powers, whereas the di- and tri-substituted derivatives are believed to be without action and mere diluents for the active constituents. The conditions which are maintained during the aging period depend, to a large extent, upon the conditions maintained during the initial heating stage. Thus, for example, condensation at the higher temperatures is found to form greater percentages of dialkylolamide esters and consequently, longer aging periods are required to convert these materials into the mono-substituted derivatives found to be active for the purpose of this invention. Although the undesirable compounds are present in smaller amount at the lower temperatures, the time periods required for accomplishing the initial condensation are prohibitive.

A primary object of the invention is to provide an improved detergent containing an agent which improves detergent action and prevents or inhibits the precipitation of insoluble soaps in the presence of polyvalent metal ions. Another ob-

ject is to provide an improved soap product in which reaction products of dialkylolamines and certain acylating materials are added to a soluble soap to prevent the deposition of insoluble soaps when the product is employed with hard water. Another object of the invention is to provide an improved agent which can be employed with detergent compositions to prevent the deposition of insoluble precipitates therefrom. Another object is to provide a reagent having improved cleanser action. A further object of the invention is to provide a method of making a soap product containing an agent capable of effectively preventing the precipitation of insoluble soaps. Another object is to provide a method of making an improved agent for preventing the precipitation of insoluble soaps when soluble soaps are brought into contact with hard water. A still further and important object is the manufacture of improved agents by condensation of dialkylolamines and certain acylating materials under conditions controlled to produce predominating amounts of compounds having the effect of preventing precipitation of insoluble soaps from solutions. An additional object is the conditioning of reaction products resulting from the condensation of alkylolamines and higher fatty acids at temperatures designed to suitably shift the equilibrium for the recovery of optimum quantities of the desired products for use with detergents. Another object is to provide improved rinse water.

More particularly, in accordance with the present invention, improved detergents are manufactured which include the reaction product of a dialkylolamine with an acylating material in a two stage process under reacting conditions controlled to produce a product predominating in monosubstituted acid derivatives of the dialkylolamine. The time of the initial reaction may be governed by the specific reactions selected, the temperature employed, and is preferably carried out in an excess of dialkylolamine. The initial stage of the process comprises the reaction of dialkylolamine and an acylating material at a temperature sufficiently high to cause substantial condensation of said reactants, followed by treatment of the reaction mixture in the presence of excess dialkylolamine at a lower temperature for a sufficient time to shift the equilibrium to form compounds having the desired inhibiting action. As a general rule, where a carboxylic acid is employed as the acylating material, it is preferred to carry out the initial phase of the reaction at a sufficiently elevated temperature to reduce the dialkylolamine-fatty acid soap to about 10% or less by weight of the reaction mixture. Alternatively, the reaction may be carried out until about 1 mol of water is removed from the reaction mixture for each mol of acid employed, or until the amount of dialkylolamine reacted determined by titration corresponds with the triglyceride fat employed, followed by reaction at a lower temperature to shift the equilibrium of the resulting mixture of compounds to the formation of predominating quantities of monosubstituted derivatives. The latter compounds are themselves in equilibrium in the reaction mixture. Preferably, following the initial heating stage, the dialkylolamine-fatty acid soap content is adjusted to from approximately 3 to 15 per cent by weight of the reaction product, for example, by the addition of the required amount of higher fatty acid. Alternatively, the reaction temperature may be reduced somewhat prior to the point of soap elimination,

so as to provide the desired soap concentration prior to heating at the lower temperature. The presence of small percentages of soap is found to accelerate the aging process, and where a triglyceride fat provides the source of acylating material, soap is preferably added after the initial stage of reaction, as by the addition of carboxylic acid followed by treatment at the lower temperature. The reaction product resulting from the process is then incorporated preferably as such into a detergent or soap composition wherein it functions to prevent the precipitation of insoluble soap in the presence of calcium and magnesium salts.

The initial heating stage for performing the soap decomposition may be carried out at temperatures of from 120° C. to 250° C. for a period of from 15 minutes to 16 hours in the presence of a substantial excess of a dialkylolamine, followed by the incorporation of additional dialkylolamine when the reaction has proceeded to the desired stage. Reaction at the higher temperature is sufficient in the smaller time period. It is considered to be essential that an excess of dialkylolamine be maintained during the second stage of the reaction to accomplish the desired shift in equilibrium. Successful results have been obtained with ratios of 1½ mols of the amine to 1 mol of carboxylic acid and also with ratios of 10 mols of amine to 1 mol of acid. The preferred lower limit of ratios of amine to acid, however, is approximately 1¾ mols of dialkylolamine to 1 mol of carboxylic acid. Any molar excess of amine tends to shift the reaction in the desired direction but mol to mol ratios are unsatisfactory in the final reaction stage since amide esters result comprising 40 per cent and up of the resulting product. At a molar ratio of approximately 1½ of amine to 1 of acid, the amount of amide ester is reduced to a small quantity. Since the dialkylolamine itself is not effective in preventing the precipitation of insoluble soaps, there is an upper practical limit to the molar excess of the dialkylolamine, although the presence of the excess dialkylolamine is not deleterious in the composition and tends to maintain a favorable equilibrium in the soap solution. Thus, in most cases, three mols of the dialkylolamine to 1 mol of carboxylic acid is sufficient to substantially inhibit the formation of compounds having more than one active acylatable hydrogen replaced by a carboxylic acid radical when the reaction conditions are properly controlled.

Since the formation of the dialkylolamide or dialkylolamine acid ester requires the splitting out of water, it is preferred to carry on the reaction under vacuum conditions to provide for evaporation of the water at relatively low temperatures. Although the reaction under vacuum can be run at temperatures ranging from 120° to 250°, the boiling point or vapor pressure of the amine is a limiting factor. The rate at which water is removed is controlled by its vapor pressure and the rate at which it is liberated, both a function of the temperature. The initial stage of the reaction has proceeded to the proper point when a quantity of water is liberated substantially equivalent to the molar quantity of carboxylic acid employed. In order to prevent complicated secondary reactions as well as the loss of dialkylolamine, it is preferable to employ temperatures not above 170° C. At 250° C. secondary dehydration and decomposition takes place to form not only amide esters but even morpholine compounds, which compounds are

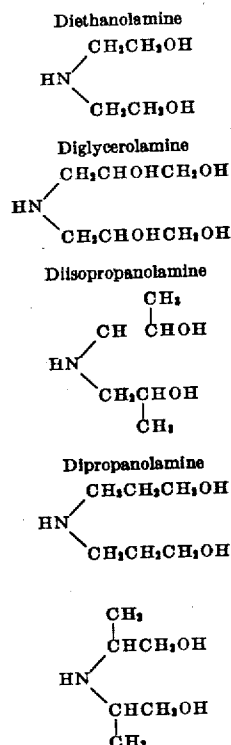
not active for the purpose of the present invention. Furthermore, the equilibrium shifts with the temperature and the equilibrium at 260° is not conducive to producing the desired compounds. Very low temperatures are not practical because of the period of time, which may extend to days, required to carry the reaction to the desired extent. Thus, temperatures much below 100° C. result in very slow reactions which may require days to bring to the desired point. We have found that temperatures of 140° to 160° C. enable the reaction to be completed to the desired extent in a relatively short period of time and also to inhibit the formation of undesired compounds. At these temperatures, 2 to 4 hours is usually sufficient to properly reduce the soap content in the reaction mixture. As soon as about 1 mol of water for each mol of mono-basic acid has been removed, the reaction has been carried to the desired point. It is desirable to stop the vacuum and heating when the proper amount of water has split out, otherwise some of the excess amine tends to volatilize. Any amine lost cannot, of course, assist in shifting the equilibrium in the proper direction to inhibit formation of compounds having more than one reactive acylatable hydrogen substituted.

The initial heating stage above described produces a composition which may contain some dialkylolamide and dialkylolamine monoacid esters, but also contains substantial amounts of dialkylolamide acid esters and possibly dialkylolamine diester, particularly if a relatively low molar excess of alkylolamine to carboxylic acid is employed when the reaction is continued past the stage of soap reduction in accordance with this invention. A large proportion of the amide esters can be reconverted into the amide by reaction with excess amine and this product then converts into the amine monoacid ester until an equilibrium between the two compounds is reached. The most desirable equilibrium exists in the range of temperatures from 40° to 90° C. At these temperatures, aging periods of from 4 to 100 hours may be employed. Use of temperatures above this range may be used, but tend to promote secondary reactions. The time of aging, however, is a function of the temperature and decreases with increase of temperature. The lower the temperature, however, the less the amount of the amide monoacid ester which remains and the greater the potency of the mixture. The time of aging likewise depends on the temperature employed in the condensation reaction, since higher temperatures increase the formation of the di- and tri-substituted derivatives which require a longer aging period for conversion. The aging is carried out at lower temperatures than those employed during condensation in order to accomplish the desired conversion. A range of temperatures between 50° C. and 80° C. is preferred during the aging process since at these temperatures the reaction is relatively rapid and the amide esters are largely converted into the active compounds for the purpose of the invention. At the above temperature, 24 to 48 hours may be required. However, 10 hours is usually sufficient to reach substantial equilibrium, resulting in a satisfactory product. A longer period of time, for example, 70 to 100 hours, in some cases produces a product having somewhat greater potency. The presence of amino soap tends to promote or catalyze the aging reaction and it is, therefore, advantageous to add an additional amount of carboxylic

acid after the main reaction treatment and before the aging treatment. Thus, it has been found that the addition of enough free carboxylic acid at the beginning of the aging to form dialkylolamine soap equal to approximately 3 to 15 per cent of the mixture causes the aging process to go forward at a more rapid rate and an insoluble soap precipitating inhibitor of a given potency is produced. The latter procedure is generally preferred although, in some cases, the temperature may simply be lowered when the desired soap content is reached. The resulting reaction products are soluble or dispersible in water and form the soap improving agents of the present invention.

When a triglyceride fat or other material is employed as the source of acylating material, conditions may vary somewhat depending upon the particular compounds employed and the results desired. In the case of a triglyceride fat, the proportions of dialkylolamine and triglyceride fat employed are calculated on the basis of the fatty acid group content of the fat.

The preferred agents of the present invention are prepared by reacting secondary alkylolamines with carboxylic acids containing no less than 8 nor more than 14 carbon atoms within their molecule. Examples of suitable secondary alkylolamines are as follows:



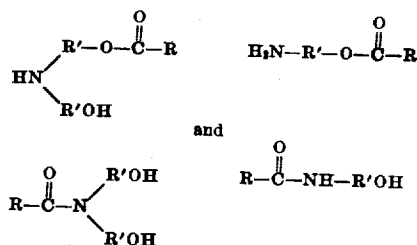
Examples of carboxylic acids which have been found particularly suitable for reaction with the secondary alkylolamines are as follows:

Lauric acid, $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
 Capric, $\text{CH}_3(\text{CH}_2)_8\text{COOH}$
 Caprylic, $\text{CH}_3(\text{CH}_2)_6\text{COOH}$
 Myristic acid, $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$

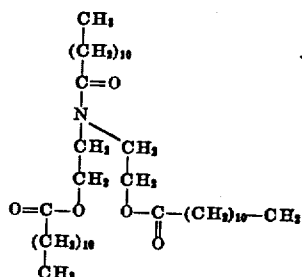
The above lists of suitable secondary alkylolamines and carboxylic acids are given merely by way of example and are not intended to be complete as other secondary alkylolamines and carboxylic acids can be employed. Reaction prod-

ucts with carboxylic acids having less than 8 or more than 14 atoms within their molecules are not as active for the purposes of the present invention, carboxylic acids having 12 carbon atoms or a number of carbon atoms close to 12 forming the most active reaction products. Thus, lauric acid is the preferred acid of the above list. Reaction products with carboxylic acids having more than 14 carbon atoms also tend to become less soluble in water.

During the aging process, predominating quantities of compounds having the following general formulas are apparently formed:



In these formulas R is a carbon containing nucleus having no less than 7 nor more than 13 car-

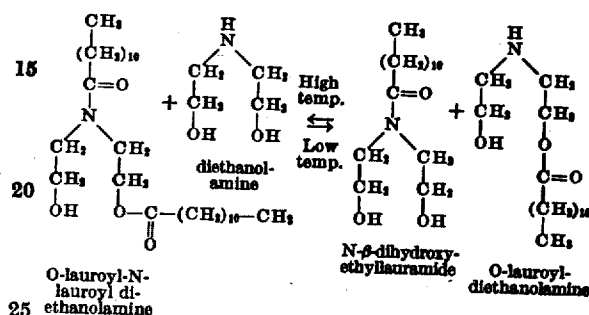


(bis- β -O-lauroylethoxy-N-lauramide)

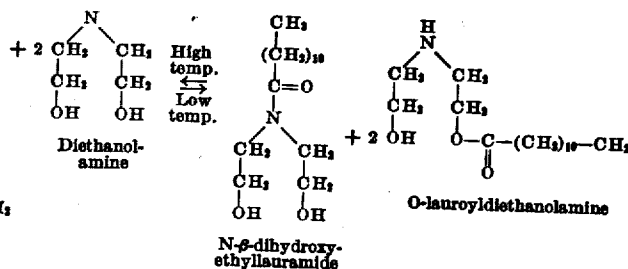
bon atoms and is preferably an alkyl group either saturated or unsaturated such as those derived from fats and oil, but may be a substituted alkyl group, or an aromatic, hydroaromatic, heterocyclic or other carbon containing nucleus. The radical R' is a carbon containing radical linked on one hand to the nitrogen and on the other hand to an oxygen of a hydroxyl or ester group and is preferably an alkyl or a hydroxy alkyl group but may be a substituted alkyl group or other carbon containing radical.

When the mixture resulting from the condensation of dialkylolamine and carboxylic acid is heated in the presence of free dialkylolamine, a shift in equilibrium apparently occurs to form a predominating quantity of dialkylolamine derivatives having a single acylatable hydrogen replaced by a carboxylic group. These compounds predominate in the reaction mixture when they exceed in quantity the di- and tri-substituted dialkylolamine derivatives. At the high temperature and reduced pressure employed in the condensation, the reaction splitting out the most water probably predominates. For example, the initial stage of the reaction between lauric acid and diethanolamine produces predominating quantities of O-lauroyl-N-lauroyl diethanolamine and (bis- β -O-lauroylethoxy)-N-lauramide. These substances are ineffective in detergents

and, in fact, insoluble in water, therefore, their formation must be suppressed. This is accomplished by heating or aging, preferably at a lower temperature, where conditions are found to promote the formation of active compounds such as N- β -dihydroxy-ethyl-lauramide. The overall chemical reaction during secondary heating or aging period is probably as follows in the case of the condensation product of diethanolamine and lauric acid:



and



It is noted that during the heating period at relatively low temperatures, the di- and tri-substituted derivatives of diethanolamine react with free diethanolamine to form the monosubstituted derivatives.

The following examples illustrate the method of manufacturing the improved detergents of the present invention:

Example 1.—One mol of molten lauric acid (200 g.) is mixed with three mols (315 g.) of diethanolamine with constant stirring. The heat of neutralization is sufficient to keep the diethanolamine laurate soap liquid. Heat is then applied and the temperature raised from 150° C. to 170° C. A short air condenser permits the water produced to escape, but retains any volatilized diethanolamine. Heating is continued under vacuum until approximately one mol of water is liberated in the reaction for every mol of acid employed, at which point the soap content has fallen to about 2% or less. This usually requires about 4 hours. Sufficient melted lauric acid is then added with stirring after the temperature has dropped to 70° C. to raise the soap content to 10%. The temperature is then lowered to about 60° C. and the heating continued for a period of about 24 hours. Fifteen parts of the resulting product are gradually worked into a hard soap while in a melted or softened condi-

tion until a homogeneous and uniform mixture results. The soap is then molded or framed and allowed to cool, following which it is cut into bars.

Example 2.—One mol (200 g.) of molten lauric acid is mixed with three mols (315 g.) of diethanolamine. The heat of neutralization is sufficient to maintain the diethanolamine laurate soap a liquid. The material is then heated at 140° C. under a reduced pressure of about 25 to 50 mm. of mercury, until roughly one mol of water is liberated for each mol of acid employed and a soap content of about 2% is reached. This will take ordinarily about 4 hours. After the temperature has dropped to 70° C. sufficient molten lauric acid is added to bring the soap concentration up to 10% and the heating continued at 60° C. for a period of 48 hours. A soap of medium hardness is prepared by incorporating 8 parts of the reaction product into 92 parts of a melted soap of medium hardness. The product is well homogenized, cooled and molded.

Example 3.—One mol of coconut oil fatty acids (209 g.) is mixed with 3 mols (315 g.) of diethanolamine. The melted soap and excess amine is then heated at 150° to 160° C. under reduced pressure (50 mm. of mercury) for 4 hours. At the end of this time, approximately one mol of water has been removed for each mol of acid employed and the mixture is cooled to 70° C. Sufficient coconut oil fatty acids are thereupon added to raise the soap content to 10% and the product is then aged for 36 hours at 60° C. A soft soap is prepared by embodying 5 parts of the active reagent into 95 parts of melted soft soap. The mixture is agitated and molded into suitable shapes.

Example 4.—One mol of molten lauric acid (200 g.) and 1½ mols (184 g.) of diethanolamine are mixed with constant stirring until the heat of reaction liquifies the diethanolamine laurate soap formed, and, in this condition, it is heated under reduced pressure with a minimum of foaming at a temperature of from 150° to 160° C. at 50 mm. of mercury pressure until roughly an equivalent amount of water is removed for each mol of acid employed. After approximately 4 hours, the reaction is complete and the material is cooled to 70° C. and sufficient molten lauric acid is added to bring the soap content up to about 10%. The product is then aged at 60° C. for a period of 48 hours.

Example 5.—One mol of coconut oil (665 g.) is mixed with 9 mols (945 g.) of diethanolamine. The two substances form two layers with the coconut oil on top and heat is gradually applied after the pressure is reduced to 25 mm. of mercury. After approximately 2 hours, the two layers merge and form a homogeneous solution. The product is then further heated for about 45 minutes to complete the reaction. The product is then deodorized and treated with sufficient lauric acid to produce a soap content of 10%. Alternatively, in the absence of deodorization, the product is cooled under vacuum to 70° C. and the proper amount of lauric acid or coconut oil fatty acids is added. The product is then aged for 30 hours. A soft soap is prepared by embodying 5 parts of the agent into 95 parts of melted soft soap. After homogenizing, the mixture is molded in suitable shapes.

A suitable soap, the action of which is improved in accordance with the invention, may consist of a mixture of about 10 parts of the saponifica-

tion products of coconut oil with about 90 parts of the saponification products of tallow. The saponification products of coconut oil are a mixture of fatty acid soaps comprising sodium laurate, sodium myristate, and sodium caprylate, whereas the saponification products of tallow are mainly sodium palmitates, stearates, and oleates. The hardness of the resulting soap is determined by the final moisture content. A comparatively hard soap ordinarily contains from 12 to 14 per cent moisture, a medium soap from 15 to 20 per cent moisture and a relatively soft soap from 30 to 35 per cent moisture. Although the foregoing is given as illustrative of a common type of soap, it is to be understood that the present agents are applicable to any soap whatsoever which tends to form a precipitate in the presence of the polyvalent metal ions of hard water.

When amounts between approximately 5 and 10 per cent of the inhibiting agent prepared as described in the above examples, are added to water soluble soap, it has been found that insoluble soaps are not deposited in fabrics or upon surfaces being cleaned and no scum is formed when the resulting soap is added to hard water or other aqueous media containing calcium, magnesium or other polyvalent metal salts. In some cases, upon long standing, a gradual precipitation of the insoluble soap occurs to form a flocculent mass. This flocculent mass, however, is not of the characteristic insoluble soap curd type, but is in a form which is readily redispersible upon mild agitation, and does not produce a scum or a ring around the container at the surface of the liquid. Furthermore, it is not of the type which adheres to and is deposited in fabrics or upon surfaces being washed or rinsed. The redispersed insoluble soap will remain in suspension for some time after agitation. The improving agents of the present invention do not depress foaming or inhibit the production of suds in the presence of calcium and magnesium or other polyvalent metal soaps but promote foaming or sudsing. No scum or adherent insoluble soap deposits are formed even upon excessive dilution of the soluble soap solution with hard water.

The amount of improving agent which is employed in various soaps may vary within a wide range depending upon the kind and quantity of soap, the particular properties of the individual improving agent and the hardness of the water against which protection is to be afforded. For the usual hard waters encountered, 5 to 10% of improving agent on the basis of the soap is entirely adequate. For extremely hard waters, the proportion of improving agent may be increased; for example, up to 50%, but for most purposes, 5 to 10% of the improving agent is sufficient to prevent deposition of the insoluble soap upon fabrics or the formation of a scum upon the surface of the water.

The improving agent or reaction products may be embodied in the soap in any desired way, since it is the presence of the improving agent rather than the manner of incorporating the same into the soap which is effective. Thus, the improving agent may be added to the soap at substantially any time after the soap has been formed and purified. For bar soaps, it may be incorporated into the soap mixture during plasticizing or plodding or may be incorporated into the kettle or neet soap. The same procedure may be employed when producing soap chips, soap flakes,

powdered soap products, spray dried soap and the like.

There is a minimum concentration of the improving agent which must be present in hard water to which soap is to be added in order to inhibit completely the precipitation of insoluble soaps. If the improving agent is added to the hard water prior to the soap, levels of from 0.1 to 0.001% based on the weight of water are sufficient. If added to the soap, the level is much higher, based upon the weight of soap; for example, 5, 10, 20, or even 50%, depending upon the softness desired in the final product. By the same token, our improving agent as added to soap which is rinsed off the washed material by infinite dilution can be incorporated at lower levels than in more conventional home methods of washing. For example, a washing machine charged with clothes, water, and soap containing 5 or 10% improving agent can be rinsed by continued dilution and draining without formation of scum or soap curd. If, on the other hand, the washed clothes are removed, wrung and placed in the rinse, a higher level of improving agent is required. This is necessary because the rinse water must have the improving agent at a certain level in the vicinity of the soap as it strikes the hard water. To insure such a condition, a higher level of the agent in the soap is required in home washing machines than in commercial machines which rinse by dilution. Newer types of home machines work on the commercial basis and hence require less improving agent than wringer type machines that rinse separately after laundering.

Particular application for the improved agent is found in the cleanser field. The ordinary cleanser may consist of a mixture of abrasives such as volcanic ash and silica with about 3% of soy bean foots soap and some alkali. The addition of from a quarter of 1% up to 2% in place of or in conjunction with the ordinary soap has been found to impart marked improvement to the ordinary cleanser. The agent may be sprayed into the abrasive so as to wet the individual particle surfaces. Among the advantages derived from use of the agent in connection with a cleanser resides in the fact that dust is eliminated, primarily because of the oily physical characteristics of the improving agent. Likewise, by virtue of its high sudsing power, it may be substituted for the soap ordinarily employed retaining its properties in the presence of hard water salts whereas the ordinary soap is inactivated. In the case of conventional cleansers containing soap, the sudsing characteristics are considerably impaired because the amount of soap employed is not sufficient to overcome the hardness of the water. Furthermore, and in addition to improvement in sudsing characteristics, the agent imparts a fluffy body to the powdered cleanser, thus reducing outage and simultaneously improving "shaking out" characteristics.

In laundering fabrics or other materials, after the washing step, the fabrics are generally rinsed to remove the soap which adheres to the fabrics. If calcium or magnesium salts or salts of other polyvalent metals are present in the rinse water, insoluble soap is deposited on and around the fibers of the fabric or upon the surfaces as the soap solution is diluted due to the rinsing. The presence of the improving agent of this invention in the soap will prevent this action and, furthermore, it is possible to prevent such deposi-

tion of insoluble soaps by adding a small amount of improving agent directly to the rinse water. Very small amounts, for example, 0.001% to 0.1% of the modifying agent based on the amount of water incorporated in the rinse water gives effective results. In order to obtain best results, the soapy material should be rinsed with water containing the modifying agent rather than attempting to remove deposited insoluble soap as the agent inhibits precipitation of the insoluble soaps much more effectively than it disperses the soap curd after it is once formed. Obviously the present invention is not only applicable to the washing of fabrics but may be employed in washing other materials and articles such as glass, silverware, painted walls, automobiles, and the like.

Likewise, our improving agent is particularly desirable as an ingredient in dusty soap products since its soft, oily body effectively renders the product dustless. This is an outstanding improvement in the art because paraffin oil and other materials ordinarily used for killing dust in soaps depress sudsings through defoamer action. In accordance with this invention, dust may be effectively killed and hard water performance simultaneously improved. This application is a continuation-in-part of our copending application, Serial No. 396,202, filed May 31, 1941, now abandoned.

The term "acylating substance" as used in the claims is intended to mean any substance capable of the formation or introduction of an acyl radical in or into the material to be acylated. Such acylating substances include carboxylic acids and triglyceride fats.

While we have disclosed the preferred embodiments of our invention, it is understood that the details thereof may be varied within the scope of the following claims.

We claim:

1. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a higher fatty acid acylating group having from about 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanolamine with a higher fatty acid acylating substance having fatty acid groups of about 8 to 14 carbon atoms at a temperature of between about 120° and 250° C. for a period of between about 15 minutes and 16 hours so that the diethanolamine-carboxylic acid soap content is reduced below about 10 per cent, then aging the reaction mixture in the presence of a substantial amount of free diethanolamine at a temperature of about 40° C. to 90° C. for a period of between 4 and 100 hours to produce acylated carbons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature, whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

2. A detergent composition consisting essentially of a fatty acid detergent soap normally

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tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a higher fatty acid acylating group having from about 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanolamine with a higher fatty acid acylating substance having fatty acid groups of about 8 to 14 carbon atoms at a temperature of between about 140° C. and 160° C. for a period of between about 2 to 4 hours so that the diethanolamine-carboxylic acid soap content is reduced below about 10 per cent, then aging the reaction mixture in the presence of a substantial amount of free diethanolamine at a temperature of about 50° C. to 80° C. for a period of about 24 to 48 hours to produce acylated carbons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

3. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a higher fatty acid acylating group having from about 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanolamine with a higher fatty acid acylating substance having fatty acid groups of about 8 to 14 carbon atoms at a temperature of between about 120° C. and 250° C. for a period of between about 15 minutes and 16 hours, adjusting the diethanolamine soap content to about 3 to 15 per cent by adding a higher fatty carboxylic acid to the reaction mixture, and aging the resulting mixture in the presence of a substantial amount of free diethanolamine at a temperature of about 40° C. to 90° C. for a period of between 4 and 100 hours to produce acylated carbons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

4. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a higher fatty acid acylating group having from about 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanol-

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amine with a triglyceridic ester of a carboxylic acid, said acid having from about 8 to 14 carbon atoms, at a temperature of between about 120° C. and 250° C. for a period of between about 15 minutes and 16 hours, adjusting the diethanolamine soap content to about 3 to 15 per cent by adding a higher fatty carboxylic acid to the reaction mixture, and aging the resulting mixture in the presence of a substantial amount of free diethanolamine at a temperature of about 40° C. to 90° C. for a period of between 4 and 100 hours to produce acylated carbons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

5. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a higher fatty acid acylating group having from about 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanolamine with a triglyceridic ester of a carboxylic acid, said acid having about 8 to 14 carbon atoms per molecule, at a temperature of between about 140° C. and 160° C. for a period of about 2 to 4 hours, adjusting the diethanolamine soap content to between about 3 to 15 per cent by adding a higher fatty carboxylic acid to the reaction mixture, and aging the resulting mixture at a temperature of about 50° C. to 80° C. for a period of about 24 to 48 hours to produce acylated carbons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

6. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a higher fatty acid group having from about 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanolamine with a carboxylic acid having about 8 to 14 carbon atoms per molecule at a temperature of between about 120° C. and 250° C. for a period of between 15 minutes and 16 hours so that said diethanolamine-carboxylic acid soap content is reduced to below about 10 per cent, and aging the reaction mixture in the presence of a substantial amount of free diethanolamine at a temperature of about 40° C. to 90° C. for a period of between about 4 to 100 hours to produce acylated carbons having a predominance of compounds with a single acyl-

atable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

7. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a higher fatty acid group having from about 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanolamine with a carboxylic acid having about 8 to 14 carbon atoms per molecule at a temperature of between about 120° C. and 250° C. for a period of about 15 minutes to 16 hours, adjusting the diethanolamine-carboxylic acid soap content to between about 3 to 15 per cent by adding a higher fatty carboxylic acid to the reaction mixture, and aging the resulting mixture by maintaining at a temperature of between about 40° C. and 90° C. for a period of about 4 to 100 hours to produce acylated carbons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

8. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a higher fatty acid group having from about 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanolamine with a carboxylic acid having about 8 to 14 carbon atoms per molecule at a temperature of between about 140° C. and 160° C. for a period of about 2 to 4 hours to reduce the diethanolamine soap content below about 10 per cent, and aging the resulting product at a temperature of between about 50° C. and 80° C. for a period of about 24 to 48 hours to produce acylated carbons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

9. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a pre-

dominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a higher fatty acid group having from approximately 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanolamine with a carboxylic acid having approximately 8 to 14 carbon atoms per molecule at a temperature of between approximately 140° C. to 160° C. for a period of about 2 to 4 hours, adjusting the diethanolamine soap content to between approximately 3 to 15 per cent by adding a higher fatty carboxylic acid to the reaction mixture, and aging the resulting mixture at a temperature of about 50° C. to 80° C. for a period of about 24 to 48 hours to produce acylated carbons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

10. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a lauric acid acylating group having from about 8 to 14 carbon atoms, said condensation product being obtained by reacting an excess of diethanolamine with lauric acid at a temperature of between about 120° C. and 250° C. for a period of between about 15 minutes and 16 hours so that said diethanolamine-lauric acid soap content is reduced below about 10 per cent, and aging the reaction mixture in the presence of a substantial amount of free diethanolamine at a temperature of between about 40° C. and 90° C. for a period of about 4 to 100 hours to produce acylated carbons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

11. A detergent composition consisting essentially of a fatty acid detergent soap normally tending to form an insoluble precipitate in hard water and between about 5 and 50 per cent based on the weight of the said soap of an acylated diethanolamine condensation product having a predominant proportion of the diethanolamine product with a single replaceable hydrogen of the diethanolamine substituted with a lauric acid acylating group having from about 8 to 14 carbon atoms, said condensation product obtained by reacting an excess of diethanolamine with lauric acid at a temperature of between about 140° C. and 160° C. for a period of about 2 to 4 hours, adjusting the soap content to between about 3 to 15 per cent by the addition of a higher fatty carboxylic acid to the reaction mixture, and aging the resulting mixture at a temperature of between about 50° C. and 80° C. for a period of between 24 and 48 hours to produce acylated car-

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bons having a predominance of compounds with a single acylatable hydrogen atom replaced by the fatty acid acyl group, the duration of each of said periods of heating varying within the specified range inversely with the temperature; whereby the resulting product has the property of inhibiting the precipitation from aqueous solutions of insoluble compounds of fatty acid detergent soap and the polyvalent ions of hard water.

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