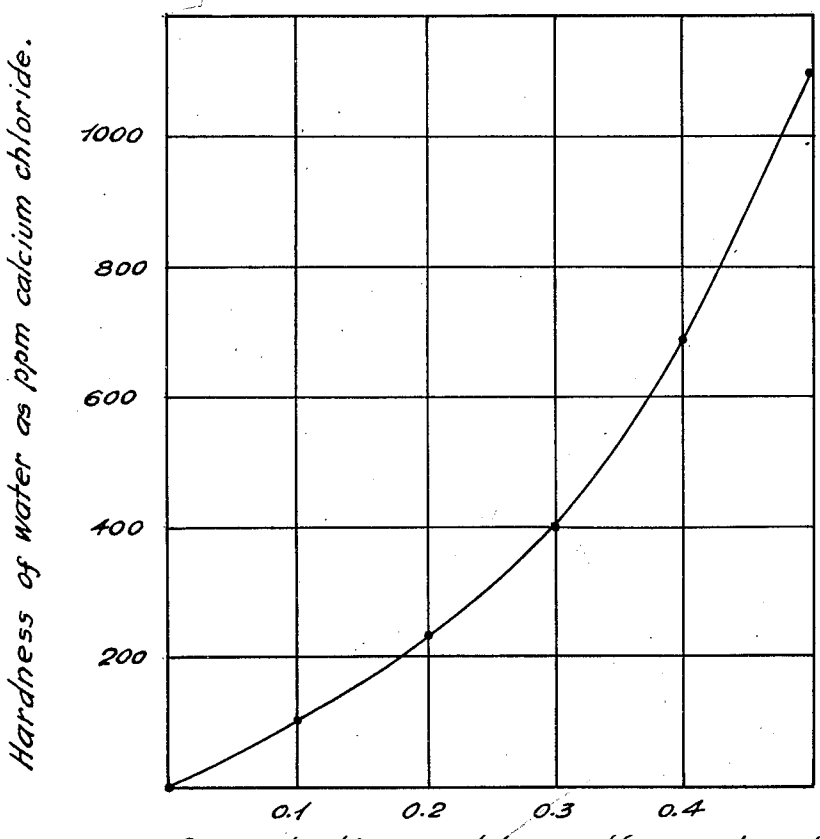
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SAPONACEOUS DETERGENT HAVING IMPROVED HARD-WATER CHARACTERISTICS

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Detergent prepared as in example 1.



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SAPONACEOUS DETERGENT HAVING IMPROVED HARD-WATER CHARACTERISTICS

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This invention relates to a saponaceous detergent in solid form and the method of combining the constituents therefor, which detergent is capable of softening hard water. This invention also relates to products moulded in the shape of conventional bar soap, but which unlike such soaps can be satisfactorily used in hard waters or sea water without significant reduction in detergent action, sudsing, and without the formation of undesirable scums and precipitates.

It has previously been proposed to incorporate such inorganic materials as the ortho-, pyrophosphates, poly- and hexametaphosphates with the alkali metal soaps to prevent calcium and magnesium ions in hard water from reacting with the alkali metal soaps precipitating insoluble soaps. But because of the large amount of said phosphates necessary to soften the water such composite hard water soaps are grainy in appearance and have an undesirable gritty feel.

It has been proposed to overcome the well-known shortcomings of common soap in hard water and sea water by mixing with it certain synthetic detergents or dispersing agents. Laboratory tests and actual usage have shown that most of these additions are not entirely satifactory. In some cases the color and general appearance of the composite bar soaps are particularly unattractive. In other cases, the cleansing properties are not sufficiently superior to those of common alkali soap to justify the added cost. Very often, in fact, the sudsing properties are seriously impaired. Moreover, the synthetic detergents may be crystalline and/or contain inorganic salts; when incorporated into common bar soap, these detergents produce a grainy soap of non-uniform structure. Some such combinations are occasionally difficult to dissolve except in hot water. Other combinations tend to become slimy after short use. Products containing filling agents which do not disperse like starch, produce objectionable surface scums. Over a period of time in use these composite bar soaps tend to crack and disintegrate because of the uneven rate of solution of the ingredients.

It is an object of our invention to produce bar soaps consisting primarily of ordinary soaps, but containing other constituents, combined in such proportions and processed in such a manner that the resulting product has none of the disadvantages hereinbefore described.

Another object of this invention is to make soaps which have the smooth, uniform appearance, feel and general attractiveness of common soap but unlike it form no precipitates in hard

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water or sea water, and possess superior detergent, foaming and rinsing properties in hard water.

A still further object is to produce soaps which are homogeneous in structure, dissolve easily and smoothly, and neither soften unduly, nor crack, nor fall apart in use.

An additional object is to provide aqueous solutions of saponaceous products possessing superior detergent, foaming and rinsing properties in hard water or sea water.

Other objects and advantages of the invention will be apparent by reference to the following specification wherein the details and preferred embodiments of the invention are described.

According to this invention a carboxylic amide of the alkylol amines, and a water-soluble organic nitrogenous base are mixed and heated with a water-soluble soap, which soap forms the major component of these three, or is equal in amount to the amide, and preferably the former. The heating should be in the range of 100° C. to 190° C. for a time period of about 60 minutes to 10 minutes, but preferably in the range of 125° C.–160° C. for a period of 45–15 minutes. It will be understood that with the lower temperatures the time is correspondingly longer; hence at 125° C. the time interval will be substantially 45 minutes, whereas at 160° C. it will be substantially 15 minutes. Mixing does not have to precede the heating but may be simultaneous therewith. It will be understood that mixtures of the amides or mixtures of water-soluble nitrogenous bases or mixtures of water-soluble soaps can be employed instead of a single representative of the three essential components. It will be further understood that this process may be performed stepwise by heating at 125–190° C. for 45 to 15 minutes a mixture of the carboxylic acid alkylol amide containing some free water soluble organic nitrogenous base and a small amount of a soap in which the cation may be an alkali metal, ammonia, or a substituted ammonia compound, and then incorporating this mix by cold crutching, without further heating, into a large amount of water-soluble soap, so that the latter component becomes the major component or equal in amount to the amide, preferably the former.

The products so prepared exhibit remarkable detergent, wetting out, and emulsifying properties. It has been found that mixing any two of the three constituents and omitting the third, then treating the mixture according to the procedures described in detail below, produces inferior products as compared with that product

which contains the three essential constituents heat treated together, namely: the carboxylic acid alkylol amide, the water soluble nitrogenous organic base, and the soap.

It has also been found that the thorough admixture of these three essential ingredients without heating to form a homogeneous mixture, results in a product which is unsuitable for use in hard water, precipitating insoluble calcium and magnesium soaps, and having no detergency. If this same mixture is heated for 30 to 45 minutes at 125° C., a product is obtained which disperses readily and shows excellent detergent properties in 0.25% solution in water containing 200 P. P. M. calcium chloride. A similar product is obtained by the alternate stepwise procedure consisting of heating the carboxylic acid amide with the water soluble nitrogenous base and a small amount of soap for 30 to 45 minutes at 125° C., then cold mixing with a larger amount of soap, so that the soap is now the major component. It should be noted that no change in the composition of the heat treated products as compared with the cold mixture could be detected by such chemical and physico-chemical measurements, such as total acid, index of refraction, hydrogen ion concentration; but the surface active properties of the heat treated compositions are considerably enhanced. This result is unexpected from previous knowledge in the art, in that no chemical change is involved and that the new detergent-active product is the result of a physical transformation. As indicated in the Harry H. Kroll application Serial No. 489,674, filed June 4, 1943, these results can be best explained by the modern theories of viscous liquids.

The amines from which the carboxylic acid amides are derived are the alkylol amines. There is a wide choice of such amines: among these are mono-, and diethanolamine, mono- and dipropanolamine, mono- and di-glycerol amines, mono and di-isopropanol amines, amino ethyl ethanol amine, di-hydroxyethyl ethylene diamine, 2.amino 2.methyl 1:3 propanediol, 2.hydroxy 1:3 diaminopropane. Any suitable combination of one or more of these amines may also be used. The preferred amides are those whose acyl radicals contain 12 to 14 carbon atoms such as N, N.di-hydroxyethyl lauramide and N.hydroxyethyl coconut fatty acid amides.

However, the carboxylic acid nucleus of the amide, and of the soap as well, should contain at least 8 but not over 30 carbon atoms. These will be designated "higher molecular weight carboxy acids," and when derived from fats and oils, "higher fatty acids." They are the detergent forming acids, i. e. those acids which combine with alkalis to produce soap or soap like bodies. The detergent forming acids include naturally occurring fatty acids, resin acids such as abietic acid, naturally occurring petroleum acids such as the naphthenic acids and carboxy acids produced by the oxidation of petroleum. As will be subsequently indicated, there are other acids which have somewhat similar characteristics and are derived from somewhat different sources and are different in structure, but can be included in the broad generic term previously indicated.

Among sources of such acids may be mentioned straight chain and branched chain, saturated and unsaturated, aliphatic, alicyclic, hydroaromatic, and aralkyl carboxylic acids, including caprylic, stearic, palmitic, myristic, oleic, ricinoleic, linoleic lauric, undecylenic acids; mixed higher fatty acids derived from animal or vegetable sources: for example, coconut oil, palm kernel oil, rapeseed oil, sesame oil, palm oil, olive oil, corn oil, cottonseed oil, tallow, lard, soybean oil, peanut oil, castor oil, teaseed oil, or marine oils such as seal oils, whale oil, shark oil, fish oils, or partially or completely hydrogenated animal and vegetable oils such as those mentioned; hydroxy acids such as dihydroxy stearic acid, alpha hydroxy stearic acid, and the like; fatty and similar acids derived from various waxes such as beeswax, spermaceti, and montan wax. As suggested, one may also employ higher molecular weight carboxylic acids derived by oxidation and other methods from paraffin wax, petroleum, and similar hydrocarbons; resin acids such as hydrogenated naphthoic, naphthenic, and abietic acid, aralkyl and aromatic acids, Twitchell fatty acids, naphthoic acid, and the like.

Among the water soluble organic bases are the mono, di, tri-alkylolamines, wherein the alkylol group is methylol, ethylol, or the like, or the alkyl alkylolamines wherein the alkylol group has the same significance, and the alkyl group is methyl, ethyl, or the like, or can be substituted alkyl groups as in mono-, di-, tri-glycerol amines, hydroxyalkyl alkylene polyamines where the alkyl group has this same significance, and the alkylene group is methylene, ethylene, or the like. Specific compounds of this type which have been found useful are the mono-, di-, tri-ethanolamines, 2.amino 2.methyl 1:3 propanediol, morpholine, N.ethyl diethanolamine, N.methyldiethanolamine, and 2·ethanol pyridine.

The water soluble soaps are not restricted as to cation, to sodium and potassium, but embrace also ammonium, substituted ammonium and other basic nitrogenous derivatives. The soaps of the last three cation types may, strictly speaking, be designated addition compounds, since no water is formed in the formation thereof. It is preferred to have two types of soaps because the conventional alkali metal soap possesses poor foaming qualities. By addition of soaps made from triethanol amine and the fatty acids of between twelve and fourteen carbon atoms such as lauric acid, the coconut fatty acids, or the palm kernel fatty acids, a saponaceous detergent possessing excellent foaming properties in hard water is obtained.

The addition to these products of dispersing agents such as glycol laurate or glyceryl stearate does not essentially change the qualities of the soap although they may improve the dispersing properties and the physical appearance of the soap. They are not capable of producing good hard water soaps without the presence of the carboxylic acid amide and the organic nitrogenous base.

The condensation product of the alkylolamine and higher molecular weight carboxylic acids, such as the naturally occurring fatty acids, preferably has a ratio of 1 mol alkylol amine to 1 mol of fatty acids. The nitrogenous base may vary from 0.1 to 4.0 mols and yet give a satisfactory hard water bar soap.

Satisfactory hard water saponaceous products have been made from components with the following range of percent concentration in the composition:

	Minimum	*Maximum*
Sodium soap	40	80
Fatty acid alkylol amide	20	40
Water soluble alkylolamine	5	20
Triethanolamine soap	1	20

Suitable fillers, assistants, or addition agents such as starch, dextrin, abrasive agents, alkali, metaphosphates, glycols, glycerine, fatty acid esters of glycols or glycerine or other alcohols, fatty alcohols, fatty amides, etc., may be incorporated into the soap to improve its physical characteristics for special uses, or modify its physical appearance or feel.

The following examples will further illustrate this invention, but the invention is not restricted to these examples:

Example 1

Components	Percent
(a) Sodium soap (commercial)	55
(b) N,N-dihydroxyethyl coconut acid amide	30½
(c) Diethanolamine	14½

The three components are heated together at 125° C. For 45 minutes. On cooling, the product is compressed in a mold to form a white smooth surfaced soap. It has remarkably good detergent and emulsifying properties in hard water. It was found that a 0.2% solution of this composition in water of 250 P. P. M. calcium chloride hardness would remove 95% of a standard soil from wool almost instantaneously.

The drawing represents as a graph the concentration of the composition required to remove 95% of the standard soil from wool in water of increasing hardness. It should be noted that a 0.5% solution of the composite soap retains excellent detergent properties in water containing more than 1000 P. P. M. calcium chloride.

Example 2

Components	Percent
(a) Sodium soap (commercial)	80
(b) Triethanolamine laurate soap	7
(c) N-hydroxy ethyl lauramide	9
(d) N-hydroxy ethyl ammonium laurate	1
(e) Monoethanolamine	3

(c), (d) and (e) are heated at 150° C. for 20 minutes, cooled to substantially 100° C. and (b) melted into same. This molten mixture is thoroughly dispersed in (a) and then this resulting mixture compressed in a mold to form a smooth bar soap, which has excellent detergent and emulsifying properties in hard water.

Example 3

Components	Percent
(a) Sodium soap (commercial)	80
(b) Triethanolamine laurate soap	8
(c) N-hydroxyethyl coconut fatty acid amides	6½
(d) N,N-di (hydroxyethyl) ammonium laurate	1
(e) Diethanolamine	4½

(c), (d) and (e) are heated at 150° C. for 20 minutes. This is blended in with (b) and (a) as in Example 2, then compressed in a mold to form a smooth surfaced soap. It has remarkably good detergent and emusifying properties in hard water.

Example 4

Components	Percent
(a) Sodium soap (commercial)	80
(b) Triethanolamine laurate soap	8½
(c) N-hydroxyethyl lauramide	6½
(d) Triethanolamine	5

(c) and (d) are heated at 150° C. for 20 minutes. This is blended in with (b) and (a) as in Example 2, then compressed in a mold to form a smooth surfaced soap. It has very good washing and emulsifying properties in hard water.

Example 5

Components	Percent
(a) Sodium soap (commercial)	80
(b) Triethanolamine laurate soap	8
(c) N-N-di(hydroxyethyl) coconut fatty acid amide	7½
(d) Diethanolamine coconut fatty acid soap	1
(e) Diethanolamine	3½

(c), (d) and (e) are heated at 125° C. for 45 minutes. This is blended in with (b) and (a) as in Example 2, then compressed in a mold to form a smooth surfaced soap. It has excellent detergent and emulsifying properties in hard water.

Example 6

Components	Per cent
(a) Sodium soap (commercial)	80
(b) Triethanolamine laurate soap	7½
(c) N,N-di (hydroxyethyl) coconut fatty acid amide	9
(d) Monoethanol ammonium laurate	1
(e) Monoethanolamine	1½

(c), (d) and (e) are heated at 140° C. for 25 minutes. This is blended with (b) and (a) and made into bar soap as in Example 2. This soap bar is smooth surfaced. It has very good emulsifying and detergent action in hard water.

Example 7

Components	Per cent
(a) Sodium soap (commercial)	80
(b) Triethanolamine laurate soap	7
(c) N,N-di (hydroxyethyl) coconut fatty acid amide	8
(d) Sodium palmitate	1
(e) Diethanolamine	4

c), (d) and (e) are heated at 150° C. for 20 minutes. This is blended with (b) and (a) and made into bar soap as in Example 2. This soap bar is smooth surfaced. It has excellent detergent, emulsifying, and lime resistant action in hard water.

Example 8

Components	Per cent
(a) Sodium soap (commercial)	80
(b) Triethanolamine laurate soap	8
(c) N,N-di (hydroxyethyl) coconut fatty acid amide	7¼
(d) Potassium laurate	1¼
(e) Diethanolamine	3½

(c), (d) and (e) are heated at 150° C. for 20 minutes. This is blended with (b) and (a) to form a smooth surfaced bar soap as in Example 2. It has exceptionally good detergent, emulsifying, and lime resistant properties in hard water.

Example 9

Components	Per cent
(a) Sodium soap (commercial)	80
(b) Triethanolamine laurate soap	7½
(c) Coconut fatty acid amide of 2 amino 2 methyl 1,3 dihydroxy propane	6½
(d) Diethanol ammonium laurate	1
(e) Diethanolamine	5

(c), (d) and (e) are heated at 150° C. for 20 minutes. This is blended with (b) and (a) to form a smooth surfaced bar soap as in Example 2. This soap has very good detergent, emulsifying, and lime resistant properties in hard water.

Example 10

Components	Per cent
(a) Sodium soap (commercial)	80
(b) Triethanolamine laurate soap	8½
(c) Coconut fatty acid amide of trishydroxymethyl amino methane	8
(d) Diethanolamine coconut fatty acid soap	1
(e) Diethanolamine	2½

(c), (d) and (e) are heated together at 150° C. for 20 minutes. This is blended in with (b) and (a) as in Example 2, then compressed in a mold to form a smooth surfaced soap. This has very valuable detergent, emulsifying, and lime resistant properties in hard water.

Example 11

Components	Per cent
(a) Sodium soap (commercial)	40
(b) Triethanolamine laurate soap	24
(c) Coconut fatty acid amide of diethanolamine	22½
(d) Diethanolamine coconut fatty acid soap	3
(e) Diethanolamine	10½

(c), (d) and (e) are heated at 125° C. for 45 minutes. This is blended in with (b) and (a) as in Example 2, then compressed to form a smooth soap. It has excellent detergent and emulsifying properties in hard water.

Example 12

Components	Per cent
(a) Sodium soap (commercial)	93
(b) Triethanolamine laurate soap	3
(c) Coconut fatty acid amide of diethanolamine	2½
(d) Diethanolamine coconut fatty acid soap	½
(e) Diethanolamine	1

(c), (d) and (e) are heated at 125° C. for 45 minutes. This is blended with (b) and (a) as in Example 2, then compressed to form a smooth soap. It has good detergent and emulsifying properties in hard water.

Example 13

Components	Per cent
(a) Sodium soap (commercial)	89
(b) N-hydroxyethyl coconut acid amides	6½
(c) Diethanolamine	4½

The three components are heated together at 150° C. for 20 minutes, then compressed in a mold to form a smooth surfaced soap. It has good detergent and emulsifying properties in hard water.

Example 14

Components	Per cent
(a) Sodium soap (commercial)	55
(b) N,N-dihydroxyethyl coconut acid amide	30½
(c) Diethanolamine	12½
(d) Glycol laurate	2

The four components are heated together at 150° C. for 20 minutes, then compressed in a mold to form a smooth bar soap.

It should be noted that we do not intend that our invention shall be limited to these compositions in the form of bar soap alone. These compositions may also be flaked or put into other physical forms or shapes. Also a phase of this invention involves the preparation of paste, gel or liquid soaps therefrom of various concentrations by merely adding or dissolving in water, soft or hard. Such liquid soaps find use as liquid hand soap or textile soap.

While this invention has been described herein with reference to particular embodiments and specific examples thereof, we do not intend that our invention shall be limited to such embodiments and examples except as hereinafter defined in the appended claims.

What we claim as new is:

1. A detergent having improved hard water characteristics comprising a water-soluble organic amine, an amide of an alkylol amine and a higher molecular weight carboxy acid, and a water-soluble soap, in the ranges 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of these said three components, which detergent has the form of a bar or cake with a smooth uniform appearance and the smooth feel of bar soap and which is produced by heating the aforesaid components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

2. A detergent having improved hard water characteristics comprising a water-soluble basic organic nitrogen compound, an amide of an alkylol amine and a higher molecular weight carboxy acid, and a water-soluble soap, in the ranges 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of these said three components, which detergent has the form of a bar or cake with a smooth uniform appearance and the smooth feel of bar soap and which is produced by heating the aforesaid essential components at 100°–190° C. for a period of 60–10 minutes.

3. A detergent having improved hard water characteristics comprising a water-soluble organic amine, an amide of an alkylol amine and a higher fatty acid, an alkali metal- and an alkylolamine soap of fatty acids of 12–14 carbon atoms, in the ranges of 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of said three components, which detergent has the form of a bar or cake with a smooth uniform appearance and the smooth feel of bar soap, and which is produced by heating the aforesaid components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

4. A detergent having improved hard water characteristics comprising a water-soluble basic organic nitrogen compound, a neutral amide formed from substantially 1 mol. of an alkylol amine and 1 mol. of higher molecular weight carboxy acid, and a water-soluble soap, in the ranges 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of these said three components, which detergent has the form of a bar or cake with a smooth uniform appearance and the smooth feel of bar soap and which is produced by heating the aforesaid components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

5. A detergent having improved hard water characteristics comprising a water-soluble basic organic nitrogen compound, a neutral amide formed from substantially 1 mol. of an alkylol amine and 1 mol. of higher molecular weight car-

boxy acid, an alkali metal- and an alkylolamine soap of fatty acids of 12–14 carbon atoms, in the ranges of 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of said three components, which detergent has the form of a bar or cake with a smooth uniform appearance and the smooth feel of bar soap and which is produced by heating the aforesaid components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

6. A detergent having improved hard water characteristics comprising a water-soluble organic amine, a neutral amide formed from substantially 1 mol. of an alkylol amine and 1 mol. of higher molecular weight carboxy acid, an alkali metal- and an alkylolamine soap of fatty acids of 12–14 carbon atoms, in the ranges of 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of said three components, which detergent has the form of a bar or cake with a smooth uniform appearance and the smooth feel of bar soap and which is produced by heating the aforesaid components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

7. A detergent having improved hard water characteristics comprising a water-soluble basic organic nitrogen compound, an amide of an alkylol amine and a fatty acid of 12–14 carbon atoms and a water-soluble soap of a fatty acid of 12–14 carbon atoms, in the ranges 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of these said three components, which detergent has the form of a bar or cake with a smooth appearance and the smooth feel of bar soap and which is produced by heating the aforesaid essential components at 100°–190° C. for a period of 60–10 minutes.

8. A detergent having improved hard water characteristics comprising a water-soluble basic organic nitrogen compound, an amide of an alkylol amine and a fatty acid of 12–14 carbon atoms and a water-soluble soap of a fatty acid of 12–14 carbon atoms, in the ranges 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of these said three components, which detergent has the form of a bar or cake with a smooth appearance and the smooth feel of bar soap and which is produced by heating the aforesaid essential components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

9. A detergent having improved hard water characteristics comprising a water-soluble alkylol amine, an amide of an alkylol amine and fatty acid of 12–14 carbon atoms and a water-soluble soap of a fatty acid of 12–14 carbon atoms, in the ranges 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of these said three components, which detergent has the form of a bar or cake with a smooth appearance and the smooth feel of bar soap and which is produced by heating the aforesaid essential components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

10. A detergent having improved hard water characteristics comprising a water-soluble alkylol amine, an amide of an alkylol amine and a fatty acid of 12–14 carbon atoms an alkali metal- and an alkylolamine soap of fatty acids of 12–14 carbon atoms, in the ranges of 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of said three components, which detergent has the form of a bar or cake with a smooth appearance and the smooth feel of bar soap, and which is produced by heating the aforesaid components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

11. A detergent having improved hard water characteristics comprising a water-soluble alkylol amine, a neutral amide formed from substantially 1 mol. of an alkylol amine and 1 mol. of fatty acid of 12–14 carbon atoms and a water-soluble soap of fatty acid of 12–14 carbon atoms, in the ranges 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of these said three components, which detergent has the form of a bar or cake with a smooth appearance and the smooth feel of bar soap and which is produced by heating the aforesaid essential components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

12. A detergent having improved hard water characteristics comprising a water-soluble alkylol amine, a neutral amide formed from substantially 1 mol. of an alkylol amine and 1 mol. of fatty acid of 12–14 carbon atoms an alkali- and an alkylolamine soap of fatty acid of 12–14 carbon atoms, in the ranges of 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of said three components, which detergent has the form of a bar or cake with a smooth appearance and the smooth feel of bar soap, and which is produced by heating the aforesaid components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

13. A detergent having improved hard water characteristics comprising a water-soluble alkylol amine, a neutral amide formed from substantially 1 mol. of an alkylol amine and 1 mol. of fatty acid of 12–14 carbon atoms an alkali- and an alkylolamine soap of fatty acid of 12–14 carbon atoms, the soaps being present in at least substantially two-thirds the amount of the other two essential components the amount of amide being greater than the amount of amine, which detergent has the form of a bar or cake with a smooth appearance and the smooth feel of bar soap, and which is produced by heating the aforesaid components at substantially 125°–160° C. for a period of substantially 45–15 minutes.

14. A detergent having improved hard water characteristics comprising a water-soluble organic amine, an amide of an alkylol amine and a higher fatty acid, an alkali- and an alkylolamine soap of fatty acids of 12–14 carbon atoms, in the ranges of 5–20%, 20–40% and 40–80% respectively, said percentages being based on the amount of said three components, which detergent has the form of a bar or cake with a smooth appearance and the smooth feel of bar soap, and which is produced by heating the aforesaid components at substantially 100°–190° C. for a period of 60–10 minutes.

15. A detergent having improved hard water characteristics comprising a water-soluble alkylol amine, a neutral amide formed from substantially 1 mol. of an alkylol amine and 1 mol. of fatty acid of 12–14 carbon atoms and two water-soluble soaps, one of which is a sodium soap and one of which is an alkylolamine soap of 12–14 carbon atoms, the sodium soaps being present in at least substantially 80% of the total amount of these said three components, the amount of amide being greater than the amount of the said alkylol amine, which detergent has the form of a bar or cake with a smooth appearance and the smooth feel of bar soap, and which is produced by heating the aforesaid components at substan-

tially 125°–160° C. for a period of substantially 45–15 minutes.

16. A detergent having improved hard water characteristics comprising 5–20% of a water-soluble basic organic nitrogen compound, 20–40% of an amide of an alkylol amine and a higher molecular weight carboxy acid, and 40–80% of water-soluble soaps, said percentage being based on the amount of these said three components, which detergent has the form of a bar or cake with a smooth uniform appearance of bar soap and which is produced by heating the first two components with less than the final percentage of soap at substantially 125°–160° C. for a period of substantially 45–15 minutes, then mixing without substantially added heat with the balance of the soap.

17. A detergent having improved hard water characteristics comprising 5–20% of a water-soluble basic organic nitrogen compound, 20–40% of an amide of an alkylol amine and a higher molecular weight carboxy acid, and 40–80% of water-soluble soaps, said percentage being based on the amount of these said three components, which detergent is produced by heating the first two components with less than the final percentage of soap at substantially 125°–160° C. for a period of substantially 45–15 minutes, then mixing without substantially added heat with the balance of the soap.

18. A detergent having improved hard water characteristics comprising 5–20% of a water-soluble basic organic nitrogen compound, 20–40% of an amide of an alkylol amine and a higher molecular weight carboxy acid, and 40–80% of water-soluble soaps, said percentage being based on the amount of these said three components, which detergent is produced by heating the aforesaid components at substantially 100°–190° C. for a period of 60–10 minutes.

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