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# TOILET BAR

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9 Claims. (Cl. 252—152)

This application is a continuation in part of copending application Ser. No. 233,947, filed Oct. 29, 1962 and now abandoned.

This invention relates to the provision of a bar of nonionic detergent substance for personal use. A solid nonionic detergent substance, preferably in bar form, is advantageous for a number of reasons. For one thing, the nonionic synthetic detergents treated of herein have superior mildness characteristics as compared either with ordinary soaps or with the generality of ionic, synthetic, non-soap detergents. For another, certain ionic additive substances, such as anti-bacterial agents, ultraviolet light absorbers, and the like, are more efficiently deposited upon the skin from, and more compatible with, a nonionic toilet bar matrix. At the same time, a toilet bar, of which the detergent component is a synthetic, non-soap material, has the usual advantage of avoiding the production of hard water soap curd. In addition, nonionic detergents are compatible with cationic materials, affording a broader range of formulation possibilities.

It is difficult to produce toilet bars of which the detergent ingredients consist essentially of nonionic synthetic detergent substances without encountering one or more of the following difficulties:

Excessive solubility or softening of the bar when wetted;
Excessive wastage of the bar in use;
Physical characteristics of the bar which differ markedly in hardness or softness from bars of milled soap;
A consistency of the product which makes it difficult to manufacture and stamp the bars;
Insufficient suds/lather in use, especially in the presence of oily/lipid soils; and
A "feel" of the product during use (including the feel of the lather) which is markedly different from that of soap.

A preferred product of this invention is a toilet bar or the like which has the feel, performance characteristics, and physical characteristics in the range of a good milled soap bar, but which at the same time will be very mild in its action on the skin, and which will not produce an objectionable amount of sticky soap curd in hard water. It is an object of this invention to provide such a bar.

It is an object of the invention to provide a satisfactory, essentially nonionic, toilet bar in which the primary detergent component is a nonionic synthetic detergent, but which can be produced in milled form, having sufficient firmness to permit stamping and to resist marring in handling.

It is an object of the invention to provide a toilet bar in which the synthetic detergent component is nonionic in character and which will act as a superior vehicle for depositing desirable ionic substances upon the skin.

It is an object of the invention to provide a toilet bar in which the primary detergent component is a nonionic synthetic detergent, but whose performance in use will be similar to that of good quality milled soap.

These and other objects of the invention, which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications, are accomplished in that composition of matter and by that process of manufacture of which certain exemplary embodiments will now be described.

Briefly, in the practice of this invention, a toilet bar



having unique performance in mildness and lather characteristics, freedom from soap curd, freedom from excessive solubility in water, and sufficient firmness to permit stamping and to be resistant to marring, is produced by blending together suitably chosen nonionic detersive substances and a slightly soluble lithium soap, as hereinafter more fully described.

By the term "toilet bar" is meant a bar formed from such a blend, with or without ionic additives for special effects upon the skin, together with such adjuvants as may be desired, the bar being suitable for use upon the person as in bathing or washing the hands. The bars of this invention are preferably made by milling operations such as have been applied to soaps; but with some formulations satisfactory bars can also be made by framing and stamping, or by casting in suitable molds.

In the investigations which led to the development of this invention, many hundreds of synthetic nonionic detergents and their mixtures were evaluated. It was found that every nonionic material tested had one or more properties which precluded its use as the sole ingredient for an acceptable toilet bar. In particular, a number of the nonionic detergents were of liquid character or were so soft as to preclude the formation of a bar. While some mixtures could be made showing an improvement in one or more of the characteristics, many of the nonionic substances were physically unacceptable in admixture with others in the amounts required to produce an improvement in lathering effects and bar "feel."

In a copending application of the same inventor entitled, Toilet Bar, filed Oct. 29, 1962, and now abandoned, Ser. No. 233,868, the manufacture is taught of a bar produced entirely from nonionic detergents which bar has acceptable physical characteristics and is capable of producing a highly acceptable lather.

It was therein stated that in order to solve the problems enumerated above with respect to forming a toilet bar from nonionic detergent materials, the principle of a two-component nonionic bar system was found to be essential. This two-component nonionic principle is not essential in the present invention, but is preferred as hereinafter described. "Component," as used herein, can refer to one material or a mixture of materials. In the two-component system, the first nonionic component hereinafter referred to as "base" or "base mixture" aids in imparting to the bar sufficient firmness and acceptable solubility characteristics. The second nonionic component hereinafter referred to as "lathering component" imparts to the bar good lathering properties, especially volume and feel of the lather. Both components of the bar by virtue of their nonionic character are mild to the skin; are compatible with ionic additives; and impart desirable cleaning properties. These two components are selected as hereinafter described so that neither component will interfere with the function of the other component.

The bars of this invention contain from (1) 0% to 70%, preferably 30% to 70%, of a base component of high molecular weight normally solid nonionic polymer or mixture of polymers of which a major portion (preferably at least about 70% by weight) is oxyethylene (2) as a lathering component, from 10% to 70% of a nonionic detergent surfactant which will lather under normal personal washing conditions (i.e., about 1% solution in cool to tepid water), and (3) from 10% to 80% of lithium soap as hereinafter more fully described.

Examples of preferred base components suitable for use in the practice of this invention alone or in admixture are the following high molecular weight polymers:

(a) Propylene oxide-ethylenediamine-ethylene oxide condensates;

b) Propylene oxide-propylene glycol-ethylene oxide condensates; and

c) Polymerized ethylene glycol.

Polymer (a) is a condensate, for example, resulting rom the reaction of propylene oxide and ethylenediamine nd then a subsequent reaction with ethylene oxide. This olymer will have only about one mole of ethylene iamine per polymer molecule which can be represented y the following formula

$$(=NCH_2CH_2N=)\ (C_3H_6O)_x(C_2H_4O)_yH_4$$

herein $x$ ranges from 1 to about 160 and $y$ ranges from bout 300 to about 700. An example of this condensate s the material sold under the trademark "Tetronic 908." he condensate, "Tetronic 908," has an average molecular veight of about 27,000 and an oxyethylene content of bout 85% by weight. Condensates of this type having molecular weight of from about 20,000 to about 30,000, nd an oxyethylene content of about 70% or more by veight are suitable for use in the detergent bars of this nvention.

Polymer (b) is a condensate, for example, resulting rom the reaction of propylene oxide and ethylene glycol nd then a subsequent reaction with ethylene oxide. This olymer can be represented by the following general ormula:

$$HO(-CH_2CH_2O-)_z(-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O-)_x(-CH_2CH_2O-)_yH$$

herein $x$ ranges from 1 to about 100 and the sum of $y+z$ ranges from about 160 to about 450.

An example of this condensate is the material sold under the trademark "Pluronic F108." "Pluronic F108" has an average molecular weight of about 16,000 and an oxyethylene content of about 80% by weight. Condensates of this type having a molecular weight of from about 10,000 to 20,000 and an oxyethylene content of 70% or more by weight are suitable for use in the detergent bars of this invention.

Polymer (c) is a condensate, for example, resulting from the polymerization of ethylene oxide with ethylene glycol or water. This polymer can be represented by the general formula:

$$HO(-CH_2CH_2O-)_xH$$

wherein $x$ ranges from about 100 to about 500.

Examples of this condensate include materials sold under the trademark "Polyglycol E6000" and the material sold under the trademark "Carbowax 6000." These materials have a molecular weight of about 7,000.

Condensates of this type having a molecular weight of from about 4,000 to 20,000 are suitable for use in the bars of this invention.

Other oxyethylene polymers than those hereinafter specifically mentioned can be used in the practice of this invention. For example, those condensates which result from the condensation of ethylene oxide with other hydrophobic bases can be used so long as those condensates have molecular weights and ethylene oxide contents generally in the ranges of the above examples and so long as said condensates are solids.

Mixtures can be made of these above polymers in substantially any proportions; the optimum mixture depends upon the nature of the lathering components and the amount of lithium soap present, as hereinafter described more fully, and is determined empirically. The amount of base component which can and should be used also depends upon the nature of the lathering components since when the lathering component is itself a solid, a smaller percentage of base component can be used and when the lathering component is a liquid, a larger percentage of the base component is used. The preferred amount of base component will vary for the same reasons. A base made up of "Tetronic 908" and "Polyglycol E6000" is approximately a 1:1 ratio, was determined to

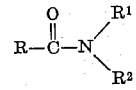


be the most soap-like in feel and is a preferred base mixture. None of these bases or base mixtures were suitable for the making of a satisfactory bar by themselves since none of these base materials provide lather under personal washing conditions. The bases or base mixtures are preferably used in amounts ranging from approximately 30% to 70% by weight of the bar.

Examples of preferred nonionic detergent surfactants as the lathering component of the bar include:

(a) Polyoxyethylene ethers of an alkyl alcohol;

(b) Polyhydroxy amides having the formula

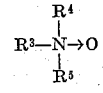


wherein



contains from about 10 to about 14 carbon atoms (preferably at least about 50% of the acyl radicals contain 12 carbon atoms), and wherein $R^1$ and $R^2$ are each selected from the group consisting of hydrogen and alkyl groups containing from 1 to about 6 carbon atoms, said alkyl groups containing a total number of carbon atoms of from 2 to about 7 and a total number of substituent hydroxyl groups of from 2 to about 6;

(c) Amine oxide detergents having the formula



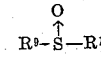
wherein $R^3$ is a hydrocarbon group containing from about 10 to about 20 carbon atoms, from 0 to about 3 ether linkages, and from 0 to about 3 hydroxyl groups, there being at least one moiety of $R^3$ which constitutes a carbon chain containing no ether linkages and containing from about 10 to about 14 carbon atoms (preferably at least 50% of said moieties contain 12 carbon atoms), and wherein $R^4$ and $R^5$ are each short alkyl chains containing from 1 to about 3 carbon atoms having from 0 to 2 hydroxyl groups attached to each of said short alkyl chains;

(d) Phosphine oxide detergents having the formula



wherein $R^6$ is a hydrocarbon group containing from about 10 to about 20 carbon atoms, from 0 to about 3 ether linkages, and from 0 to about 3 hydroxyl groups, there being at least one moiety of $R^6$ which constitutes a carbon chain containing no ether linkages and containing from about 10 to about 14 carbon atoms (preferably at least 50% of said moieties contain 12 carbon atoms), and wherein $R^7$ and $R^8$ are each short alkyl chains containing from 1 to about 3 carbon atoms having from 0 to 2 hydroxyl groups attached to each of said short alkyl chains;

(e) Dialkyl sulfoxide detergents having the formula



wherein $R^9$ is a hydrocarbon group containing from about 10 to about 20 carbon atoms, from 0 to about 3 ether linkages, and from 0 to about 3 hydroxyl groups, there being at least one moiety of $R^9$ which constitutes a carbon chain containing no ether linkages and containing from about 10 to about 14 carbon atoms (preferably at least 50% of said moieties contain 12 carbon atoms), and wherein $R^{10}$ is a short alkyl chain containing from 1 to about 3 carbon atoms having from 0 to 2 hydroxyl groups attached to said short alkyl chain;

(f) Stearoyl N-methyl glucamide;

(g) Polyethylene glycol tertdodecyl thioether containing from about 8 to about 30 moles of ethylene oxide per mole of thioether; such as "Nonic 218"; and

(h) Mixtures thereof.

Lathering component (a) is a condensate of (1) an alkyl alcohol wherein the alkyl group contains from about 10 to about 16 carbon atoms and (2) ethylene oxide wherein the ethylene oxide:alkyl alcohol mole ratio is in the range of 10:1 to 25:1. An example of such a substance is the condensation product of one mole of tridecanol with 15 moles of ethylene oxide sold under the trademark "Sterox AP–100." Other examples include decanol, dodecanol, and the mixture of alcohols derived from coconut oil condensed with respectively 10, 15, 20 and 25 moles of ethylene oxide per mole of alcohol.

Examples of lathering component (b) include lauroyl diethanol amide, coconut diethanol amide, coconut dimethanol amide, coconut monoethanol amide, lauroyl glyceryl amide, lauroyl N-methyl glucamide, lauroyl trimethanol methyl amide, lauroyl diisopropanol amide, lauroyl ethylene glycol amide and lauroyl di-N-propanol amide. This list is by no means exhaustive of the acyl polyhydroxy amides suitable for use in the bars of this invention. It will be understood that these amides can be prepared from mixtures of fatty acids and amines wherein the carbon chains are derived from naturally occurring substances or petroleum derived substances, or mixtures or fractions thereof, and that this will normally be the case.

Preferred amides are lauroyl (or coconut) diethanol amide, and lauroyl (or coconut) glyceryl amide. Lauroyl glyceryl amide and glyceryl amides in which the acyl chain is a close homolog of lauric acid, have unique performance characteristics in the compositions of this invention. In addition to acting as a lathering agent, (like the other amides used in the bars of this invention) they also act in part as agents to firm the bars and they are particularly valuable in reducing excessive solubility in the bar.

Examples of lathering component (c) include:

dimethyldodecylamine oxide
dimethyltetradecylamine oxide
ethylmethyltetradecylamine oxide
cetyldimethylamine oxide
dimethylstearylamine oxide
cetylethylpropylamine oxide
diethyldodecylamine oxide
diethyltetradecylamine oxide
dipropyldodecylamine oxide
bis-(2-hydroxyethyl)dodecylamine oxide
bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropylamine oxide
(2-hydroxypropyl)methyltetradecylamine oxide
dimethyloleylamine oxide
dimethyl-(2-hydroxydodecyl)amine oxide

and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds. The preparation of amine oxides containing ether linkages and/or hydroxyl groups is taught in U.S. Patent 3,202,714. The preparation of amine oxides containing multiple ether linkages is taught in the commonly assigned copending application of Davis, Ser. No. 370,036, filed May 25, 1964.

Examples of lathering component (d) include:

dimethyldodecylphosphine oxide
dimethyltetradecylphosphine oxide
ethylmethyltetradecylphosphine oxide
cetyldimethylphosphine oxide
dimethylstearylphosphine oxide
cetylethylpropylphosphine oxide
diethyldodecylphosphine oxide
diethyltetradecylphosphine oxide
dipropyldodecylphosphine oxide
bis-(hydroxymethyl)dodecylphosphine oxide
bis-(2-hydroxyethyl)dedocylphosphine oxide
(2-hydroxypropyl)methyltetradecylphosphine oxide
dimethyloleylphosphine oxide
dimethyl-(2-hydroxydodecyl)phosphine oxide

and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds. The preparation of phosphine oxides containing hydroxyl groups is taught in the commonly assigned co-pending application of Yoke, et al., Ser. No. 173,834, filed Feb. 16, 1962.

Examples of lathering component (e) include:

octadecyl methyl sulfoxide
dodecyl methyl sulfoxide
tetradecyl methyl sulfoxide
3-hydroxytridecyl methyl sulfoxide
3-methoxytridecyl methyl sulfoxide
3-hydroxy-4-dodecoxybutyl methyl sulfoxide
2-hydroxyundecyl methyl sulfoxide
2-hydroxydecyl methyl sulfoxide
2-decoxyethyl-2-hydroxyethyl sulfoxide.

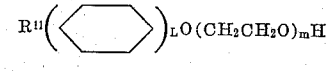
The preparation of dialkylsulfoxides containing ether linkages and/or hydroxyl groups is disclosed in the commonly assigned co-pending applications of Lyness et al., Ser. Nos. 444,069 and 448,228, filed Mar. 30, 1965.

It will be understood that the above oxides (c, d, and e) can be prepared from mixtures of alkyl groups derived from naturally occurring substances or petroleum derived substances, or mixtures or fractions thereof, and this will normally be the case.

Preferred lathering components include components (a) and (b) since they are relatively inexpensive, have good lathering characteristics, and are very mild. Other preferred lathering components include (c), (d) and (e) where the compounds contain hydroxyl groups and/or ether linkages. They are preferred over components (c), (d) and (e) which do not contain hydroxyl groups and/or ether linkages because the former are milder. Especially preferred lathering components are 2-hydroxyalkyl methyl sulfoxides wherein alkyl refers to dodecyl, tridecyl and/or tetradecyl groups. These lathering components are milder than shorter chain homologs and have excellent lathering characteristics. The 2-hydroxydodecyl methyl sulfoxide is preferred for lather volume, but the 2-hydroxytetradecyl and 2-hydroxytridecyl homologs can be mixed with the 2-hydroxydodecyl methyl sulfoxide to improve the creaminess of the lather without appreciably diminishing the lather volume.

Components (c), (d) and (e), especially the preferred compounds hereinbefore described, are made milder by the presence of the insoluble lithium soap.

It has been discovered that lather (suds) builder compounds having the formula



wherein $R^{11}$ is an alkyl radical containing from about 8 to about 20 carbon atoms, wherein L is selected from the group consisting of 0 and 1, and wherein M is a number between about 10 and about 60, can be mixed with lathering components (c), (d) and/or (e) to provide more lather volume and a more stable lather. The above definition comprises component (a) and accordingly, the total of component (a) and the above lather builder compound is desirably from 0% to about 200% by weight, preferably 20% to 70%, of the rest of the lathering components present. An especially preferred lather builder is prepared by condensing dodecanol with about 45 moles of ethylene oxide per mole of dodecanol.

Although the primary use of the lather builder compound is in admixture with lathering components (c), (d) and/or (e), it can also be used as the sole lathering component or in combination with the other lathering components.

Other mixtures of the above lathering agents can be sed.

The present invention is dependent upon the discovery f a new coaction between essentially insoluble lithium aps and the nonionic synthetic detergents described bove. By "essentially insoluble lithium soap" is meant ie lithium salts of fatty acids containing 12 to 18 carbon toms. The lithium soaps as hereinafter described proide a number of advantages not hitherto obtained. For ne thing, they improve the physical characteristics of ars containing nonionics, making them more "soap-like." or another, they permit one to mill the detergent comosition. For yet another thing, they radically affect the feel" and performance characteristics of the bar.

Nonionic detergents, as described above, have many lesirable properties for toilet bars. However, certain haracteristics of such nonionic detergents can be spoken f as "not soap-like" in feel and physical properties and, onsequently, many people find these characteristics undeirable.

For instance, at high concentrations, the lather of ionionic detergents is more slimy and slippery than soap ather. Furthermore, as the lather is rinsed away there s a transition from the more slimy and slipper feel to "squeaky clean" effect as a result of the removal of surace fats and oils from the skin and the relatively poor ubricity of nonionic lather relative to the lather of soap. This relative lack of lubricity is also noted in the feel of the toilet bar itself.

As has been described hereinbefore, it is difficult to form toilet bars from nonionic synthetic detergents because of the generally excessive solubility of such detergents and the consistency of the product which makes it difficult to manufacture and stamp the bars. This lack of "workability" is apparently due to the lack of plasticity of nonionic detergents which have a tendency to be either soft and sticky or hard and brittle relative to soap.

The addition of lithium soap to a toilet bar wherein the active detergent substances consist primarily of synthetic nonionic detergents provides unique benefits. In combination with nonionic detergent surfactant materials such as are hereinbefore described, the lithium soap makes the toilet bar more plastic and "soap-like."

This is equally true whether the other materials in the bar would be hard and brittle or soft and sticky by themselves in a toilet bar formulation. In one case the improvement is in the direction of a softer bar and in the other the improvement is in the direction of a harder bar. In both cases the improvement is toward a plastic, "soap-like," ideal structure which is considered desirable. The improvement is such that materials which cannot be used in bars in and of themselves, can be made into bars in combination with lithium soap. Lithium soap acts as a type of base and indeed can be substituted entirely for the base component hereinbefore described. It is preferred, however, to use lithium soap in combination with one or more of the base components hereinbefore described.

As a result of the improved plasticity imparted to the formulation by the inclusion of lithium soap it is possible to mill the detergent compositions of this invention. This ability to "work" the detergent compositions enables the manufacturer of a bar to shape, stamp, etc., more economically and with less equipment than would be required for the same production if a molding method were used.

Certain other bar performance characters are improved. For instance, due to the relative insolubility in water of lithium soap, its inclusion in toilet bars, reduces the generally excessive solubility of the nonionic detergents. This reduction makes the bars much more acceptable and economical to use since the bar will not dissolve away as rapidly when in contact with water.

A very important and unique effect of lithium soap is that it imparts a slippery soap-like feeling not only to the bar containing nonionic detergents but also the lather. When combined with nonionic detergents the "feel," or slip, of the lather is altered so that the initial slimy and slippery feeling of the lather and the subsequent squeaky-clean feeling are modified or eliminated and the lather is slippery like the lather of soap. (It is believed that this slip effect is due to the crystal structure of lithium soaps and is not a result of soap in solution since small amounts of sodium soap added to a nonionic bar formulation do not improve the lathering characteristics noticeably.)



Lithium soap itself is a pliable, substantially water insoluble material having no appreciable detergent qualities. As a result of the substantially insoluble nature of lithium soap it does not affect the nonionic character of the bar. The performance and mildness benefits on the nonionics are retained while at the same time the unusual physical and performance characteristics of the toilet bars are modified to conform to the generally desirable ideal of soap.

Lithium soaps appear to be unique in the practice of this invention, and identical effects are not obtained from the use of other insoluble or difficultly soluble soaps such as the soaps of the alkaline earth metals in general. Nevertheless, the lithium soaps herein contemplated can be somewhat diluted by the addition of magnesium, zinc or calcium soap of similar fatty acids if desired. So long as the lithium soap or soaps preponderate in the soap mixture, the quantities hereinafter given will serve to bring about the advantages derivable from the invention. Additional quantities of other difficultly soluble soaps, if added, can be regarded as filler materials primarily.

The fatty acid radicals in the lithium soaps encompass a range from lauric through steraic; but inasmuch as the fatty acids will normally be derived from vegetable, animal or marine oils, the use of such oils as a source of the fatty acids is within the scope of this invention despite the fact that they may contain some small quantity of fatty acids having carbon contents outside the stated range. Thus, fatty acids derived from coconut oils can be used as such with or without fractional distillation, as can oils from other vegetable, animal or marine origins. However, the greater part of the fatty acids should contain from about 12 to about 18 carbon atoms.

Mixtures of fatty acids from different sources may also be used. Thus, the slightly soluble metallic soaps may be lithium salts of mixtures of fatty acids derived from tallow and coconut oils. A preferred fatty acid mixture is one containing about 80% tallow fatty acids and 20% coconut fatty acids, such as is used in the manufacture of much of the milled soaps of commerce. In this preferred blend an increase in the amount of tallow decreases the slippery feeling somewhat. An increase in the amount of coconut increases solubility and decreases plasticity somewhat. Other preferred lithium soaps are lithium ricinoleate, lithium oleate and mixtures containing said soaps. Soaps containing hydroxyl substituents and/or unsaturation are operable and even desirable. Any of these fatty acid mixtures may be saponified by the use of lithium compounds, e.g., LiOH or $Li_2CO_3$.

The triglycerides or the fatty acids may be hardened by hydrogenation if they contain too many unsaturated components, to the end of minimizing the development of rancidity in the final product.

The useful range of usage of the lithium soap in the formulation is quite wide. An improvement in the soap-like characteristics (slip) of the bar and the lather can be noted as soon as a few percent, say 10 percent or so, of the lithium soap is added. A larger percent of about 40% or more is preferred to effect an improvement in the physical properties. For milling of the bar components, it is preferred to have from 30% to 80% of the lithium soap by weight in the formulation; and considering smear and wear rate a somewhat narrower range of about 50% to 80% will be found best for a bar. When the lithium soap is the only base component

present in the bar, it should not be present in an amount less than about 50% by weight of the bar.

A desirable component which can be incorporated in the bars of this invention, in an amount of from about 0.1% to about 10% by weight of the bar, is a fatty acid monoester of ethylene glycol wherein the fatty acid contains from about 14 to about 20 carbon atoms. Bars containing this component last longer. However, this component acts to suppress the lather if used in too large a quantity.

Preferably, this fatty acid monoester component is used at a level of about 5% by weight of the bar. It is also preferably used with the better lathering components such as 2-hydroxydodecyl methyl sulfoxide. The preferred fatty acyl groups in the monoester are those derived from tallow, e.g., $C_{16}$ and/or $C_{18}$, but the fatty acyl groups can be derived from other sources such as fatty acids which have been synthetically produced.

In the manufacture of a milled product, the nonionic surfactants are melted and sufficient water is added to make the mass fluid. The lithium soap is added and the mixture is agitated vigorously until it is creamy. The mixture is then treated to reduce the moisture content to about 5% or less, which can be done in known ways. When the dried mixture is firm, it is then milled in the usual manner, extruded, and stamped into bars. A moisture content which is less than about 5% is important in controlling bar firmness in manufcture and in use. The optimum moisture level is dependent on the level of the lithium soap and the nature of the nonionic portion.

It may be noted that bars may be made by casting the nearly anhydrous materials provided the amount of lithium soap is not too great, say, not above about 30% by weight of the formulation.

It will further be understood that the bars can contain ionic additives such as ionic germicides (either cationic or anionic) and ultraviolet light absorbers as well as adjuvants which are common in the toilet bars of commerce including, but without limitations, perfumes, emollients, coloring matters and the like. These ionic additives can be present in amounts up to about 10%. Due to the nonionic character of the bar matrix, functional ionic additives will be especially effective (as noted above). In order to obtain the advantages of this invention the bars should be substantially free from anionic detergent and/or alkaline builder materials.

For convenience or economic reasons it may be desirable to "fill" or dilute the bar composition with a normally solid impalpable substance which does not adversely affect the performance of the detergent bar composition. Fillers can be used in the bar compositions in amounts up to about 40%, preferably not more than 30% by weight of the bar.

Materials which can be used as fillers or diluents for detergent bars are, for the most part, commonly used and well known in the art. These materials are naturally impalpable such as those of a waxy nature or are finely ground to a size of about 75 microns or smaller. Conventional filler materials include: substantally insoluble, finely ground minerals such as talc, felspar, quartz, calcium carbonate, bentonite, fuller's earth, clay, kaolin; finely ground organic materials of low solubility such as starch, and calcium and magnesium soaps.

*Example I*

A blend was made of the following ingredients, trade names, hereinbefore described, being used for certain of the nonionic ingredients for the sake of brevity:

| | Percent |
|---|---|
| Lithium soap (80% tallow, 20% coconut) | 50 |
| Tetronic 908 | 24 |
| Sterox AP100 | 12 |
| Lauroyl diethanol amide | 12 |
| Water | 2 |



The percentages are by weight.

This blend was milled at a moisture content of about 3%, and gave a bar having a soap-like lather and possessing the other unique characteristics set forth above.

*Example II*

A mixture was made by blending:

| | Percent |
|---|---|
| Lithium soap (80% tallow, 20% coconut) | 65 |
| Lauroyl diethanol amide | 15 |
| Polyglycol E–6000 | 15 |
| Remainder water and adjuvants. | |

The percentages are by weight.

The product was milled at a moisture content of about 2%, and gave a toilet bar of excellent character and performance.

*Example III*

Another product was prepared by blending together the following ingredients, the percentages given being on a dry basis:

| | Percent |
|---|---|
| Lithium stearate | 10 |
| Lauroyl diethanol amide | 27 |
| Sterox AP100 | 27 |
| Tetronic 908 | 18 |
| Polyglycol E–6000 | 18 |

Milling was done at 2% moisture.

The bars prepared from the milled mixture of this example gave good performance and had lathering characteristics generally similar in volume, creaminess and "feel" to those of conventional milled soaps. The wear rates of the bars were higher than those of Examples I and II above, but were substantially lower than those of a bar containing only the synthetic nonionic detergent surfactants.

*Example IV*

All percentages in this example are on a dry basis.

| | Percent |
|---|---|
| Lithium soap (80% tallow, 20% coconut) | 55 |
| Lauroyl diethanol amide | 10 |
| Tetronic 908 | 30 |
| Dimethyl dodecyl amine oxide | 5 |

This mixture was milled as above. The resulting bars performed well with amine oxide instead of the Sterox AP 100 of Example III as a sudsing agent.

*Example V*

Yet another toilet bar of excellent characteristics was prepared by milling the following formula:

| | Percent |
|---|---|
| Lithium soap (80% tallow, 20% coconut) | 50 |
| Tetronic 908 | 15 |
| Sterox AP100 | 15 |
| Lauroyl diethanol amide | 15 |
| Water | 5 |

Formulations of the type set forth above have been found to be entirely compatible with and efficient carriers for ionic additives. For example, up to about 10% by weight of sodium para-aminobenzoate as an ultraviolet light absorbent in the formula did not adversely affect bar performance. The same is true for a cationic anti-bacterial agent commercially known as "Hyamine 1622" which is a di-isobutyl phenoxy ethoxy dimethyl benzyl ammonium dichloride monohydrate. This anti-bacterial agent retained its anti-bacterial activity in the bars of this invention.

In the above cases, the ionic additive was found to be deposited on the skin when the bar was used for personal washing. Further, the additives were deposited on the skin from the nonionic formulations of this invention

much more efficiently than from alkali metal soaps, e.g., allow-coconut soaps.

*Example VI*

As an example of an excellent milled bar formulation containing a material intended to be deposited on the skin, the following is given:

| | Percent |
|---|---|
| Lithium soap (80% tallow, 20% coconut) | 53 |
| Tetronic 908 | 25 |
| Lauroyl diethanol amide | 10 |
| Dimethyl dodecyl amine oxide | 5 |
| Sodium para-amino benzoic acid | 5 |
| Water | 2 |

The percentages are by weight.

Excellent bars are also obtained when stearoyl N-methyl glucamide, "Nonic 218," dodecyl dimethyl phosphine oxide or dodecylmethyl sulfoxide are substituted for the amine oxide of this example.

*Example VII*

Yet another exemplary formula of an excellent milled bar including a skin treatment substance is:

| | Percent |
|---|---|
| Lithium soap (80% tallow, 20% coconut) | 53 |
| Tetronic 908 | 30 |
| Lauroyl diethanol amide | 10 |
| Hyamine 1622 | 5 |
| Water | 2 |

The percentages are by weight.

*Example VIII*

When in the above examples the following lathering components are substituted either wholly or in part for the Sterox AP100, lauroyl diethanol amide, and/or the dimethyl dodecyl amine oxide, substantially equivalent results are obtained in that the bars are excellent bars giving a substantial lather; the condensation products prepared by condensing, respectively, 1 mole of decanol, dodecanol, tridecanol, or alcohols derived from coconut oil with either 10, 15, 20 or 25 moles of ethylene oxide per mole or alcohol; lauroyl diethanol amide, coconut diethanol amide, coconut dimethanol amide, coconut monoethanol amide, lauroyl glyceryl amide, lauroyl N-methyl glucamide, lauroyl trimethanol methyl amide, lauroyl diisopropanol amide, lauroyl ethylene glycol amide, lauroyl di-N-propanol amide, dimethyldodecylamine oxide, dimethyltetradecylamine oxide, ethylmethyltetradecylamine oxide, cetyldimethylamine oxide, dimethylstearylamine oxide, cetylethylpropylamine oxide, diethyldodecylamine oxide, diethyltetradecylamine oxide, dipropyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropyl amine oxide, (2-hydroxypropyl)methyltetradecylamine oxide, dimethyloleylamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, the corresponding decyl, hexadecyl, and octadecyl homologs of the above amine oxides; dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, cetyldimethylphosphine oxide, dimethylstearylphosphine oxide, cetylethylpropylphosphine oxide, diethyldodecylphosphine oxide, diethyltetradecylphosphine oxide, dipropyldodecylphosphine oxide, bis-(hydroxymethyl)dodecylphosphine oxide, bis-(2-hydroxyethyl)dodecylphosphine oxide, (2 - hydroxypropyl)methyltetradecylphosphine oxide, dimethyloleylphosphine oxide, dimethyl-(2-hydroxydodecyl)phosphine oxide, bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropylphosphine oxide, the corresponding decyl, hexadecyl, and octadecyl homologs of the above phosphine oxides; octadecy methyl sulfoxide, dodecyl methyl sulfoxide, tetradecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide, 2-hydroxyundecyl methyl sulfoxide, 2-hydroxydecyl methyl sulfoxide, 2-decoxyethyl-2-hydroxyethyl sulfoxide, 2-hydroxydodecyl methyl sulfoxide, 2-hydroxytridecyl methyl sulfoxide, 2-hydroxytetradecyl methyl sulfoxide, the corresponding decyl, hexadecyl and octadecyl homologs of the above sulfoxides and mixtures thereof in, e.g., a 1:1 ratio by weight.

*Example IX*

When in the above examples Pluronic F108 and/or Carborwax 6000, either alone or in 1:1 mixtures by weight, are substituted either wholly or in part for either the Tetronic 908, the Polyglycol E–6000, or both of these base components, substantially equivalent results are obtained in that the bars are excellent bars having good physical characteristics.

*Example X*

When in the above examples lithium ricinoleate and/or lithium oleate, either alone or in 1:1 mixtures by weight, are substituted either wholly or in part for the lithium soaps, substantially equivalent results are obtained in that the bars formed have better physical characteristics and are more soap-like in lathering characteristics and bar feel than similar bars prepared without the lithium soaps being present.

*Example XI*

When in the above examples about 5% by weight of the bar components of stearoyl monoester of ethylene glycol is substituted for one of the base components, substantially improved results are obtained in that the bars last longer in use.

*Example XII*

When in the above examples which contain amine oxide, phosphine oxide, and/or sulfoxide lathering components, sufficient amounts of the following components are added so that the total of the amounts of these components and lathering components coming within the scope of lathering component (a) is 100% by weight of the amine oxide, phosphine oxide, and/or sulfoxide present, substantially improved results are obtained in that the bars provide more lather volume and a more stable lather than when the following components are not present: the condensation product of dodecanol with about 45 moles of ethylene oxide per mole of dodecanol; the condensation product of nonyl phenol with 40 moles of ethylene oxide per mole of nonyl phenol, and mixtures thereof in, e.g., a 1:1 ratio of weight.

*Example XIII*

An example of a particularly desirable milled bar is:

| | Percent |
|---|---|
| 2-hydroxydodecyl methyl sulfoxide | 20 |
| 2-hydroxytetradecyl methyl sulfoxide | 20 |
| The condensation product of one mole of fatty alcohols derived from coconut oil and about 45 moles of ethylene oxide | 20 |
| Lithium laurate | 40 |

This bar was mild and had good lather characteristics.

A similar bar was prepared in which lithium ricinoleate replaced the lithium laurate in the above example and this bar also was mild and had good lather characteristics.

When in the above example, lithium oleate or a 1:1 mixture of lithium oleate and lithium ricinoleate is substituted for the lithium laurate, substantially equivalent results are obtained in that the bar is mild and has good lather characteristics.

*Example XIV*

The following is a desirable formula for a milled bar having an improved wear rate.

| | Percent |
|---|---|
| 2-hydroxydodecyl methyl sulfoxide | 30 |
| The condensation product of one mole of dodecyl phenol and about 40 moles of ethylene oxide | 20 |
| Ethylene glycol monostearate | 5 |
| Lithium laurate | 45 |

In the claims which follow, the term "consisting essentially of" is not to be construed as excluding minor proportions of adjuvants, fillers, and ionic substances, whether of surfactant or skin treatment character and the like.

Modifications may be made in the invention without departing from the spirit of it. The invention having been described in certain exemplary embodiments, what is claimed as new and desired to be secured by Letters Patent is:

1. A solid toilet bar substantially free of anionic detergents and alkaline builder materials and consisting essentially of:

(1) a base of high molecular weight, normally solid, polymeric nonionic detergent of which at least about 70% by weight is oxyethylene selected from the group consisting of:

(a) propylene oxide-ethylenediamine-ethylene oxide condensates, having the formula

$$(=NCH_2CH_2N=)(C_3H_6O)_x(C_2H_4O)_yH_4$$

wherein $x$ ranges from 1 to about 160 and $y$ ranges from about 300 to about 700 and wherein the molecular weight ranges from about 20,000 to about 30,000 and the percentage by weight of oxyethylene in the condensates is at least about 70% by weight,

(b) propylene oxide-propylene glycol-ethylene oxide condensates, having the formula

$$HO(-CH_2-CH_2O)_z(-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2O)_x(-CH_2CH_2O)_yH$$

wherein $x$ ranges from 1 to about 100 and the sum of $y$ and $z$ ranges from about 160 to about 450, and wherein the molecular weight ranges from about 10,000 to about 20,000 and the percentage by weight of oxyethylene in the condensates is at least about 70% by weight,

(c) polymerized ethylene glycol having the formula

$$HO(-CH_2CH_2O-)_xH$$

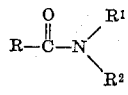
wherein $x$ ranges from about 100 to about 500, and

(d) mixtures thereof;

(2) a nonionic lathering component selected from the group consisting of:

(a) polyoxyethylene ethers of an alkyl alcohol wherein said alkyl group contains from about 10 to about 16 carbon atoms and the mol ratio of ethylene oxide:alkyl alcohol is in the range of 10:1 to 25:1;

(b) polyhydroxy amides having the formula

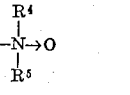


wherein



contains from about 10 to about 14 carbon atoms and wherein $R^1$ and $R^2$ are each selected from the group consisting of hydrogen and alkyl groups containing from 1 to about 6 carbon atoms, said alkyl groups containing a total number of carbon atoms of from 2 to about 7 and a total number of substituent hydroxyl groups of from 2 to about 6;

(c) amine oxide detergents having the formula



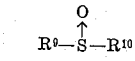
wherein $R^3$ is selected from the group consisting of alkyl and monohydroxy alkyl groups containing from about 10 to about 20 carbon atoms and from 0 to about 3 ether linkages, there being at least 1 moiety of $R^3$ which constitutes a carbon chain containing no ether linkages and containing from about 10 to about 14 carbon atoms, and wherein $R^4$ and $R^5$ are each selected from the group consisting of alkyl and monohydroxyalkyl groups containing from 1 to about 3 carbon atoms;

(d) phosphine oxide detergents having the formula



wherein $R^6$ is selected from the group consisting of alkyl and monohydroxyalkyl groups containing from about 12 to about 18 carbon atoms, and wherein $R^7$ and $R^8$ are each selected from the group consisting of alkyl and monohydroxy alkyl groups containing from 1 to about 3 carbon atoms;

(e) dialkyl sulfoxide detergents having the formula



where in $R^9$ is selected from the group consisting of alkyl monohydroxyalkyl, alkoxyalkyl and alkoxymonohydroxyalkyl groups containing from about 10 to about 18 carbon atoms, there being at least one moiety of $R^9$ which constitutes a carbon chain containing no ether linkages and containing from about 10 to about 14 carbon atoms, and wherein $R^{10}$ is selected from the group consisting of alkyl and monohydroxyalkyl groups containing from 1 to about 3 carbon atoms;

(f) stearoyl N-methyl glucamide;

(g) polyethylene glycol tertdodecyl thioether containing from about 8 to about 30 moles of ethylene oxide per mole of thioether;

(h) mixtures thereof; and

(3) Lithium soap of fatty acids containing from about 12 to about 18 carbon atoms; the base (1) ranging from zero percent to about 70% of the composition of the bar by weight; the lathering component (2) ranging from about 10% to about 70% of the composition of the bar by weight; the lithium soap (3) ranging from about 10% to about 80% by weight of the bar, and the bar being firm at room temperatures.

2. The bar of claim 1 in which the base is from about 30% to about 70% by weight of the bar.

3. The bar of claim 1 in the form of a milled bar, the amount of said lithium soap being from about 40% to about 80% by weight of the bar.

4. The bar of claim 1 wherein the lathering component is 2-hydroxydodecyl methyl sulfoxide.

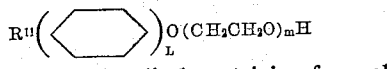
5. The bar of calim 1 containing as an additional ingredient from 0.1% to about 10% by weight of the bar of a fatty acid monoester of ethylene glycol wherein the fatty acid contains from about 14 to about 20 carbon atoms.

6. The bar of claim 5 wherein the fatty acid monoester is at a level of about 5% by weight of the bar.

7. The bar of claim 1 wherein the lithium soap is selected from the group consisting of lithium ricinoleate, lithium oleate and mixtures thereof.

8. The bar of claim 1 containing as an additional component, from 0% to about 200% by weight of the lather-

ıg components present of a lather builder compound aving the formula



/herein $R^{11}$ is an alkyl radical containing from about 8 ɔ about 20 carbon atoms, wherein L is selected from the roup consisting of 0 and 1, and wherein *m* is a number ɛtween about 10 and about 60, the total amount of athering component (a) and the lather builder com-ıound being from 0% to about 200% by weight of the est of the lathering components present.

**9.** The bar of claim **8** wherein the lather builder com-ɔund is the condensation product of fatty alcohols de-ived from coconut oil with about 45 moles of ethylene ɔxide per mole of fatty alcohols derived from coconut oil.


**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,678,921 | 5/1954 | Turck | 252—161 |
| 2,703,798 | 3/1955 | Schwartz | 252—152 X |



| | | | |
|---|---|---|---|
| 2,774,735 | 12/1956 | Becher | 252—117 |
| 2,787,595 | 4/1957 | Webb | 252—138 |
| 2,868,731 | 1/1959 | Henderson et al. | 252—117 |
| 2,972,583 | 2/1961 | Hewitt | 252—161 |
| 3,081,267 | 3/1961 | Laskey | 252—135 |
| 3,159,581 | 12/1964 | Diehl | 252—137 X |
| 3,197,509 | 7/1965 | Drew et al. | 252—152 X |
| 3,202,714 | 8/1965 | Zimmerer | 252—152 X |

FOREIGN PATENTS

| | | |
|---|---|---|
| 229,443 | 7/1960 | Australia. |

OTHER REFERENCES

Martin: The Modern Soap and Detergent Industry, vol. 1, section 1, p. 11 (1950).


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