This invention relates to improvements in the manufacture of detergents, more particularly in milled soaps and especially milled soaps of the type employed for toilet purposes. It relates to improvements in milled soap compositions containing a hard soap and a synthetic detergent of the higher petryl aromatic sulfonate type and especially of the higher petryl aromatic sulfonate type, and to improvements in the processes of manufacturing milled soaps containing a hard soap and a synthetic detergent of the higher petryl sulfonate type and especially of the higher petryl aromatic sulfonate type.

As employed throughout this specification and claims, the term “soap” denotes and includes the water-soluble alkali metal, ammonium, and organic amine salts of higher fatty acids containing 10 to 20 carbon atoms; the term “hard soap” denotes and includes those “soaps” which form solid masses under normal atmospheric conditions; and the terms “higher petryl sulfonate” and “higher petryl aromatic sulfonate” denote and include mixtures of organic sulfonates and substituted aromatic sulfonates, respectively, in which an organic radical which is a part of the organic sulfonate, or which is a constituent of the aromatic nucleus of the aromatic sulfonate, is derived from a polycyclic hydrocarbon mixture of the type of a petroleum distillate (a petroleum distillate or a synthetic mixture whose composition is similar to a petroleum distillate) boiling for the most part within the range 100° to 300° C. at atmospheric pressure. Examples of such soaps are the sodium, potassium, ammonium, and triethanolamine salts of saturated and unsaturated higher fatty acids derived from coconut oil, palm oil, olive oil, tallow, cottonseed oil, and the like, and mixtures thereof, well known to those skilled in the soap-making art. Detergents of the higher petryl aromatic sulfonate type are disclosed, for example, in United States Patents 2,196,985; 2,218,472; 2,220,099; 2,233,364; 2,233,408; 2,267,725; 2,364,723; and British Patent 416,379. Other examples of detergents of the higher petryl sulfonate type are petroleum sulfonates obtained in the refining of lubricating oils, and sulfonated products obtained by treating mineral oil fractions by the process of United States Reissue Patent No. 29,988 and United States Patents Nos. 2,197,000; 2,202,731; 2,239,974; and 2,276,090.

It is known to produce soap compositions containing a hard soap and a higher petryl sulfonate for use as effective detergents and washing agents in water of varying degrees of hardness, and in sea water. Such compositions have been prepared, for example, by mixing a higher petryl aromatic sulfonate with molten kettle soap in a crutcher, allowing the resulting mixture to cool and solidify in frames, and cutting the resulting solid soap composition into bars or cakes.

A milled soap cannot be prepared from the resulting framed soap compositions because the high content of water present in said compositions (30% or more) renders them soft and mushy, so that plodding cannot be satisfactorily effected. Preparation of a milled soap product by mixing a hard soap in a form usually employed for milling (e.g., in the form of ribbons, beads, particles, flakes, grains, or the like), containing 5% to 15% of mixture) with a higher petryl sulfonate in a substantial amount (e.g., 15% of the weight of the soap) presents difficulties; the mixture becomes sticky and tough so that it opposes milling and plodding in the usual commercial soap-making equipment. If it is attempted to improve the plasticity of such mixture by the addition of water, the mixture merely becomes more tacky and its working properties are not materially improved. In view of these difficulties, heretofore the manufacture of soap bars and cakes containing mixtures of soap and higher petryl sulfonates has been largely restricted to framed soap products.

According to the present invention, the production of milled soaps containing a hard soap and a higher petryl sulfonate can be effectively carried out in the ordinary soap-making equipment and with the use of commercially available higher petryl sulfonate detergents, by incorporating a substantial amount of starch, in the ordinary insoluble form, into a mixture of the higher petryl sulfonate and hard soap containing moisture. In accordance with the present invention, it has been found that the presence of starch in the insoluble form serves to overcome the stickiness and toughness of the composition, with the result that the mixtures flow readily through the plodder without requiring greater pressure than is normally employed in the manufacture of the usual milled toilet soaps, and the resulting bars issuing from the plodder are smooth and light colored. Further, the presence of the starch in the resulting soap products imparts a satiny feel to the products.

Corn starch is ordinarily employed, because of its low cost and general availability, but any other water-insoluble starch may be used; such as, wheat starch, tapioca starch, potato starch, etc. The starch is present in the novel compositions.
The amount of starch employed in accordance with the present invention relative to the amount of higher petryl sulfonate and hard soap will depend upon a number of factors; such as, the amount of soap and higher petryl sulfonate employed, the amount of sodium sulfate and other inorganic salts present in the mixture, and the use to which the product is to be put. In general, the amount of starch should be at least sufficient to provide compositions which may be milled and plodded without difficulty in the usual soap-making machinery to form bars possessing satisfactory physical properties. It is generally preferred to employ an amount of starch equal to between 10% and 40%, and especially between 20% and 30%, of anhydrous starch, based on the "total weight of basic components." An amount less than 10% of starch (e.g., 5%) may in some cases affect the desired improvement in workability; but it is preferable to employ a larger amount in order to obtain a more highly diluted milled detergent composition. The presence of substantially more than 40% of starch tends to reduce unduly the concentration of active cleaning agents in the resulting products, to deprive them of their slippery feel, and to detract otherwise from the desirability of the bars or cakes. It was surprising to find that soap--higher petryl benzene sulfonate--starch mixtures of the type of the present invention containing as high as 40% by weight of starch will yield milled bars possessing a feel and appearance comparable with a milled bar of high-grade toilet soap, even when the proportion of soap contained in such mixtures is as low as 25%.

As employed herein, the expression "total weight of basic components" refers to the sum of the weights of the following components of the compositions: (1) hard soap (on an anhydrous basis), (2) higher petryl sulfonate (on an anhydrous, inorganic-salt-free basis), (3) starch (on an anhydrous basis), and (4), if present, sodium sulfate and/or other inorganic salts.

In preparing the milled soaps in accordance with the present invention, the hard soap, in the form of ribbons, flakes, beads, or other form commonly employed for making milled soaps, is mixed with a higher petryl sulfonate and starch in suitable mixing apparatus, such as a soap mill, and the resulting mixture is introduced into a plodder from which the mixture is extruded in the form of the usual bars, which are then stamped or otherwise converted into the desired form. As in usual in the making of milled soaps, the mixtures contain water, which is ordinarily introduced in the form of moisture present in the soap. The amount of water preferably should not exceed 15% of the "total weight of basic components." Greater amounts of moisture render the composition too soft for satisfactory working. Preferably, the mixtures contain an amount of water equal to at least 6% of the "total weight of basic components," to provide desirable working properties. In general, amounts of water equal to 10% to 12% of the "total weight of basic components" provide optimum workability. Usually, commercial forms of starch also contain moisture, and a part of the total moisture is introduced with the starch. The amounts of hard soap and higher petryl sulfonate components will depend to some extent upon the uses to which the resulting products are to be put. In general, an amount of higher petryl benzene sulfonate (on an anhydrous, inorganic-salt-free basis) equal to at least 6%, preferably at least 10% of the "total weight of basic components" is preferred. For use in water of relatively high degree of hardness, and especially for use in seawater, the amount of higher petryl sulfonate (salt-free basis) is preferably at least 20% of the "total weight of basic components". In general, an amount of hard soap (on an anhydrous basis) equal to at least 15% of the "total weight of basic components" is employed to provide the desired workability of the composition and to impart the characteristics of a milled dust soap to the resulting products. Further, in connection with the use of the products in sea water, such a minimum amount of soap is desirable to provide the products with advantageous washing ability in sea water.

Within these limits, the proportions of soap and higher petryl sulfonate will depend to some extent upon the amount of inorganic salt in the higher petryl sulfonate detergent employed. For example, in preparing a milled soap from a tallow soap, or other toilet soap bases, by ordinarily employed in making milled soaps, and commercially available sodium higher petryl benzene sulfonate detergent composition derived from a kerosene fraction of petroleum distillate and containing about 80% to about 85% of sodium higher petryl benzene sulfonate and about 20% to about 40% of inorganic salts (mainly sodium sulfate), the proportions of ingredients (in terms of 100 parts of the total weight of the three components on an anhydrous basis) may be as follows:

**Component:**
- **Sodium higher petryl benzene sulfonate composition**
  - Parts: 20 to 60
- **Soap**
  - Parts: 15 to 55, preferably 25 to 45
- **Starch**
  - Parts: 5 to 40, preferably 20 to 30

Another commercially available higher petryl benzene sulfonate composition, containing about 85% to about 95% of sodium higher petryl benzene sulfonate derived from a kerosene fraction of petroleum and about 5% to about 15% of inorganic salts (mainly sodium sulfate), is particularly advantageous for use in connection with the present invention in view of its low content of inorganic salt. When using a higher petryl sulfonate composition of the latter type, a relatively larger amount of soap is employed to compensate for the lesser amount of salt present in the mixture. For example, the proportions of ingredients (in terms of 100 parts of the total weight of the three components on an anhydrous basis) may be as follows:

**Component:**
- **Sodium higher petryl benzene sulfonate composition**
  - Parts: 30 to 60
- **Soap**
  - Parts: 20 to 50, preferably 40 to 70
- **Starch**
  - Parts: 5 to 20, preferably 20 to 30

Other forms of commercially available higher petryl sulfonates may be employed, a number of which are disclosed in the patent, above referred to. Of these, the higher petryl aromatic sulfonates are preferred. The higher petryl aromatic sulfonates are mixtures of substituted derivatives of aromatic sulfonates which preferably contain not more than two benzene nuclei in the aromatic radical and of which a substituent in the aromatic radical nucleus is derived from a polycrystalline, non-aromatic hydrocarbon mixture of the type of a
petroleum distillate, and preferably of mineral origin, of which at least 80% boils (distills) between 150° and 280° C. The term "poly-component non-aromatic hydrocarbon mixture" as employed herein means a hydrocarbon mixture, such as petroleum or a petroleum distillate or otherwise refined petroleum fraction, or other mixture of similar composition, containing straight and/or branched chain alkanes and/or alkenes, but does not contain more than 20% of aromatic hydrocarbons. For convenience, the mixture of substituted derivatives of aromatic sulfonates are referred to as "mixtures of alkyl aromatic sulfonates," the term "alkyl" being used in its broad sense to include straight or branched, open-chain aliphatic hydrocarbon radicals, as well as radicals derived from cyclo-aliphatic and aromatic hydrocarbon radicals which may be present in the polycomponent hydrocarbon mixture.

They are mixtures of water-soluble products represented by the general formula

\[ R - A X \text{SO}_3 Y \]

wherein \( A \) represents an aromatic nucleus preferably containing no more than two benzene nuclei which may be condensed or not (for example, a benzene nucleus, a naphthalene nucleus, a diphenyl nucleus, or a diphenyl oxide nucleus); \( R \) represents an "alkyl" group which is directly attached to a carbon atom of the nucleus represented by \( A \) and which is derived from the hydrocarbon mixture and corresponds with a component thereof; \( X \) represents a representative hydrogen of the aromatic nucleus represented by \( A \) or a substituent such as an alkyl group containing 1 to 8 carbon atoms, a hydrocyclo group, an alkyloxy group, or an aryloxy group containing 1 to 6 carbon atoms, or halogen; \( Y \) represents the numbers 1, 2, or 3; and \( \text{SO}_3 Y \) represents a sulfonate group which is attached to a carbon atom of the aromatic nucleus represented by \( A \) and in which \( Y \) is hydrogen or the stochiometric equivalent of a salt-forming metal or radical; such as sodium, potassium, ammonium, alkyl ammonium, hydroxyl-alkyl ammonium, and the like. Thus, the mixtures of higher petroly aromatic sulfonates may be derived from benzene, toluene, xylene, phenol, cresol, anisole, phenol, chlorobenzene, diphenyl, hydroxydiphenyl, diphenyl oxide, naphthalene, alpha-naphthol, beta-naphthol, etc. Those derived from mononuclear aromatic compounds, and especially benzene, are preferred. Ordinarily the sodium salts are preferred by reason of their lower cost.

Preferably, they are mixtures obtained by a process comprising chlorinating the polycylic hydrocarbon mixture to form mixed alkyl chlorides, condensing resulting mixed alkyl chlorides with a mononuclear aromatic hydrocarbon or a derivative thereof to produce a mixture of mixed alkyl derivatives of said aromatic hydrocarbon or derivative and sulfonating a mixture of said or derivative, and sulfonating a mixture of said or derivative.

The following example illustrates the preparation of such a higher petroly benzene sulfonate by such a process. The parts by weight are:

**Example A**

A Pennsylvania kerosene boiling from 180° C. to 280° C., 80% of which boiled between 190° and 255° C., was chlorinated between 70° and 75° C. until the specific gravity of the latter had increased from 0.788 at 24° C. to 0.918 at 24° C. 10 parts of the resulting chlorinated kerosene were divided equally and kept at 25° C. for 75 minutes into a mixture of 20 parts of benzene and 0.5 part of aluminum chloride, while gradually raising the temperature to 45° C., after which the mixture was agitated at 45° C. for 15 minutes and then allowed to stratify. The upper layer of oil was removed from the lower layer and distilled, and the fraction which boiled between 95° and 240° C. at 3 to 7 mm. of mercury absolute pressure was collected separately. The collected fraction was refined by agitating it with 18.4% of the weight of 100% sulfuric acid at about 40° C. for 30 to 40 minutes, allowing the mass to settle 30 minutes, discarding the lower acid layer. The refined oil was mixed with 1.35 times its weight of 100% sulfuric acid at 30° C., the mixture was warmed to 55° to 60° C., agitated at that temperature for 1 hour and allowed to stratify for 4 hours, and the lower layer was drawn off. The remainder containing higher petroly benzene sulfonic acid was rendered neutral to Nitrazine Yellow paper by stirring it into about one and one-half times its weight of water simultaneously with 50% aqueous caustic soda. To the neutralized mass, which contained about 35% of inorganic salt (mostly sodium sulfate) and about 65% of sodium higher petroly benzene sulfonate on a dry basis, sufficient sodium sulfate was added to give a dry composition containing 40% of inorganic salts and about 60% of sodium keryl benzene sulfonate, and the resulting mixture was drum dried.

In addition to the essential components above referred to, other substances usually incorporated in milled soaps may be included in the compositions of the present invention. Thus, perfumes, pigments, coloring agents, antiseptics, and the like may be incorporated into the compound prepared from the sodium salts of higher petroly aromatic sulfonates in the proportions of the present invention. Further, substances imparting supplementary surface activity to the above essential components may be included, especially when the amount of higher petroly sulfonate is relatively small; for example, lower alkyl aromatic sulfonates, particularly sodium isopropyl naphthalene sulfonate, sodium di-isopropyl naphthalene sulfonate, sodium butyl naphthalene sulfonate, the ingredients may be mixed and converted into bar form in any suitable equipment. Thus, the mixture may be milled, plodd ed and stamped in apparatus commonly used for manufacturing high-grade toilet soaps. Where highly concentrated compositions are employed, relatively little milling may be required to achieve the desired degree of homogeneity, and such compositions may be formed directly into bars by passage through a plodder, which itself provides some milling action.

To promote easy working, it is helpful to warm the composition, say to 90° to 120° F. Such temperatures may be developed in part or completely by the friction of the milling and plodding action. The shaping dies of the plodder may be heated, say to about 140° F, to facilitate the ex-
A mixture of 45 parts of powdered corn starch, 515 parts of "2" soap (a pure soap of 39\% titre sold by John Powell and Company, Inc., New York city), adjusted to contain 110 parts of moisture, and 675 parts of the product of Example 1 (a sodium higher petryl benzene sulfonate detergent containing about 40\% of sodium sulfate and about 60\% of a sodium higher petryl benzene sulfonate derived from a kerosene fraction of Pennsylvania petroleum) was intimately mixed in a Day soap mixer. A small amount of water-soluble coloring matter and 0.5\% of emulsified perfume oil were added. The resulting mixture, which was a free-flowing powder essentially devoid of lumps or "doughiness," was transferred to the hopper of a Houchin soap plodder. The mixture flowed into the plodder without external pressure and issued therefrom in the form of a uniform, tough bar, which looked like a bar of well-made toilet soap, notwithstanding the fact that the soap content of the bar was only 27\%. The resulting bar, when shaped to the desired form in a stamping machine, did not "sweat" on exposure to the atmosphere, or "frost," disintegrate or become soft in use, and lathered and washed well in water of various degrees of hardness, as well as sea water. Strikingly inferior results were obtained by replacing the starch in this example with equal amounts of soap or other d理uents. Thus, when urea, "Cerelose," cane sugar, wheat flour, or bentonite were employed in place of starch in this example, mixtures were obtained which, when moistened in the Day mixer, became doughs of varying toughness and tachiness. Such compositions required pressure to feed them from the hopper to the plodder, they tended to adhere to the plodder parts, and issued from the plodder in the form of bars which were rough, crumbly, or sticky, or if smooth they lacked the gloss and finish of toilet soap. In general, the workability, ability to feed itself from the hopper into the mill or plodder, speed of passage through the plodder, and time of milling required to give a satisfactory bar of such compositions was considerably poorer than that of corresponding compositions employing starch.

The following examples illustrate additional soap-higher petryl sulfonate-starch mixtures which, in accordance with this invention, when milled and plodded into bar form in the foregoing manner, showed better workability in the 80 plodder than mixtures wherein the starch was replaced by soap or others of the d理uents mentioned previously, and yielded smooth bars that possessed good firmness and appearance, and did not "sweat," "frost," disintegrate, or become soft in use.

Example 2

"818" soap chips (a pure tallow soap of 41\% titre sold by Armour & Company) adjusted to contain about 7 parts of moisture.
Sodium higher petryl benzene sulfonate detergent employed in Example 1.
Corn starch

Example 3

Parts
"#818" soap chips adjusted to contain about 7 parts of moisture.
Detergent composition containing approximately 15.8 parts of inorganic salts (mostly sodium sulfate) and 29.2 parts of a mixture consisting of a sodium higher petryl benzene sulfonate derived from a kerosene fraction of Pennsylvania petroleum (11.7 parts) and sodium di-isopropynaphthene sulfonate (17.5 parts).
Corn starch

Example 4

Parts
"#818" soap chips adjusted to contain about 9 parts of moisture.
Sodium higher petryl benzene sulfonate detergent employed in Example 1.
Corn starch

Example 5

Parts
"#818" soap chips adjusted to contain about 8 parts of moisture.
Sodium higher petryl benzene sulfonate detergent employed in Example 1.
Corn starch

Example 6

Parts
"#818" soap chips adjusted to contain about 10 parts of moisture.
Sodium higher petryl benzene sulfonate detergent employed in Example 1.
Corn starch

Example 7

Parts
"Harris" soap chips (10\% coconut oil soap and 90\% tallow soap) containing about 10 parts of moisture.
Sodium higher petryl benzene sulfonate detergent containing about 10\% of inorganic salts (mostly sodium sulfate) and about 90\% of a sodium higher petryl benzene sulfonate derived from a kerosene fraction of Pennsylvania petroleum.
Corn starch

Example 8

Parts
"Lux" soap flakes adjusted to contain about 9 parts of moisture.
Detergently composition containing approximately 9.1 parts of inorganic salts (mostly sodium sulfate), and 27.4 parts of a mixture consisting of a sodium higher petryl benzene sulfonate derived from a kerosene fraction of Pennsylvania petroleum (11 parts) and sodium di-isopropynaphthene sulfonate (16.4 parts).
Corn starch

Example 9

Parts
"#818" soap chips adjusted to contain about 10 parts of moisture.
Sodium higher petryl benzene sulfonate detergent employed in Example 7.
Corn starch
Sodium higher petryl sulfonate detergent

Example 10

<table>
<thead>
<tr>
<th>Parts</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lux soap flakes adjusted to contain about 8 parts of moisture..........................</td>
<td>26</td>
</tr>
<tr>
<td>Sodium higher petryl sulfonate detergent sold by E. I. du Pont de Nemours &amp; Company, Inc. under the name &quot;MP-188&quot; and containing about 11 parts of inorganic salts and about 21 parts of sodium higher petryl sulfonate of the type described in U. S. Reissue Patent No. 20,968 and U. S. Patents No. 2,197,800; 2,202,791; 2,239,974 and 2,276,590</td>
<td>5</td>
</tr>
<tr>
<td>Corn starch</td>
<td>27</td>
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Example 11

<table>
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<tr>
<th>Parts</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toilet soap stock adjusted to contain about 7 parts of moisture..........................</td>
<td>59</td>
</tr>
<tr>
<td>Sodium higher petryl benzene sulfonate detergent employed in Example 7</td>
<td>30</td>
</tr>
<tr>
<td>Corn starch</td>
<td>11</td>
</tr>
<tr>
<td>Titanox (titanium oxide pigment)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Example 12

<table>
<thead>
<tr>
<th>Parts</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toilet soap stock adjusted to contain about 8 parts of moisture..........................</td>
<td>43</td>
</tr>
<tr>
<td>Sodium higher petryl benzene sulfonate detergent employed in Example 1</td>
<td>29</td>
</tr>
<tr>
<td>Corn starch</td>
<td>30</td>
</tr>
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</table>

Example 13

<table>
<thead>
<tr>
<th>Parts</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toilet soap stock adjusted to contain about 10 parts of moisture..........................</td>
<td>48</td>
</tr>
<tr>
<td>Sodium higher petryl benzene sulfonate detergent employed in Example 1</td>
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</tr>
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<td>Corn starch</td>
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Example 14

<table>
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<tr>
<th>Parts</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toilet soap stock adjusted to contain about 10 parts of moisture..........................</td>
<td>52</td>
</tr>
<tr>
<td>Sodium higher petryl benzene sulfonate detergent employed in Example 1</td>
<td>25</td>
</tr>
<tr>
<td>Corn starch</td>
<td>25</td>
</tr>
</tbody>
</table>

Example 15

<table>
<thead>
<tr>
<th>Parts</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toilet soap stock adjusted to contain about 10 parts of moisture..........................</td>
<td>56</td>
</tr>
<tr>
<td>Sodium higher petryl benzene sulfonate detergent employed in Example 1</td>
<td>35</td>
</tr>
<tr>
<td>Corn starch</td>
<td>20</td>
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</table>

Example 16

<table>
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<tr>
<th>Parts</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toilet soap stock adjusted to contain about 9 parts of moisture..........................</td>
<td>59</td>
</tr>
<tr>
<td>Sodium higher petryl benzene sulfonate detergent employed in Example 1</td>
<td>40</td>
</tr>
<tr>
<td>Corn starch</td>
<td>27</td>
</tr>
</tbody>
</table>

It will be realized by those skilled in the art that the invention is not limited to the above specific examples and that changes may be made in the compositions and processes of preparing them, within the scope of the appended patent claims.

Thus, instead of the specific components employed in the above examples, others of the substances referred to above may be substituted in equal amounts. Further, as above noted, additional substances may be incorporated into the compositions besides the essential components: a hard soap, a higher petryl sulfonate, and starch.

As above noted, the amount of salt employed relative to the amount of higher petryl sulfonate will depend upon several factors, one of which is the amount of sodium sulfate and/or other inorganic salts present in the higher petryl sulfonate or otherwise incorporated into the composition or otherwise incorporated into the mixture or otherwise incorporated into the admixture. In general, the amount of soap is reduced to compensate for the amount of sodium sulfate and other inorganic salts present in the composition.

Thus, in accordance with the present invention, the compositions subjected to milling may contain the following compositions: (1) a hard soap, (2) a higher petryl sulfonate, and (3) starch, together with (4) inorganic salt in an amount ranging from 0% to 25% of the weight of the admixture, in the following proportions by weight of said components (1), (2), and (3), on the basis of a total weight of 100 parts of said four components:

Component: Higher petryl sulfonate | at least 6

Soap | 15 to (85-50), where 50 equals the weight of inorganic salt

Starch | 5 to 40

In this case, the minimum amount of soap is 15 parts by weight, and the maximum amount is 85 parts by weight, and the weight less the weight of inorganic salt.

It is noted that the amount of sodium sulfate and/or other inorganic salts present in the higher petryl sulfonate will depend upon several factors, one of which is the amount of sodium sulfate and/or other inorganic salts present in the higher petryl sulfonate or otherwise incorporated into the composition or otherwise incorporated into the admixture. In general, the amount of soap is reduced to compensate for the amount of sodium sulfate and other inorganic salts present in the composition.

Thus, in accordance with the present invention, the compositions subjected to milling may contain the following components: (1) a hard soap, (2) a higher petryl sulfonate, and (3) starch, together with (4) inorganic salt in an amount ranging from 0% to 25% of the weight of the admixture, the proportions by weight of said components (1), (2), and (3), on the basis of a total weight of 100 parts of said four components, may be within the following ranges:

Component: Higher petryl aromatic sulfonate | at least 10

Soap | 30 to 85, less the weight of sodium sulfite

Starch | 10 to 40

In this instance, the amount of soap may vary from 30 parts by weight, minus the weight of the sodium sulfite, to 80 parts by weight, minus the weight of sodium sulfite.

I claim:

1. In the manufacture of a milled soap from a mixture comprising water and at least the following components: (1) a soap which forms solid masses under normal atmospheric conditions and which is selected from the group consisting of the alkali metal, ammonium, and organic amine salts of higher fatty acids containing 12 to 22 carbon atoms, and (2) a higher petryl sulfonate, the improvement which comprises incorporating (3) starch into a mixture of said type containing an amount of (4) inorganic salt ranging from 0% to 25% of the weight of the mixture, milling and plodding the resulting mixture, and controlling the workability of the mixture in the milling and plodding operations by proportioning the amounts of components (1), (2), and (3) so that the relative weights and the total weight of 100 parts of components (1), (2), and (3), and (4), lie within the following ranges:

Component: Parts

Soap | 15 to (85-50), where 50 equals the weight of inorganic salt

Higher petryl sulfonate | at least 6

Starch | 5 to 40

and limiting the amount of water in said mixture to 6 to 15 parts per 100 parts of the total weight of components (1), (2), (3), and (4).
In the manufacture of a milled soap from a mixture comprising water and at least the following components: (1) a soap which forms solid masses under normal atmospheric conditions and which is selected from the group consisting of the alkali metal, ammonium, and organic amine salts of higher fatty acids containing 10 to 20 carbon atoms, and (2) a higher petryl sulfonate, the improvement which comprises incorporating (3) starch into a mixture of said type containing an amount of (4) sodium sulfate ranging from 0% to 20% of the weight of the mixture, milling and plodding the resulting mixture; and controlling the workability of the mixture in the milling and plodding operations by proportioning the amounts of components (1), (2), (3), and (4), so that their relative weights, on the basis of a total weight of 100 parts of components (1), (2), (3), and (4), lie within the following ranges:

Component:  
Parts
Soap------------- 15 to 85-X, where X equals the weight of sodium sulfate
Higher petryl sulfonate ----------- at least 10
Starch----------  10 to 40

and limiting the amount of water in said mixture to 6 to 15 parts per 100 parts of the total weight of components (1), (2), (3), and (4).

3. In the manufacture of a milled soap from a mixture comprising water and at least the following components: (1) a soap which forms solid masses under normal atmospheric conditions and which is selected from the group consisting of the alkali metal, ammonium, and organic amine salts of higher fatty acids containing 10 to 20 carbon atoms, and (2) a higher petryl aromatic sulfonate, milling and plodding the resulting mixture; and controlling the workability of the mixture in the milling and plodding operations by the improvement which comprises incorporating (3) starch into a mixture of said type containing an amount of (4) sodium sulfate ranging from 0% to 20% of the weight of the mixture; milling and plodding the resulting mixture; controlling the workability of the mixture in the milling and plodding operations by proportioning the amounts of components (1), (2), (3), and (4), so that their relative weights, on the basis of a total weight of 100 parts of components (1), (2), (3), and (4), lie within the following ranges:

Component:  
Parts
Soap------------- 15 to 85-X, where X equals the weight of sodium sulfate
Higher petryl aromatic sulfonate ----------- at least 8
Starch----------  5 to 40

and limiting the amount of water in said mixture to 6 to 15 parts per 100 parts of the total weight of components (1), (2), (3), and (4), and forming the plodded mixture into bars.

4. In the manufacture of a milled soap from a mixture comprising water and at least the following components: (1) a soap which forms solid masses under normal atmospheric conditions and which is selected from the group consisting of the alkali metal, ammonium, and organic amine salts of higher fatty acids containing 10 to 20 carbon atoms and (2) a higher petryl aromatic sulfonate, the improvement which comprises incorporating (3) starch into a mixture of said type containing an amount of (4) sodium sulfate ranging from 0% to 20% of the weight of the mixture; milling and plodding the resulting mixture; controlling the workability of the mixture in the milling and plodding operations by proportioning the amounts of components (1), (2), (3), and (4), so that their relative weights, on the basis of a total weight of 100 parts of components (1), (2), (3), and (4), lie within the following ranges:

Component:  
Parts
Soap------------- 30 to 80, less the weight of sodium sulfate
Higher petryl aromatic sulfonate ----------- 6 to 40
Starch----------  10 to 40

and limiting the amount of water in said mixture to 6 to 15 parts per 100 parts of the total weight of said components (1), (2), (3), and (4), and forming the plodded mixture into bars.

5. In the manufacture of a milled soap from a mixture comprising water and at least the following components: (1) a soap which forms solid masses under normal atmospheric conditions and which is selected from the group consisting of the alkali metal, ammonium, and organic amine salts of higher fatty acids containing 10 to 20 carbon atoms, and (2) a higher petryl mononuclear aromatic sulfonate, the improvement which comprises incorporating (3) starch into a mixture of said type containing an amount of (4) sodium sulfate ranging from 0% to 20% of the weight of the mixture; milling and plodding the resulting mixture; controlling the workability of the mixture in the milling and plodding operations by proportioning the amounts of components (1), (2), (3), and (4), so that their relative weights, on the basis of a total weight of 100 parts of components (1), (2), (3), and (4), lie within the following ranges:

Component:  
Parts
Soap------------- 30 to 80, less the weight of sodium sulfate
Higher petryl mononuclear aromatic sulfonate ----------- 6 to 40
Starch----------  10 to 40

and limiting the amount of water in said mixture to 6 to 15 parts per 100 parts of the total weight of said components (1), (2), (3), and (4), and forming the plodded mixture into bars.

6. In the manufacture of a milled soap from a mixture comprising water and at least the following components: (1) a soap of said type and (2) a higher petryl benzene sulfonate, the improvement which comprises incorporating (3) starch into a mixture of said type containing an amount of (4) sodium sulfate ranging from 0% to 20% of the weight of the mixture; milling and plodding the resulting mixture; and controlling the workability of the mixture in the milling and plodding operations by proportioning the amounts of components (1), (2), (3), and (4), so that their relative weights, on the basis of a total weight of 100 parts of components (1), (2), (3), and (4), lie within the following ranges:

Component:  
Parts
Soap------------- 30 to 80, less the weight of sodium sulfate
Higher petryl benzene sulfonate ----------- 10 to 40
Starch----------  10 to 40

and limiting the amount of water in said mixture to 6 to 12 parts per 100 parts of the total weight of said components (1), (2), (3), and (4).

7. In the manufacture of a milled soap from a mixture comprising water and at least the following components: (1) a sodium soap adapted for toilet use and (2) a sodium higher petryl benzene sulfonate composition containing 80% to 60% of its weight of a sodium higher petryl benzene sulfonate and 30% to 40% of its weight.
of inorganic salts, the improvement which comprises incorporating (3) starch into a mixture of said type; milling and plodding the resulting mixture; and controlling the workability of the mixture in the milling and plodding operations by proportioning the amounts of components (1), (2), and (3) so that their relative weights, based on a total weight of 100 parts of said components (1), (2), and (3), lie within the following ranges:

Component:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Soap</th>
<th>Sodium higher petryl benzene sulfonate composition</th>
<th>Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 to 55</td>
<td>20 to 60</td>
<td>5 to 40</td>
<td></td>
</tr>
</tbody>
</table>

and limiting the amount of water in said mixture to 6 to 15 parts per 100 parts of the total weight of said components (1), (2), and (3).

8. In the manufacture of a milled soap from a mixture comprising water and at least the following components: (1) a sodium soap adapted for toilet use and (2) a sodium higher petryl benzene sulfonate composition containing 85% to 85% of its weight of sodium petryl benzene sulfonate and 5% to 15% of its weight of inorganic salts, the improvement which comprises incorporating (3) starch into a mixture of said type; milling and plodding the resulting mixture; and controlling the workability of the mixture in the milling and plodding operations by proportioning the amounts of components (1), (2), and (3) so that their relative weights, based on a total weight of 100 parts of said components (1), (2), and (3), lie within the following ranges:

Component:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Soap</th>
<th>Sodium higher petryl benzene sulfonate composition</th>
<th>Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 to 80</td>
<td>10 to 40</td>
<td>5 to 40</td>
<td></td>
</tr>
</tbody>
</table>

and limiting the amount of water in said mixture to 6 to 15 parts per 100 parts of the total weight of said components (1), (2), and (3).

9. A milled soap composition comprising as its essential components: (1) a soap which forms solid masses under normal atmospheric conditions and which is selected from the group consisting of the alkali metal, ammonium, and organic amine salts of higher fatty acids containing 10 to 20 carbon atoms, (2) a higher petryl sulfonate, and (3) starch, together with (4) inorganic salt in an amount ranging from 0% to 20% of the total weight of said four components, the proportions by weight of said components (1), (2), and (3), on the basis of a total weight of 100 parts of said four components, lying within the following ranges:

Component:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Soap</th>
<th>Higher petryl sulfonate</th>
<th>Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 to 55</td>
<td>10 to 40</td>
<td>at least 8</td>
<td></td>
</tr>
</tbody>
</table>

said composition containing not more than 15 parts of water per 100 parts of the total weight of said four components.

10. A milled soap composition comprising its essential components: (1) a soap which forms solid masses under normal atmospheric conditions and which is selected from the group consisting of the alkali metal, ammonium, and organic amine salts of higher fatty acids containing 10 to 20 carbon atoms, (2) a higher petryl sulfonate, and (3) starch, together with (4) sodium sulfate in an amount ranging from 0% to 20% of the total weight of said four components, the proportions by weight of said components (1), (2), and (3), on the basis of a total weight of 100 parts of said four components, lying within the following ranges:

Component:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Soap</th>
<th>Higher petryl sulfonate</th>
<th>Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 to 55</td>
<td>at least 10</td>
<td>10 to 40</td>
<td></td>
</tr>
</tbody>
</table>

said composition containing not more than 15 parts of water per 100 parts of the total weight of said four components.
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15 parts of water per 100 parts of the total weight of said four components.

14. A milled soap composition comprising as its essential components (1) a sodium soap, (2) a sodium higher petryl benzene sulfonate detergent containing about 60% of its weight of sodium higher petryl benzene sulfonate derived from a kerosene fraction of petroleum and about 40% of its weight of inorganic salts, and (3) starch, in the following proportions by weight based upon a total of 100 parts by weight of said three components:

Component: | Parts |
---|---|
Soap | 15 to 45 |
Sodium higher petryl benzene sulfonate detergent | 40 to 60 |
Starch | 10 to 40 |

said composition containing not more than 15 parts of water per 100 parts of the total weight of said three components.

15. A milled soap composition comprising as its essential components (1) a sodium soap, (2) a sodium higher petryl benzene sulfonate detergent containing sodium sulfate, and (3) starch, the amount of sodium sulfate ranging from 20% to 40% of the weight of the higher petryl benzene sulfonate detergent, the proportions by weight of said components (1), (2), and (3) on the basis of a total weight of 100 parts of said three components lying within the following ranges:

Component: | Parts |
---|---|
Soap | 25 to 45 |
Sodium higher petryl benzene sulfonate detergent | 20 to 60 |
Starch | 10 to 40 |

said composition containing not more than 15 parts of water per 100 parts of the total weight of said three components.

16. A milled soap composition comprising as its essential components: (1) a sodium soap adapted for toilet use, (2) a higher petryl aromatic sulfonate detergent containing sodium sulfate, and (3) starch, the amount of sodium sulfate ranging from 5% to 15% of the weight of the higher petryl aromatic sulfonate detergent, the proportions by weight of said components (1), (2), and (3) on the basis of a total weight of 100 parts of said three components lying within the following ranges:

Component: | Parts |
---|---|
Soap | 40 to 80 |
Higher petryl aromatic sulfonate detergent | 10 to 40 |
Starch | 5 to 40 |

said composition containing not more than 15 parts of water per 100 parts of the total weight of said three components.

17. A milled soap composition comprising as its essential components: (1) a sodium soap adapted for toilet use, (2) a sodium higher petryl benzene sulfonate detergent containing sodium sulfate, and (3) starch, the amount of sodium sulfate ranging from 5% to 15% of the weight of the higher petryl benzene sulfonate detergent, the proportions by weight of said components (1), (2), and (3) on the basis of a total weight of 100 parts of said three components lying within the following ranges:

Component: | Parts |
---|---|
Soap | 40 to 80 |
Sodium higher petryl benzene sulfonate detergent | 10 to 40 |
Starch | 5 to 40 |

said composition containing not more than 15 parts of water per 100 parts of the total weight of said three components.

LESTER FRANCIS HOYT.

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