The oxidized starches, which may be prepared by treating starch with an alkaline hypochlorite are easier to use in preparing the actual product than the unoxidized starches. These oxidized starches may be gelatinized with much less water than the untreated starch; normally a ratio of 4 parts of water to one of oxidized starch is sufficient in the presence of synthetic detergents and soaps, both of which are retarders of gelatinization. The oxidized starches are readily available from starch manufacturers. The compositions of our invention contain at least 10% of sodium soaps of fatty acids, preferably from tallow or coconut oil. These may be added in whole or in part to the aqueous solution and dispersion used to gelatinize the starch, but it is conducive to better appearance if these sodium soaps are added after the starch preparation has been dried.

Our preferred method for gelatinizing the starch is to add to a mixer, commonly called a crutcher in the soap industry, enough hot water so that the mix will contain from about 55 to about 70% of water when all ingredients including the synthetic detergent that are to go into the crutcher are placed therein. The synthetic detergent or detergents and any other ingredients that it is desirable to add at this time are then added and dispersed in the water. The oxidized starch is then added, and thoroughly dispersed with an auxiliary high speed mixer. On a pilot plant scale this may be accomplished with a hand-held, motor driven, propeller type mixer.

The crutcher is then run with the regular agitation. The mix is roll dried and the completion of the gelatinization of the starch takes place on the rolls. The temperature required to effect the completion of gelatinization is achieved when the rolls are supplied with steam at about 60 lbs. pressure, and will vary with different starches. As indicated in Figure 1 of the drawing, gelatinization of cornstarch may be effected at about 80°C. and of potato starch at about 90°C. Time is, of course, a factor and, generally speaking, lower temperatures may be employed when the starch is heated for a longer period of time.

Figure 2 shows the appearance of oxidized starch in a crutcher mix. The dark cross dividing each granule into four parts is typical of the birefringence shown by ungelatinized starches. Figure 3 shows the complete disappearance of birefringence in the finished bar.

The dried crutcher mix may be milled, extruded, and stamped in conventional soap making equipment. If the sodium soap was not added to the crutcher it should be added before milling. The sodium soap may be added as dried flakes or pellets, or part of it may be added as neat soap containing about 30% water, if the dried mix requires water to bring the moisture content up to that desired in the finished bar. When we refer to sodium soap we mean a soap where the alkali is predominantly sodium, a small amount, about 5 to 10%, of potassium soap may be present without softenning the bar unduly.

The sodium soap is conveniently mixed with the roll dried mix in the amalgamator—a device for mixing materials with dried soaps. An amalgamator is commonly used to mix perfume and coloring matter with soaps before milling. In small scale work, such as some described hereafter, the mixing may be accomplished with and the mixing achieved by an extra pass thru the milling rolls.

The synthetic detergents that may be employed in the practice of the invention are the normally solid synthetics, commonly referred to as anionic organic sulfonic reaction products. Cationic detergents are not suitable, being incompatible with soap, and nonionic detergents are commonly either liquid or paste, and are often nonlathering.

This invention relates to a detergent bar containing, as the detergent constituent, synthetic detergent and soap, and containing starch acting as a binder and filler. It is an object of the invention to provide a detergent bar of this type having improved properties.

Synthetic detergents in bar form containing starch have hitherto lacked the characteristic "feel" of ordinary toilet soap, having what is referred to in the art as a "draggy feel." Furthermore, bars of this type usually have tendency to smear or develop a slimy outer surface when left in contact with water, which detracts markedly from the appearance of the bar, necessitates frequent cleaning of the soap dish, and results in excessive waste.

We have discovered that these and other defects of starch filled detergent bars may be overcome, and the characteristics of such bars otherwise improved, if the starch be properly gelatinized as hereinafter described.

Further objects and features of the invention will be apparent from the following description taken in connection with the accompanying drawings, in which:

Figure 1 is a graphical representation of the effect of temperature on gelatinization of certain starches, and

Figures 2 and 3 are photomicrographs of compositions containing starch in normal and gelatinized form, respectively.

If starch is suspended in water and heated, a gradual taking up of water (gelatinization) occurs. This is described in Radley, "Starch and Its Derivatives," 2d ed., vol. 1, pages 89 and 90. Figure 1, taken from the publication by Radley, shows how the gelatinization of potato and corn starch proceeds. We prefer to determine the extent of gelatinization by means of a microscope fitted with cross Nicol prisms. The ungelatinized particles show a birefringence when thus viewed. In the practice of the present invention, we prefer to gelatinize to the point B, Fig. 1, where all of the anisotropy as shown by birefringence has disappeared. As stated by Radley in speaking of gelatinization generally, some workers in the field consider the point of gelatinization to be the point A, where anisotropy disappears from the majority of the granules, but for use of the gelatinized starch in synthetic bar formulations, we find the characteristics we desire to be more fully developed if we gelatinize until all anisotropy disappears.

The starch used should be a normal (non-waxy) starch. The amylose content of these non-waxy starches is reported to be from about 15 to about 25 percent and this type of starch appears necessary for the attainment of the characteristics we desire. The waxy starches, containing little or no amylose, do not yield a satisfactory product.

The normal starch may be brought to the desired condition in a number of ways. It may be suspended in water and heated. This has the disadvantage of introducing a large amount of water into the composition because normal starch will not gelatinize unless suspended in more than about 15 times its weight of water.

2,982,735
DETERGENT MILLED BAR AND PROCESS OF PREPARING SAME
Joseph Blinka and Preston W. Grounds, Jr., Cincinnati, Ohio, assignors to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio
Filed Sept. 8, 1955, Ser. No. 533,681
12 Claims. (Cl. 252—121)
The following examples of suitable water-soluble synthetic detergents are given only for the purpose of illustrating the wide variety of types of detergent compounds useful in the practice of the invention and it will be appreciated that the scope of the invention is not thereby limited.

Alkyl glyceryl ether sodium sulfate in which the alkyl is 50% -docetyl.

The alkyl sulfates, typified by sodium docetyl sulfate.

The alkyl monoglyceride sulfates, such as coconut monoglyceride sodium sulfate. (These are preferably not used with alkaline builders.)

The alkyl monoglycol sulfates, such as coconut ethylene mono glycol sodium sulfate.

The alkyl monoglycerol sulfonates, such as coconut monoglycerol sodium sulfonates.

The isethionates—RCOOC₂H₅₂SO₃Na—where the RCO preferably represents acyl radicals in a mixture of fatty acids from oils of the coconut group, for example coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide.

By oils of the coconut group we mean to designate vegetable seed or nut oil having at least 50% by weight of the combined fatty acids as lauric and/or myristic.

Practically all of these are derived from nuts of the palm family such as coconut oil, palm kernel oil, tucum kernel, and babassu nut oil.

The methyl tarines RCONH₂CH₂₂SO₄Na, where RCOOCH₃ preferably represents acyl radicals contained in fatty acids derived from an oil of the coconut group specifically the sodium salt of coconut sulfonate.

Detergents made by sulfating and neutralizing the compounds made by reacting a coconut fatty amine with hydroxy acetic acid.

The alkyl benzene sulfonates, where the alkyl is a keryl or a polypropylene of C₆ to C₁₅, are satisfactory physically, if their tendency to exhibit a sticky feel is not objectionable under their circumstances of use.

There may be used with the normally solid anionic detergents listed above, a limited amount of pasty or even liquid synthetics such as the nonionic synthetics.

In the following examples the quantities are given on the "pure" basis, that is, water and sodium chloride and sulfates have been subtracted from the gross weights used.

Example 1.—700 ml. of hot water were added to a 1000 gram crucher. To this was added 45 grams of sodium salt of middle cut coconut alcohol sulfate containing about 65% C₁₂ alcohol and 21 grams of the sulfated and sodium neutralized reaction product of 1 mole of the same middle cut coconut alcohol and three moles of ethylene oxide. 30 grams of sodium soap of 80% tallow, 20% coconut oil was then added and 60 grams of sodium coconut oil soap. After these were dispersed, there was added 18 grams of sodium tripolyphosphate and this was dissolved. Then there was added 103 grams of Hercules No. 55 sizing starch (oxidized) made by Corn Products Refining Co; the starch was dispersed by high speed agitation and mixing was continued for about 20 minutes. The temperature was about 150° F, during this mixing. The mix was then rolled dried on a roll heated with steam at about 60 lbs. steam pressure at the rate of 1 lb. of dried product per hour per square foot of roll and examined for ungelatinized starch. No birefringence was noted. The mix was milled, extruded from a small plodder and stamped into 80 gram bars. The finished bar contained about 1% of sodium chloride and sodium sulfate and had a moisture content of 12%.

The bars were good in lather and excellent in resistance to smear when soaked in water overnight. The smear test was made by cutting off the stamped face of a bar to provide a flat surface. The bar was then soaked 16 hours in 70° water. The bar was weighed and then the soft "smeary" cut surface wiped off with the full force of the forefinger. The bar was then reweighed. The loss in weight compared to that of a similar bar of soap or detergent known to be satisfactory when tested in the same manner, is a measure of smear.

Example 2.—This composition was similar to Example 1, using the same ingredients, the synthetic detergents being increased over Example 1 and the starch being correspondingly decreased. The preparation was carried out exactly like Example 1, except for the change in proportions. The final product had the composition—dry basis:

<table>
<thead>
<tr>
<th>Percent</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Sodium middle cut coconut alkyl sulfate</td>
</tr>
<tr>
<td>9.5</td>
<td>Sodium soap of 80% tallow, 20% coconut oil</td>
</tr>
<tr>
<td>10</td>
<td>Sodium soap of coconut oil</td>
</tr>
<tr>
<td>6</td>
<td>Sodium tripolyphosphate</td>
</tr>
<tr>
<td>10.5</td>
<td>Salts and miscellaneous</td>
</tr>
<tr>
<td>24</td>
<td>Starch (Hercules #55)</td>
</tr>
</tbody>
</table>

The final bar had 13% moisture. This bar lathered as well as that of Example 1, and was practically the same in smear when soaked overnight in water.

The sodium middle cut coconut alkyl sulfate in this example may be replaced by sodium alkyl benzene sulfonate where the alkyl is polypropylene averaging about 12 carbons in the radical. The bar with alkyl benzene sulfonate performs as well as the one with coconut alkyl sulfate but it has a slightly sticky feel to the hands.

Example 3.—This was prepared similarly to Example 1. The finished product analysis, dry basis was:

<table>
<thead>
<tr>
<th>Percent</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Sodium middle cut coconut alkyl sulfate</td>
</tr>
<tr>
<td>6.5</td>
<td>Sodium salt of the sulfated reaction product of 3 moles of ethylene oxide to 1 mole of middle cut coconut alcohol</td>
</tr>
<tr>
<td>10</td>
<td>Sodium soap of 80% tallow, 20% coconut oil</td>
</tr>
<tr>
<td>20</td>
<td>Sodium coconut oil soap</td>
</tr>
<tr>
<td>6</td>
<td>Sodium tripolyphosphate</td>
</tr>
<tr>
<td>10.1</td>
<td>Salts and miscellaneous</td>
</tr>
<tr>
<td>27.4</td>
<td>Starch (Hercules #55)</td>
</tr>
</tbody>
</table>

Making 100 parts. To these 100 parts were added on the milling rolls 3.5 parts of middle cut coconut alcohol. The starched bar contained 12.2% of water. The coconut alcohol, a suds builder, improved the lather so that it was slightly better than that of Example 2. The overnight smear was almost the same as that of Example 2.

Example 4.—About 650 ml. of hot water at about 200° F. was added to a 1000 gram crucher. To this was added 45 grams of sodium middle cut alkyl sulfate containing about 65% C₁₂ alcohols. There was then added 9 grams of the sodium salt of the sulfated reaction product of 3 moles of ethylene oxide to 1 mole of fatty alcohol made from tallow. After these were well dispersed, there was added 103.5 grams of Hercules #55 sizing starch made by Corn Products Refining Co. The starch was dispersed with rapid agitation and then heated for about 20 minutes at about 150° F. The mix was then rolled dried, at about 60 lbs. steam pressure on the rolls at the rate of one pound of dried product per square foot of roll per hour. These conditions accomplished complete gelatinization of the starch. There was added to the milling rolls where the dried mix was milled, 75 grams of sodium soap of 80% tallow, 20% coconut oil.

There was also added 10.5 grams of middle cut coconut alcohol to act as a suds builder. These were thoroughly milled into the roll dried mix, which was then extruded and stamped.

On account of the low amount of alkyl sulfate, this
Example did not lather quite as well as the product of Example 3, and the overnight smear test was better than that of Example 3, showing that the properly gelatinized starch produces a bar that will hold together when soaked in 70° water for 16 hours. A bar with ungelatinized starch for example will lose in an overnight smear test, about twice as much weight as the formula made into a bar with gelatinized starch.

Example 5.—There was added to a 1000 gram crutcher about 650 ml of hot water at about 200° F. To this there was added 45 grams of sodium salt of middle cut fatty alcohol sulfate. To this was added 15 grams of sodium salt of the sulfated reaction product of 10 moles of ethylene oxide to 1 mole of tallow alcohol and 11.4 grams of sodium coconut oil soap. There was then added 45 grams of sodium tripolyphosphate. These were dispersed by mixing and there was added 84 grams of Hercules #55 sizing starch. The temperature had dropped to about 150° F., but this was enough to require rapid agitation to prevent the starch from gelatinizing in lumps. After the starch was well dispersed, the normal agitation of the crutcher was restored and the mixing continued for about 20 minutes. The mix was rolled dried at about 60 lb. per square inch steam pressure in the rolls, at the rate of one pound of dried product per square foot per hour. This was enough to complete the gelatinization of the starch. There was added on the mills 78.6 grams of sodium soap of 80% tallow, 20% coconut oil and 7.5 grams of middle cut coconut oil fatty alcohol. After milling, the bars were extruded and stamped. The bars contained 18% moisture. The bars were excellent in lather, but superior in resistance to smear, upon being soaked overnight in water, to those made with ungelatinized starch.

Example 6.—This was prepared like Example 5, but the proportions were different. The finished bar contained:

- Sodium salt of middle cut coconut alcohol sulfate .......................... parts by weight 20
- Sodium salt of the sulfated reaction product of 3 moles of ethylene oxide to 1 mole of tallow alcohol ............................................. parts 6.5
- Sodium soap of 80% tallow, 20% coconut oil ........................................ parts 18
- Sodium soap of coconut oil ................................................... parts 15
- Sodium tripolyphosphate .................................................... parts 5.8
- Starch (Hercules #55) ...................................................... parts 20.2
- Middle cut fatty alcohol .................................................. parts 2.5
- Moisture ................................................................... parts 13.8

This bar lathered well, and was satisfactory in smear tests.

Example 7.—In this example parts are shown by weight.

- 20 parts sodium alkyl glyceryl ether sulfonate (middle cut coconut alkyl)
- 10 parts sodium soap of 80% tallow, 20% coconut oil
- 15 parts sodium coconut oil soap
- 10 parts calcium hydrated soap of 80% tallow, 20% coconut oil
- 25 parts oxidized starch
- 10 parts water
- 10 parts miscellaneous salts.

The sodium alkyl glyceryl ether sulfonate is dissolved in enough water to constite 60 to 75% final mixture in a crutcher. The 80% tallow, 20% coconut soap to be made into calcium soap is then dissolved in the crutcher. The equivalent amount of calcium chloride is added and stirring per square foot of dispersion occurs. The dispersion is then added and dispersed with high speed agitation. After dispersion, the agitator is run at normal speed until a good mix is obtained. The crutcher mix is roll dried. The sodium soap of 80% tallow, 20% coconut oil is added as pellets and the sodium coconut soap as kettle soap to the amalgamator. After mixing, the lot is milled, plodded, and stamped. The hand lather was satisfactory.

In place of calcium chloride, magnesium sulfate in equivalent amounts stoichiometrically may be used. If it is desired to produce a mixture of calcium and magnesium soaps the chlorides of calcium and magnesium should be used to avoid the formation of relatively insoluble calcium sulfate.

The sodium salt of the coconut ester of isethionic acid may be used in place of the alkyl glyceryl ether sulfonate in the formula of Example 7 and will produce a bar of equivalent performance. While these examples contain synthetic detergents at the 20% level, it will be understood that the synthetic detergent may vary between 15 and 40% depending upon the qualities desired in a bar, and the sudsing power of the synthetic detergent used.

The detergent compositions described above are not limited to the particular detergents described. The synthetic detergents described above in the enumeration of normally solid synthetics can be substituted for detergents used in the above examples with substantially the same results.

We have prepared bars with as little as 15% starch as the only inert binder-filler and find them satisfactory, however the lowering of the starch requires the increasing of the soap or the anionic synthetic detergent or both. Increasing the soap increases the tendency to curd in hard water, and increasing the synthetic adds to the cost, with no improvement in performance. 15% of starch is about the lower limit in which starch is useful.

The upper limit is set by the fact that about 25% of active (synthetic detergent plus soluble soap) is the minimum for effective performance. There is usually about a minimum of 5% of miscellaneous inorganic salts, so the upper limit for starch in a bar is about 70%, although most of our compositions will be in the range of 15 to 45%.

The soluble soap is a desirable ingredient in a bar containing anionic synthetic detergent and starch. The soluble soap will normally be principally a sodium soap of coconut oil type or a sodium soap of tallow and coconut oil type. When the anionic synthetic detergent is used slowly as it is used, coconut soap is preferred as it acts to speed up lathering. The soluble soap will normally constitute 10 to 35% of our compositions. The soluble soap may be all tallow soap if speed of lathering is not a primary objective. The sum of the synthetic and soda soap will normally be not more than 65%.

The sodium soap may contain a minor proportion of potassium, ammonium, or substituted ammonia soap, but these will be limited in amount on account of their softness.

The synthetic bar containing properly gelatinized starch may be prepared by spray drying a detergent starch crutcher mix instead of roll drying. When this is done, it is desirable to pass the crutcher mix thru a process step involving vigorous agitation and disintegration, before spray drying. The period of heating in a spray tower is short as compared to roll drying and the gelatinization and rupturing cannot be easily carried out in the crutcher alone, because of the retarding effect of the soap and synthetic upon gelatinizing and rupturing. A suitable agitation and disintegration may be achieved by passing the crutcher mix thru a homogenizing valve at 3000 p.s.i., before spraying into the drying tower.

Another method of gelatinizing the starch is to pre-cook it before mixing with the detergents. The oxidized starches are the most useful in this procedure as they can be cooked with a water to starch ratio as low as 2:1.
to 1, although a ratio of 4 to 1 is preferred in the presence of synthetic detergents which retard gelatinization, whereas untreated corn starch will require a ratio of about 15 to 1.

The precooking of oxidized starch must be done with good agitation to prevent lumping. The mixture of the precooked starch and synthetic detergent should be controlled between the lower limit for plasticity and the upper limit for stiffness. These limits will normally be between 10 and 15%, although as little as 5% moisture may be used when the anionic sulfonic reaction product used is of a waxy nature and is used at a high level, say 35%.

It will be perceived that starch may be properly gelatinized in a number of ways for inclusion in a bar containing a synthetic detergent and we do not wish to be limited to the methods herein disclosed. The principal point to be observed is that the starch be gelatinized to the disappearance of anisotropy.

While the invention described and claimed herein resides in the use, as a binder and filler for a detergent bar containing synthetic detergent and soap, of a starch which has been fully gelatinized while the proportions of synthetic detergent and soap are not critical, the utility of the invention is best demonstrated in detergent bars containing anionic synthetic detergent within the range of 15% to 40%, and soap in the range of 10% to 35%, and in which the amount of starch is not less than 15% nor more than 70% of the bar, the percentages being by weight. The total amount of synthetic detergent and soap preferably constitutes between 35% and 60% of the bar and the moisture content is preferably not less than 5% and not more than 15%.

While the soap bar of the present invention comprises essentially detergents of the class described with starch, it will be appreciated that the incorporation in the bar of commonly used perfumes, organic and inorganic builders is contemplated as part of the instant invention.

It will be appreciated that reference herein to a synthetic detergent is intended to include mixtures of detergents of different types.

What is claimed is:

1. A detergent milled bar having a characteristic soap-like feel, comprising 10% to 35% normally solid, water-soluble sodium soap and 15% to 40% of a normally solid anionic synthetic detergent comprising a water-soluble, alkaline metal salt of an organic sulfonic reaction product and a gelatinized non-waxy starch, said gelatinized starch being characterized by the disappearance of anisotropy and consisting not less than 15%, nor more than 70% of the bar, the sum of said synthetic detergent and said sodium soap being between 25% and 65%.

2. The detergent bar of claim 1 in which the gelatinized starch is present in the range of 15% to 45%, the sum of said synthetic detergent and said sodium soap being between 35% and 60%.

3. The detergent bar of claim 1 in which the moisture content is not less than 10% and not more than 15%.

4. The detergent bar of claim 1 in which the gelatinized starch constitutes not less than 15%, nor more than 45% of the bar.

5. The detergent bar of claim 1 in which the normally solid, water soluble sodium soap is of fatty acids selected from the group consisting of tallow fatty acids, coconut oil fatty acids, and mixtures thereof.

6. In the process of preparing a milled toilet bar consisting essentially of 15% to 40% of a normally solid synthetic anionic detergent comprising a water-soluble alkaline metal salt of an organic sulfonic reaction product, 15% to 70% gelatinized non-waxy starch and 10% to 35% normally solid, water-soluble sodium soap, the sum of said synthetic detergent and said sodium soap being between 25% and 65%, the steps which comprise agitating and dispersing starch and synthetic detergent in water, the weight of said water being from about 2 to about 15 times the weight of said starch and sufficient in amount to permit complete gelatinization of said starch, heat drying the mixture, effecting substantially complete gelatinization of the starch to disappearance of anisotropy, milling and extruding the mixture and stamping same into a bar, and at any stage prior to milling and extruding, adding sodium soap to the mixture.

7. The process of claim 6 in which said starch is normal starch and it is dispersed in about 15 times its weight of water.

8. The process of claim 6 in which said starch is oxidized starch and it is dispersed in about 2 to about 4 times its weight of water.

9. The process of claim 6 in which the mixture of synthetic detergent, starch and water is roll-dried with the aid of steam at about 60 pounds per square inch pressure.

10. The process of claim 6 in which the sodium soap is added to the mixture of water, starch and synthetic detergent.

11. The process of claim 6 in which the sodium soap is added to the dried mixture.

12. The process of claim 6 in which a portion of the sodium soap is added to the mixture of synthetic detergent, starch and water and the remainder of the sodium soap is added to the dried mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,438,169 Hoyt ..................... Mar. 23, 1948
2,714,093 Blumenthal ................ July 26, 1955