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DETERGENT BAR MANUFACTURE

ABSTRACT

A process of producing a built, non-soap detergent bar containing primary alcohol sulphate of the formula

$$R^1OSO_3M$$

and/or alpha olefin sulphonate of formula

$$R^1CH = CH - (CH_2)_n - SO_3H$$

in which n is 1 or 2, M is a solubilising cation, R^1 is primary alkyl of 8 to 22 carbon atoms and $R^1CH = CH - (CH_2)_n -$ is a primary alkenyl of 8 to 22 carbon atoms, wherein the primary alcohol sulphate, olefin sulphonate or a mixture of them constitutes from 10% to 100% by weight of the detergent active material present in the bar, comprising an initial step of reacting a primary alcohol sulphate and/or alpha olefin sulphonate of respective specific formula with an acid to generate the corresponding acid, thereafter neutralising the acid, and thereafter adding further constituents of the bar composition.

This invention relates to the manufacture of built non-soap detergent (NSD) bars. Such bars are composed of detergent active, builder and usually filler(s) as the third main component and are generally used for laundering fabrics, and cleaning surfaces.

Commercial built detergent compositions contain detergent active and detergent builder materials together with optional components, for example abrasives, fillers, perfumes, alkaline salts, for example silicates, and bleaching agents.

The present invention is concerned with bars in which from 10% to 100% by weight of the detergent active is primary alcohol sulphate (PAS) of formula

$$ROSO_3H$$

and/or alpha olefin sulphonate (AOS) of formula

$$R^1CH = CH-(CH_2)_n-SO_3H$$

wherein n is 1 or 2, R is a primary alkyl group containing 8 to 22 carbon atoms, preferably 10 to 18 carbon atoms, R^1 is a primary alkyl group such that $R^1CH = CH_2-(CH_2)_n$ - contains 8 to 22 carbon atoms, again preferably 10 to 18, and M is a cation such that the detergent active is water

soluble.

Bars which contain even fairly small amounts of primary alcohol sulphate are prone to excessive breakage during handling and transport to a retailer. The present invention is concerned with ameliorating this difficulty.

Normally detergent bars of this general type are made using a paste containing the neutralised salt form of the detergent active. GB-A-2145103 mentions that bars may be made commencing from the free acid form of a detergent active, neutralising this in situ with soda ash or other suitable neutralising agent. No benefit is attributed to this use of free acid as a starting material. In the case of the acid form of primary alcohol sulphate, a strong disincentive to such a process is a tendency of the free acid form of the detergent active to decompose during storage and revert to the unsulphated alcohol. In the case of alpha olefin sulphonate there is again a disincentive. The acid mixture prepared by sulphonation of an alpha olefin contains sultone by-products which are skin sensitizers. Elimination of them necessitates use of forcing conditions (e.g. high pressure steam at 180°C in

alkaline media for 20 minutes) during neutralisation. This would complicate bar manufacture considerably, creating a strong incentive to choose the pre neutralised salt form of this detergent active as the starting point for bar manufacture.

Surprisingly, we have now found that the properties of bars can be improved by use of a manufacturing procedure commencing from the neutralised form of the detergent active, acidifying this to generate the acid form and then reneutralising the resulting mixture.

Therefore, the present invention provides a process of producing a built, non-soap detergent bar, containing primary alcohol sulphate of the formula

$$ROSO_3H$$

and/or alpha olefin sulphonate of formula

$$R^1CH = CH-(CH_2)_n-SO_3H$$

in which R or R^1, n and M are as specified above, wherein the primary alcohol sulphate, olefin sulphonate or a mixture of them constitutes from 10% to 100% by weight of the detergent active material present in the bar, comprising an initial step of reacting a primary alcohol sulphate and/or

alpha olefin sulphonate of the respective specified formula with an acid to generate the corresponding acid of formula

$$ROSO_3H \text{ or } R^1CH = CH-(CH_2)_n-SO_3H$$

thereafter neutralising the said acid so as once again to form primary alcohol sulphate and/or alpha olefin sulphonate of the specified formula and thereafter admixing further constituents of the bar composition.

Surprisingly, bars made by this procedure of converting the detergent active from its salt form to acid and then back to salt form are harder and stronger at the time of manufacture, making them easier to handle, yet after storage are less brittle and therefore less prone to excessive breakage during handling and transport. These improved properties, in particular the improved hardness at the time when the bar is first made, makes it possible to incorporate materials which are known to plasticise a bar (usually a disadvantage) but which improve the properties of the bar after storage. Examples of such material are coconut alcohol, other C_{10} to C_{20} alcohols, C_{10} to C_{20} esters and amides, and phthalate esters.

The process may be commenced using neutralised primary alcohol sulphate or alpha olefin sulphonate which is in the form of a semi solid paste or which has been dried to a particulate condition. Primary alcohol sulphate or olefin sulphonate which has been dried to a particulate condition may nevertheless still contain up to 10% of water.

This neutral detergent active is mixed with an acid to convert it to the acid form of the detergent active. The nature and amount of acid which is used may be such as to convert substantially all the alcohol sulphate or olefin sulphonate to acid form, or to convert only part of it. It is desirable to convert at least about one third of the alcohol sulphate or olefin to its acid form, preferably from about half to about three quarters.

Consequently it will generally be desirable to use from 0.3 to 10 equivalents of acid per equivalent of primary alcohol sulphate and/or alpha olefin sulphonate, preferably from 0.5 to 0.75 equivalents of acid. Suitable acids include sulphuric acid, hydrocholoric acid, phosphoric acid and dehydrated forms of phosphoric acid,

citric acid and alkyl benzene sulphonic acid.

Reaction with the acid is preferably carried out in a high shear mixer. After mixing, the reaction mixture is preferably left for a period of time to allow reaction to take place. Such a period of time is desirably not less than 2 nor more than 15 minutes, more preferably within a range from 3 to 10 minutes.

After this, the mixture which is so formed is neutralised. This may be carried out using alkali such as sodium hydroxide or a carbonate, bicarbonate or sesquicarbonate in a high shear mixer. It is desirable then to add all other constituents of the bar composition within not more than 20 minutes and this may be accomplished within a shorter space of time such as within 5 to 10 minutes of neutralising. Some constituents may be added with the neutralisation agent.

The resulting mixture is then formed into bars. This is preferably carried out by milling the mixture, for example through a roller mill, to break up any lumps and thereafter in conventional fashion, plodding, cutting, embossing and wrapping the finished product.

Bars made by the process of the invention

may suitably contain from 10%, preferably 12.5%, up to about 45% by weight of detergent active based on the total bar composition. From 10% to 100% by weight of the detergent active must be primary alcohol sulphate, alpha olefin sulphonate or a mixture of the two. This detergent active may constitute at least one third or possibly a majority of the weight of detergent active present in the bar composition.

The alkyl group of primary alcohol sulphate preferably contains 10 to 18 carbon atoms. In particular it may be derived from coconut, but other sources which are possible include hardened palm and stearin. A suitable alpha olefin sulphonate preferably has 10 to 18 carbon atoms in its $R^1CH = CH-(CH_2)_n-$ group.

Another detergent active which may be included is linear or branched alkyl benzene sulphonate with an alkyl chain length of 8 to 22 carbon atoms, preferably linear alkyl of 8 to 16 carbon atoms.

One or more of these detergent actives may provide the whole of the detergent active present, or other detergent actives may be used in addition to one or more of those mentioned above.

Detergent actives and builder components are well characterised in detergent bar technology. The components are described in "Surface Active Agents" by Schwartz and Perry (Interscience 1949) and Volume II by Schwartz, Perry and Berch (Interscience 1958). The detergent actives usable in the present invention may be found in the general classes of anionic, nonionic, amphoteric, betaine and zwitterionic actives. Specific examples of detergent actives usable in addition to those mentioned above include alkane sulphonates, secondary alcohol sulphates, olefin sulphonates, ethoxylated alcohols and ethoxylated alcohol sulphates.

Soap will generally be absent because it inhibits the formation of lather by the non-soap detergent active. Soap would tend to plasticise a bar and theoretically therefore would provide an advantage. However, an important user-perceivable property of built NSD bars is the ability to form a lather and the presence of soap reduces the rate of lather formation by the non-soap detergent active. Consequently it is preferred that soap is absent. If any quantity of soap is present the amount of it will generally be less than 2% by weight.

Bars produced in accordance with the present invention will generally contain detergency builder. The amount of detergency builder present will generally lie in the range from about 5% to about 60% by weight of the bar composition, preferably from 10% to 45%. Examples of builder components are: water soluble phosphate salts, e.g. sodium tripolyphosphate, pyrophosphate and orthophosphate; water soluble carbonates, e.g. sodium carbonate; organic builders, e.g. sodium nitrilotriacetate, sodium tartrate, sodium citrate, trisodium carboxymethyl oxysuccinate, sodium oxydisuccinate, sodium sulphonated long-chain monocarboxylic acids, polymeric polycarboxylic acids such as polyacrylates, maleic acid copolymers and oxidised polysaccharides; and aluminosilicate ion exchanger; e.g. zeolite 4A. In particular, use of phosphate builders or polyphosphate detergency builder may be such that phosphate provides at least 10% by weight of the bar composition.

Built NSD bars generally contain a proportion of filler which although chemically inert is significant in contributing to the properties of the bar. An appropriate range for such filler is

5 to 60% by weight of the composition. The filler may consist of water soluble salts such as sodium sulphate but possibly it includes water insoluble filler. The filler present may even all be water insoluble and accordingly the possible amount of water insoluble filler is 5 to 60 wt%. Examples of water insoluble fillers are talc, kaolin, calcite, bentonite, aluminosilicate and calcium silicate.

Other ingredients may also be present in the bar composition. These include silicates, e.g. sodium alkaline silicate, sodium carboxymethyl cellulose, lather enhancing agents such as coconut alkanolamides (both mono- and di - derivatives) as well as coconut alcohol, colouring materials, enzymes, fluorescers, opacifiers, germicides, humectants, hydrotropes, perfumes, and bleaching agents.

Cellulose may be added during the mixing procedure, e.g. together with the filler(s). Alkanolamines may be included, as described in our UK published patent application 2184732A. Aluminosilicate may be formed in situ, as described in our UK published patent application 2099013A.

It will be appreciated that this invention is concerned with detergent bars which will generally be substantially rigid, enabling such a bar to be rubbed against an item of laundry. Of course if a bar is soaked in water or stored under conditions of excessive humidity it may lose its strength and become plastically deformable by hand pressure.

In the Examples which follow, all percentages are by weight unless stated otherwise.

Example 1 (comparative)

Sodium coconut alcohol sulphate powder (94% active 357.5g), coconut alcohol (100% active 400g) and water (550g) were mixed in a high shear mixer for 2 to 5 minutes until the mixture was homogeneous. Excess sodium carbonate (345.3g) was next added, followed by alkyl benzene sulphonic acid of molecular weight 324 (97.4% active 216.0g). The amount of sodium carbonate was sufficient to neutralise the acid materials and also provide a quantity of sodium carbonate in the final formulation. Inter alia, it assists in hardening the bars. When the neutralisation reaction was complete alkaline silicate powder (86% active 700g) was then added followed by aluminium sulphate hydrate (1480g) and mixing continued for

a further 8 minutes. Calcite (3027g), pyrophosphate (800g), sodium tripolyphosphate (1200g), fluorescer (48g), titanium dioxide (30g) and perfume (50g) were then sequentially added. The resultant dough was then milled and plodded to produce bars, in accordance with conventional NSD bar manufacture.

Example 2

Sodium coconut alcohol sulphate powder (94% active 3575g) was added to a high shear mixer together with alkyl benzene sulphonic acid of molecular weight 324 (97.4% active 2160g) and the whole mixed for 5 minutes. Excess sodium carbonate (3453g) to neutralise the acid material and provide formulation and bar hardening requirements was then added followed by water (350g). When the neutralisation reaction was complete coconut alcohol (100% active 400g) was added and mixed in for 2 minutes. Alkaline silicate (44% active 1220g) was then added and manufacture continued using the same sequence of addition as in Example 1.

Example 3

Sodium coconut alcohol sulphate powder (94% active 3575g) was added to a high shear mixer

together with alkyl benzene sulphonic acid of molecular weight 324 (97.4% active 2160g) and concentrated sulphuric acid (98% active 360g) and the whole mixed for 5 minutes. Water (350g) was then added followed by excess sodium carbonate to neutralise the acid material and provide formulation and bar hardening requirements (3794g). When the neutralisation reaction was complete coconut alcohol (100% active 400g) was added and mixed in for 2 minutes. Alkaline silicate (48% active 1220g) was then added and manufacture continued using the same sequence of addition as in Example 1.

Examples 4 to 6

These were manufactured using the mixing procedure of Example 3, but with modified quantities of the constituents materials as shown in the Tables below. For Example 6 water was added after the sodium carbonate, instead of before it.

Example 7

Sodium coconut alcohol sulphate (74% active 3575g) was mixed with water (970g) in a high shear mixer. Alkyl benzene sulphonic acid (MW 324, 97.4% active 2160g) and sulphuric acid (98% active

360g) were added and the whole mixed for 5-10 minutes. Excess sodium carbonate (3794g) was then added and mixed until neutralisation was complete. Coconut alcohol (100% active 400g) was then added and after mixing for 2 minutes alkaline silicate powder (84% active 700g) was added. Manufacture then continued as in Example 1.

Example 8

Sodium coconut alcohol sulphate powder (94% active 6000g), water (1866g) and sulphuric acid (98% active 300g) were slurried for 5 minutes in a high shear mixer at 50-60°C. Urea (200g) and monoethanolamine (200g) were then added and mixed for a further 2 minutes. Sodium tripolyphosphate (1500g) was then added followed by excess sodium carbonate (3040g) to neutralise the acidic species and also provide a quantity of sodium carbonate in the final formulation. Then neutral sodium silicate powder (84% active 700g) was added followed by aluminium sulphate hydrate (1480g). After mixing for 5-8 minutes at 60-65°C the remaining bar ingredients were added sequentially: calcite (2300g), sodium tripolyphosphate (1500g), sodium orthophosphate (1000g), fluorescer (48g), titanium dioxide (30g) and perfume (70g). The

resultant dough was milled and plodded to produce bars, in accordance with conventional NSD bar manufacture.

Example 9 (comparative)

Alkyl benzene sulphonic acid with a molecular weight of 324 (97.4%, 2160g) and excess sodium carbonate (3453g) were mixed in a high shear mixer. The sodium carbonate served to neutralise the acid and also provide a quantity of sodium carbonate in the final formulation. When the neutralisation reaction was complete, sodium coconut alcohol sulphate powder (94%, 3575g) and water (550g) were then added. Mixing was continued for two minutes after which alkaline silicate powder (86% active, 700g) was added and manufacture then continued using the same sequence of addition as in Example 1.

Table 1 below summarises the quantities of sodium coconut alcohol sulphate (PAS, 94% active) alkyl benzene sulphonic acid (AHS, 97.6% active), 98% sulphuric acid, and sodium carbonate used in the above Examples.

TABLE 1

Example No.	1	2	3	4	5	6	7	8	9
Quantities Used (gms)									
PAS (sodium salt)	3575	3575	3575	3575	3575	1198	3575	6000	3575
ABS (acid)	2160	2160	2160	2160	2160	4309	2160	–	2160
H_2SO_4	–	–	360	200	100	150	360	300	–
Na_2CO_3	3453	3453	3794	3046	3540	3926	3974	3040	3453
H_2O	550	350	250	350	350	350	870	1866	550

The following Table 2 gives the overall formulations in percentages by weight. In Table 2 the percentages by weight of aluminium sulphate and of silicate are given as the equivalent percentage by weight of anhydrous, 100% active material. Titanium dioxide, perfume, fluorescer and non-detergent organic impurities are grouped together as "balance" of the compositions. Table 2 also quotes the nominal ratio of PAS:ABS, and the results of penetrometer tests and twist tests on bars produced by each Example.

The penetrometer test is a measure of the bar

hardness. The penetrometer used was a SUR type PNR 8 (Sommer und Runge of Berlin DDR). The needle had a point angle of 9° 10' and was forced into a plane bar surface under a total load of 100 for 10 seconds. The penetration depth was recorded in millimeters. Sample bars were tested directly after manufacture, after a delay of 1 hour and after 24 hours.

The twist test assesses bar strength, particularly resistance to breakage and deformation, at the "traying off" stage of NSD bar production where cut and embossed bars are transferred from a conveyor belt to metal trays for bar cooling and weathering. The test procedure is as follows:

One end of a hot (55-70°C) freshly cut and embossed quadruplet bar of length 33cms is clamped horizontally with its narrow edge uppermost. The free end of the bar is then held in the hand and turned through successive 90° steps. Checks are made for signs of initial bar cracking and final bar tearing/breaking. Turning is continued until problems arise up to a maximum of 3 complete turns or 12 quarter turns. The results are expressed as the number of quarter turns for initial cracking

and ultimate tearing/breaking. For example, if a bar starts cracking after 1 complete turn and tears/breaks after 1.5 complete turns the score is 4/6. If a bar is still perfect after 3 complete turns the score is 12:12.

TABLE 2

Example No	1	2	3	4	5	6	7	8	9
PAS:ABS	60:40	60:40	60:40	60:40	60:40	80:20	60:40	allPAS	60:40
Percentages of final bar formulations:-									
PAS	16.8	16.8	16.8	16.8	16.8	5.6	16.8	28.0	16.8
ABS	11.2	11.2	11.2	11.2	11.2	22.4	11.2	-	11.2
Sulphuric Acid	0	0	1.8	1.0	0.5	0.75	1.8	1.5	0
Coco Alcohol	2.0	2.0	2.0	2.0	2.0	2.0	2.0	0	0
Soda Ash	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Calcite	23.5	23.5	20.8	21.7	22.9	23.5	20.8	11.5	27.9
Ortho-phosphate	-	-	-	-	-	-	-	5.0	-
Pyro-phosphate	4.0	4.0	4.0	4.0	4.0	4.0	4.0	-	4.0
Tripoly-phosphate	11.0	11.0	11.0	11.0	11.0	11.0	11.0	15.0	11.0
Al Sulphate	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2

= 20 =

Table 2 continued

Silicate	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9
Ethanol-amine	-	-	-	-	-	-	-	1.0	-
Urea	-	-	-	-	-	-	-	1.0	-
Total Water	7.5	9.1	9.4	9.3	9.2	9.2	9.4	14.7	7.5
Total Sodium Sulphate	0.4	0.4	3.0	1.8	1.1	1.2	3.0	2.7	0.4
Penetrometry (100g/10 secs)									
Initial	12.2	9.0	6.7	6.7	7.9	6.9	6.2	3.5	10.3
1 Hour	0.8	1.6	1.6	2.2	1.0	2.6	1.0	0.5	2.2
24 Hours	0.9	0.7	0.9	0.9	0.8	1.7	0.6	0.3	1.2
Twist Test	8/10	10/12	12/12	12/12	12/12	12/12	12/12	12/12	6/8

Example 10

Sodium alpha-olefin sulphonate of predominately C_{14}-C_{16} chain length (98% active, 3,400g) was mixed with alkyl benzene sulphonic acid with a molecular weight of 324 (97% active, 2,160g) and concentrated sulphuric acid (98% active, 360g) in a high shear mixer. After mixing for 5 minutes the mass was neutralised by adding water (600g) and sodium carbonate (3,680g). On completion of the neutralisation reaction, coconut alcohol (400g), alkaline silicate powder (84% active, 680g), aluminium sulphate hydrate (1,480g) and calcite (5,100g) were added sequentially. Finally, the remaining solids sodium tripolyphosphate (2,200g), sodium pyrophosphate (800g) were added followed by fluorescer (48g), titanium dioxide (30g) and perfume (80g). The resultant dough which was produced was milled and plodded in the conventional way to produce NSD bars.

Example 11 (comparative)

Sodium alpha-olefin sulphonate of predominately C_{14}-C_{16} chain length (98% active, 3,400g) and sodium carbonate (3,500g) were mixed with water (600g) to generate a thick paste.

Alkyl benzene sulphonic acid with a molecular weight of 324 (97% active, 2160g) was then added and mixing continued until the neutralisation was complete. Coconut alcohol (400g), alkaline silicate powder (84%, 680g), aluminium sulphate hydrate (1,480g) and calcite (5,100g) were then added sequentially. The remaining solids sodium tripolyphosphate (2,200g), sodium pyrophosphate (800g) were added followed by fluorescer (48g), titanium dioxide (30g) and perfume (80g). Finally, the resultant dough was milled and plodded in the conventional way to produce NSD bars.

The bar formulations for Examples 10 and 11, with penetrometer test results, are set out in Table 3 below. Minor constituents, making the balance to 100% are not listed.

TABLE 3

	Example 10 %	Example 11 (comparative) %
AOS	16.8	16.7
Sodium carbonate	10.1	10.2
Sulphuric acid	1.8	-
ABS	11.2	11.2
Coconut alcohol	2.0	2.0
Sodium silicate (anhy)	2.9	2.9
Aluminium sulphate (anhy)	4.2	4.2
Calcite	22.2	25.5
Tripolyphosphate	11.10	11.0
Pyrophosphate	4.0	4.0
Total water	7.8	7.4
Total sodium sulphate	3.4	0.9
Penetrometry (100g/10 secs)	mm	mm
Initial	7.1	10.7
24 hours	2.3	3.0

CLAIMS

1. A process of producing a built, non soap detergent bar, containing primary alcohol sulphate of the formula

$$ROSO_3M$$

and/or alpha olefin sulphonate of formula

$$R^1CH = CH\text{-}(CH_2)_n\text{-}SO_3M$$

in which n is 1 or 2, M is a solubilising cation, R is primary alkyl of 8 to 22 carbon atoms and $R^1CH = CH\text{-}(CH_2)_n-$ is primary alkenyl of 8 to 22 carbon atoms, wherein the primary alcohol sulphate, olefin sulphonate or a mixture of them constitutes from 10% to 100% by weight of the detergent active material present in the bar, comprising an initial step of reacting a primary alcohol sulphate and/or alpha olefin sulphonate of the respective specified formula with an acid selected from sulphuric acid, hydrochloric acid, phosphoric acid, dehydrated forms of phosphoric acid, citric acid and alkyl benzene sulphonic acid, to generate the corresponding acid, thereafter neutralising the acid, and thereafter adding further constituents of the bar composition.

2. A process according to claim 1 wherein the said acid is alkyl benzene sulphonic acid

having an alkyl group of 8 to 18 carbon atoms.

3. A process according to claim 1 wherein said acid is used in an amount from 0.3 to 10 equivalents of acid per equivalent of primary alcohol sulphate and/or alpha olefin sulphonate.

4. A process according to claim 2 wherein said acid is used in an amount from 0.3 to 10 equivalents of acid per equivalent of primary alcohol sulphate and/or alpha olefin sulphonate.

5. A process according to claim 3 wherein the said acid is used in an amount from 0.5 to 0.75 equivalents of acid per equivalent of primary alcohol sulphate and/or alpha olefin sulphonate.

6. A process according to claim 4 wherein the said acid is used in an amount from 0.5 to 0.75 equivalents of acid per equivalent of primary alcohol sulphate and/or alpha olefin sulphonate.

7. A process according to claim 1 wherein the said primary alcohol sulphate and/or alpha olefin sulphonate constitutes from 50% to 100% of the detergent active in the final bar composition.

8. A process according to claim 3 wherein the said primary alcohol sulphate and/or alpha olefin sulphonate constitutes over 50% of the detergent active in the final bar composition.

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