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(54) Detergent bar

(57) A built detergent bar comprising 10 to 45% by weight of non-soap detergent active, from 5 to 60% by weight of detergency builder and at least 1% by weight of cellulose having a bulk density less than 0.6 kg/litre. Inclusion of cellulose ameliorates breakage and handling difficulties often associated with detergent bars.

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DETERGENT 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.

Various materials have been proposed for inclusion in NSD laundry bars, to improve properties of the bar. Various effects have been attributed to such materials. It is always possible that including a material to improve one property of a bar produces a detrimental effect on another property.

We have now found that bar properties can be improved by including cellulose of a low bulk density. This material is effective to modify structural properties of a detergent bar, which can give a change in the rate at which the bar wears during use, and improve resistance to brittle fracture, without other undesirable effects.

According to the present invention we provide a built detergent bar, of composition comprising from 10% or preferably 12.5% to 45% by weight of non-soap detergent active, from 5 to 60% by weight of detergency builder, and

at least 1% by weight of cellulose having a bulk density less than 0.6 Kg/litre.

The cellulose will generally not be chemically modified. Suitable is flocced cellulose, whose bulk density varies according to grade, but can be as low as 0.05 Kg/litre.

Such cellulose is available from James River Corporation under their registered trade mark Solka-Floc and Hahn & Co under their trade mark Hahnflock.

It is preferred that the amount of cellulose lies in a range from 1 to 10% by weight of the bar composition, more preferably from 2 to 6%.

The invention is particularly applicable when at least a part of the detergent active is either primary alcohol sulphate of formula

$$ROSO_3M$$

and/or fatty acyl ester sulphonate of formula

$$R^1CHCO_2R^2$$
$$|$$
$$SO_3M$$

in which R or R^1 is a primary alkyl group containing 8 to 22 carbon atoms, preferably 10 to 18, R^2 is a primary alkyl group containing 1 to 6 carbon atoms, preferably 1 to 4, and M is a cation such that the detergent active material is water soluble. These actives may in particular have R or R^1 derived from coconut, but other sources which are possible include hardened palm and stearin.

With both of these actives the inclusion of the abovementioned cellulose produces a reduction in the rate of wear of a detergent bar and an improvement in user

perceivable properties.

Bars which contain even fairly small amounts of primary alcohol sulphate are prone to excessive breakage during handling and transport to a retailer. Inclusion of the abovementioned cellulose is effective to ameliorate this difficulty. It also enables the bars to tolerate a substantial water content, which is advantageous in allowing the use of primary alcohol sulphate supplied in the form of an aqueous paste.

Fatty acid ester sulphonate, or primary alcohol sulphate, or a mixture of the two may constitute at least 10%, more particularly at least one third, or possibly a majority of the weight of detergent active present in a bar composition. 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 alkyl of 8 to 16 carbon atoms.

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

In general the amount of detergency builder present will be 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, polyacrylates and oxidised polysaccharides; and aluminosilicate ion exchanger; e.g. zeolite 4A. In particular, use of phosphate builder 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 and bentonite.

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, perfumes, and bleaching agents.

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.

The bars according to this invention may be prepared by mixing the ingredients, with water, using a high shear mixer as is conventional and then extruding. The cellulose may be added initially but preferably is added at a later stage in the mixing procedure together with the filler(s). Alkanolamines may be included, as described in

our UK published patent application 2184452A. Aluminosilicate may be formed in situ, as described in our UK published patent application 2099013A.

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

The cellulose used in Examples 1, 2, 4 and 5 was cellulose of bulk density approximately 0.2 Kg/litre from James River Corporation, Hackensack, New Jersey, USA sold under their trade mark Solka-floc. Example 3 used cellulose from Hahn & Co, D2371 Bredenbek Kromberg, West Germany. Anhydrous silica gel, used as a desiccating agent was Gasil 23 from Joseph Crosfield & Son, Warrington, UK.

Example 1

A number of bars were made, having a general formulation as follows:

Coconut alcohol sulphate	28.0%
Soda ash	15.2%
Sodium alkaline silicate (anhydrous basis)	2.9%
Aluminium sulphate (anhydrous basis)	4.2%
Sodium pyrophosphate	21.0%
Cellulose	variable
Silica gel	variable
Calcite	variable
Water	16.0%
Impurities introduced with the detergent active, minor constituents.	balance to 100%

The water could all be introduced with other constituents, especially if detergent active was provided in the form of a water-containing paste. The amount of calcite was varied so that the total amount of calcite, silica gel and cellulose was constant.

Bars were extruded, and then aged for two weeks to allow their physical properties to stabilise (although the benefits of the invention are apparent much sooner than this).

The hardness of the bars was measured by means of a penetrometer, the results being expressed as depth of penetration into the bar of a standard probe under a 100gm or 200gm load applied for a standard time.

The rate of wear of bars was measured by a standard test procedure designed to resemble use, the results being expressed as loss of weight of the bars.

The results of these tests are set out in Table 1 below.

TABLE 1

Composition No:	I	II	III	IV	V	VI	VII	VIII
Constituent:								
Silica gel %	0	2.5	5	0	2.5	5	5	5
Cellulose %	0	0	0	5	2.5	5	5	5
Calcite %	10	7.5	8	5	5	0	3	0
Water %	16	16	16	16	16	16	13	22
Hardness:								
Penetration under 100gm (mm)	9.0	8.8	6.5	8.5	6.0	3.4	4.6	8.4
Penetration under 200gm (mm)	14.0	13.9	12.0	13.0	8.7	7.5	7.5	12.5
Rate of wear (weight loss in gram)	4.9	4.7	3.7	3.2	3.6	3.1	3.0	5.3

It can be seen that incorporation of silica gel or cellulose or both gave a reduction in the rate of bar wear.

Bars of compositions I to VI were tested for resistance to fracture on impact. For this test bars were extruded into the same form as a current commercial product. This consists of an elongate bar having an overall length six times its width, and having three transversely extending indentations into its top face so as to give a reduced thickness at three points along the length of the bar.

These indentations are intended to allow the bar to be snapped into quarters prior to use.

To test the bars, six such bars were individually wrapped and placed face-to-face in a stack. This stack was placed in a cardboard carton so that a long edge of each bar was resting on the base of the carton. This carton was then placed at a standard position on a pair of downwardly opening trap doors held closed by being latched together. The latch was quickly released allowing the carton to drop through about 750mm onto a hard floor. The carton was then dropped in the same way twice more after which the bars were unpacked and inspected.

With composition I containing neither cellulose or silica gel the bars broke across their width at the centre or at one or both of the outer indentations. The breaks at the outer indentations however were not directly transverse and a number of fragments broke off along lines extending longitudinally of the bar. With compositions II and III containing silica gel but no cellulose the result was generally the same with a number of fragments broken off along lines extending longitudinally of each bar.

With composition IV which contains 5% of cellulose, however, there was a dramatic improvement. The bars broke transversely across their width at the central indentation only, and the break fairly closely followed the central indentation. Three of the six bars had no fragments broken off, the other three had only one small fragment broken off at the central break. Composition VI containing both 5% of the cellulose and 5% silica gel gave a similar

result to composition IV except that there were no small fragments broken off. Composition V containing 2.5% of the cellulose and 2.5% of the silica gel gave a result which was nearly as good as the result for composition IV. Four of the six bars broke in half at the central indentation without any small fragments being broken off. One bar broke approximately at the two outer indentations while the remaining bar broke at the centre and one outer indentation with two small fragments broken off.

A current commercial product in which the detergent active is alkyl benzene sulphonate was tested in the same way. Two of the six bars broke cleanly at the central indentation. One broke at the centre and one outer indentation, the other three broke approximately at an outer indentation. A small number of fragments broke off.

Overall, it was clearly apparent that the compositions I, II and III were inferior to the current commercial product in that there was greater creation of fragments breaking off along lines extending longitudinally of the bar. Composition V was slightly superior to the current commercial product in that there was slightly less creation of small fragments and more of the breaks extended directly across the bars. Compositions IV and VI were better still in that they displayed less breakage and less formation of small fragments.

As a comparison, bars were also produced with a formulation similar to the general formulation for bars I-VI but utilizing starch or gelatin rather than cellulose as a polymeric material to improve the bar's resistance to

brittle fracture. When tested shortly after the manufacture of the bars the incorporation of starch or gelatin did give an improvement in resistance to brittle fracture. However the improvement was short lived and could not be observed in bars which had been allowed to age for two weeks.

Assessment of Feel

Bars of compositions I, II, IV and V were tested for the feel characteristics perceived by users. This was a subjective assessment by a panel.

Each bar was rubbed 50 times on each side (by hand while wearing rubber gloves) to remove surface finish. Members of a panel of eight randomly selected assessors were then asked to rub the bars between bare hands in demineralised water at 26°C and grade the bars for three detrimental properties which were

i) gritty/abrasive feel

ii) mushy feel (i.e. surface layer too soft)

iii) slimy feel

The bars were scored for each property on a scale of

0 = no grit/mush/slimy feel

1 = very slight grit/mush/slimy feel

2 = little grit/mush/slimy feel

3 = fairly gritty/mushy/slimy feel

4 = very gritty/mushy/slimy feel

5 = extremely gritty/mushy/slimy feel

Each bar was freed from accumulated mush before being shown to the next panellist, and replaced with a new bar (freed from surface finish) after assessment by four

panellists.

The average scores for each characteristic were calculated, and are set out in Table 2 below.

TABLE 2

Composition No:	I	II	IV	V
Cellulose %	0	0	5	2.5
Silica gel %	0	2.5	0	2.5
Grit	3.2	3.1	2.1	2.4
Mush	3.0	3.4	2.6	2.7
Slime	2.9	3.3	2.4	2.8

It can be seen from the Table that composition IV and composition V had better scores than compositions I and II.

Example 2

Two further compositions VII and VIII were prepared similar to composition VI above but with different amounts of water. Composition VII contained 3% calcite but only 13% water. Composition VIII contained 22% water which necessitated reducing the level of soda ash to 10.2%. Hardness and rate of wear were measured as previously. The results are included in Table 1 above.

As can be seen from the table, increasing the water content to 22% gave some softening of the bar and a slightly increased rate of wear.

With NSD bars containing primary alcohol sulphates as the detergent active, increasing the water content of the bar reduces the bar's resistance to brittle fracture. Bars

of composition VIII were subjected to the drop test for brittle fracture as described above. It was found that four bars broke into two pieces approximately at the centre while two of the six bars produced one additional fragment. The resistance to brittle fracture was therefore at least as good as that of composition V or the commercial product with alkyl benzene sulphonate as active. This shows that incorporation of cellulose was making it possible to enhance the water content from 16% to 22% without serious detriment to the resistance to brittle fracture.

Example 3

Bars similar to composition VII were made, substituting cellulose from Hahn & Co, sold under their designations

Hahnflock H100 Bulk density 0.17Kg/litre

and Hahnflock H250 Bulk density 0.22Kg/litre

These bars, and those of composition VII were subjected to the drop test for brittle fracture. All bars of composition VII (with Solka-floc) broke at the central indentation only - a result as good as for composition VI. When Hahnflock H100 was used, four bars broke at the centre, with two small fragments broken off. Two bars broke at the centre with peices also broken off at one end. With Hahnflock H250 two bars broke at the centre only. Four bars broke in two places and there were four small fragments. The breakage patterns with both grades of Hahnflock were generally about as good as with the commercial product.

Example 4

A number of bar compositions were prepared using coconut acid methyl ester sulphonate (FAES) in admixture with C_{12} alkyl benzene sulphonate (ABS) as the detergent active. Both potassium and sodium salts were employed and varying amounts of cellulose were included. All the bars had a general composition as follows:-

Detergent active	31.0%
Sodium tripolyphosphate	3.0%
Sodium pyrophosphate	5.0%
Carbonate (variable cation)	10.0%
Aluminium sulphate (anhydrous)	4.2%
Sodium alkaline silicate (anhydrous)	3.0%
Calcite	variable
Kaolin	5.0%
Water	10.2%
Cellulose	variable
Impurities introduced with the detergent active, minor constituents	balance to 100%

The parts of the composition which were varied are set out in Table 3 below with rates of wear observed.

TABLE 3

Composition No:	IX	X	XI	XII	XIII	XIV	XV
FAES K%	21.7	21.7	21.7	21.7	0	0	27.9
FAES Na%	0	0	0	0	21.7	15.5	-
ABS Na%	0	0	0	0	9.3	15.5	3.1
ABS K%	9.3	9.3	9.3	9.3	0	0	0
K_2 CO_3 %	10.0	10.0	10.0	10.0	0	0	0
Na_2 CO_3 %	0	0	0	0	10.0	10.0	10.0
Calcite %	26.0	24.5	21.0	16.0	21.0	21.0	21.0
Cellulose %	0	2.5	5.0	10.0	5.0	5.0	5.0
Rate of wear (weight loss in gram)	10.1	7.4	6.6	4.51	6.4	6.5	7.8

Compositions IX to XII show the effect of introducing increasing amounts of cellulose with concomitant reduction of the amount of calcite while the composition remains similar in other respects. It is clearly seen that this leads to a progressive reduction in the rate of wear of the bars. Compositions XIII-XV show that generally similar results are obtained if potassium salts are replaced by sodium salts or if the proportions of the two detergent actives are varied.

Compositions IX, X and XI were assessed for feel characteristics in the manner described in Example 1. Results are set out in the following Table 4.

TABLE 4

Composition No:	IX	X	XI
Cellulose %	0	2.5%	5%
Grit	3.0	2.1	1.8
Mush	3.1	2.6	2.4
Slime	3.2	2.5	2.4

This Table shows that compositions X and XI - containing cellulose have better scores than composition IX.

Example 5

Two formulations were prepared containing a mixture of coconut alcohol sulphate (PAS) and C_{12} alkyl benzene sulphonate (ABS) as detergent active. Again, rate of wear was tested. The compositions and the rate of wear are set out in Table 5 below. Once again it can be seen that introduction of cellulose leads to a reduction in the rate of wear.

TABLE 5

PAS (Na)	16.8%	16.8%
ABS (Na)	11.2%	11.2%
Sodium tripolyphosphate	11.0%	11.0%
Sodium pyrophosphate	4.0%	4.0%
Sodium carbonate	9.4%	9.4%
Potassium carbonate	2.9%	2.9%
Aluminium sulphate	4.2%	4.2%
Sodium alkali silicate (anhydrous)	2.9%	2.9%
Calcite	22.5%	25.0%
Cellulose	2.5%	0%
Water	10.0%	10.0%
Impurities introduced with the detergent active, minor constituents		balance to 100%
Rate of wear (weight loss in gram)	5.4	7.6

CLAIMS

1. A built detergent bar, of composition comprising from 10 to 45% by weight of non-soap detergent active, from 5 to 60% by weight of detergency builder, and at least 1% by weight of cellulose having a bulk density less than 0.6 Kg/litre.

2. A bar according to claim 1 wherein at least 10% of the detergent active, by weight, is anionic detergent active selected from primary alcohol sulphate of formula

$$ROSO_3M$$

and/or fatty acyl ester sulphonate of formula

$$R^1CHCO_2R^2$$
$$|$$
$$SO_3M$$

in which R or R^1 is a primary alkyl group containing 8 to 22 carbon atoms, R^2 is a primary alkyl group containing 1 to 6 carbon atoms and M is a cation such that the detergent active material is water soluble.

3. A bar according to claim 2 wherein at least 10% by weight of the detergent active is said primary alcohol sulphate.

4. A bar according to claim 2 or claim 3 wherein the detergent active also comprises alkyl benzene sulphonate having from 8 to 22 carbon atoms in the alkyl chain thereof.

5. A bar according to any one of claims 2 to 4 wherein the cation M is an alkali metal.

6. A bar according to any one of claims 2 to 5 wherein the bar composition contains at least 20% by weight of the said primary alcohol sulphate.

7. A bar according to any one of the preceding claims wherein the amount of the said cellulose is not over 10% by weight of the bar composition.

8. A bar according to claim 7 wherein the amount of the said cellulose is 2 to 6% by weight of the bar composition.

9. A bar according to any one of the preceding claims wherein soap is substantially absent.

10. A bar according to any one of the preceding claims wherein the amount of detergent builder is 10% to 45% by weight of the bar composition.

11. A bar according to any one of the preceding claims wherein the builder comprises phosphate in an amount which is at least 10% by weight of the bar composition.

12. A bar according to any one of the preceding claims which also contains inorganic filler in an amount which is 5 to 60% by weight of the bar composition.

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