IMPROVED DETERGENT BAR COMPOSITION

A1

5000 \times 10^{-13}, \frac{[Cm^3][Cm]}{[Cm^2][s][Pa]}, (1)

Abstract: A detergent bar composition comprising: a) more than 60 \% to 95 \% by weight detergent active; and b) 0 to less than 40 \% by weight inorganic particulates and/or other conventional ingredients; wherein the external surface of the shaped detergent composition comprises a polymer coating comprising at least one polymer layer; at least one of the polymer layers being a non-radiation-curable material and having a water vapour permeability coefficient for water less than formula (1), which polymer coating is substantially water insoluble and has a melting point greater than 30\(^\circ\)C but is abrasible in use.
IMPROVED DETERGENT BAR COMPOSITION

The invention relates to shaped solid detergent compositions for cleaning hard surfaces or fabric or for personal wash, and more particularly to compositions that have improved durability and thus retain shape although in continuous contact with water.

Detergent compositions in general for fabric or hard surface cleaning typically comprise a surfactant system whose role is to assist in removal of soil. The surfactant system may predominantly be non-soap surfactants for fabric or hard surface cleaning. Detergent bars require an acceptable physical strength so that they retain their structural integrity during handling, transport and use. Various abrasives, fillers, builders, and other ingredients such as colour, perfume, preservatives, etc. may also be incorporated suitably.

Cleaning compositions in the solid form are much cheaper than liquids because of low cost packaging and these are very popular forms in developing countries. Amongst the solid form bars are gaining popularity and growing rapidly in the market of developing countries, because of better value delivery. The product dosage in the solid form is easier, it avoids spillage and the product application can be better controlled. Cleaning compositions in the bar form are economically superior to other product forms, and the dosage per swipe from the bar is highly controlled.
Detergent bars require an acceptable physical strength so that they retain their structural integrity during handling, transport and use. Various abrasives, fillers, builders, and other ingredients such as colour, perfume, preservatives, etc. may also be incorporated suitably.

Detergent bars formulated for personal washing contain over about 70 % by weight TFM, the remainder being water (about 10-20 %) and other ingredients such as colour, perfume, preservatives, etc. Structurants and fillers are also present in such compositions in small amounts which replace some of the soap in the bar while retaining the desired hardness of the bar. Personal washing compositions are formulated as transparent, non-transparent bars. They are manufactured by either the cast or extruded route.

Detergent bars for fabric, hard surface cleaning or for personal washing are in constant contact with water during usage and subsequent storage and hence get soggy and generally get disintegrated to paste form. The shape and contour of the bar is not retained satisfactorily.

This problem is generally solved by making suitable changes in the formulation of the bar. Any attempt to harden the bar if not properly controlled through formulation can result into a hard product which would not release sufficient product for cleaning purpose. Therefore, it is a major challenge to ensure that there is no disintegration of the product during use, no wastage of product through mush generation, yet the product is sufficiently soft to enable
the users to pick up right quantity of product while
cleaning dishes.

In our co-pending application 417/Mum/2001, we have
described a direct application, shaped detergent product
which comprises a water-resistant coating that is capable of
being abraded from the detergent product during use.
Preferably, the shaped detergent product is an extruded bar
and comprises an abrasive, wherein the external surface of
the said detergent bar comprises one or more materials
having a permeability coefficient for water less than

\[
1000 \times 10^{-13} \frac{[Cm^1]}{[Cm^2][s][Pa]}
\]

and with a melting point greater than 30°C, wherein \([Cm^3] =
Cm^3(273,15K; 1,013 \times 10^5 \text{ Pa.})\), as outlined in "Polymer
Immergut, (Wiley-Interscience Publication), page VI/436".

In another of our co-pending applications 1131/Mum/2001, we
have disclosed a solid shaped detergent composition
comprising:
0.5-95% by weight detergent active,
0-90% by weight inorganic particulates and/or other optional
conventional ingredients,
wherein the external surface of the shaped detergent
composition comprises at least one polymer coating or film
obtained by radiation curing or a radiation-curable resin.

However, in one of our co-pending patent applications the
active levels of the detergent bars are only up to 60% and
with high levels of abrasives, whereas personal washing bars have active levels over 70% and do not have any abrasives in the formulation. When the active levels are higher than 60% and in the absence of or very low levels of abrasives in detergent bars used in personal washing or laundry soaps, the possibility of them getting soggy is also higher.

It has now been found that it is particularly advantageous to provide the external surface of the detergent bar having active levels greater than 60% with one or more materials having a water vapour permeability coefficient for water less than $5000 \times 10^{-13} \frac{[Cm]}{[Cm^2 s Pa]}$.

Although the application 1131/Mum/2001 discloses a solid shaped detergent composition with high active levels up to 95% with an external surface comprising at least one polymer coating or film obtained by radiation curable resin, it has now been found that providing the external surface of personal washing bars or laundry soap bars with non-photo curable formulations is advantageous.

Such coatings, apart from preventing sogginess during use, have the added advantage of giving high consumer appeal as they have a high gloss, good lathering, and other in-use properties. The water-resistant film provided on the product reduces disintegration and deformation of the product during use, and also reduces wastage of product by reducing undesired mush formation. The water resistant film is inherent on the product surface, and although it gets abraded along with the product during usage, it is capable
of maintaining the shape and integrity of the product. The water resistant coating is preferably substantially insoluble in water, even under alkaline conditions.

5 It is the basic objective of the present invention to be able to provide selected coatings or films on solid shaped detergent compositions having actives greater than 60% by weight of the composition, such as detergent bars or tablets for laundry and fabric washing, for hard surface cleaning and for personal cleansing and the like. The polymer coatings are non-radiation curing and can be readily applied; in addition, the polymer coatings are able to provide desired gloss/surface finish, and at the same time improve the durability of the detergent bars, even when in prolonged contact with water.

It is another object of the invention to provide selected polymer coatings for such detergent compositions which have proper adhesion to the surface of the compositions, which are of defined thickness and have good mechanical properties.

Yet another object of the present invention is to provide solid shaped detergent compositions such as bars and tablets (hereinafter collectively referred to as "detergent bars") which are coated with selected non-radiation curable polymer coatings or films with good adhesive properties to the bar surface, with desired thickness and with good mechanical properties, thereby causing the bar to maintain desired physical shape and integrity even in contact with water.
Furthermore, it is an object of the present invention to provide a process for obtaining the detergent bars as described above.

Thus according to a first aspect of the present invention, there is provided a solid shaped detergent composition (hereinafter referred to as "detergent bar") comprising:
- 60-95 % by weight detergent active, and
- 0-90 % by weight inorganic particulates and/or other optional conventional ingredients,

wherein the external surface of the shaped detergent composition comprises at least one polymer coating that is a non radiation-curable material and having a water vapour permeability coefficient for water less than

\[
5000 \times 10^{-13} \frac{[\text{Cm}^3]}{[\text{Cm}^2] \cdot \text{s} \cdot \text{Pa}} \quad \text{where} \quad [\text{Cm}^3] = \text{Cm}^3(273.15K; 1.013 \times 10^5 \text{Pa}), \text{which is substantially water insoluble, whose melting point is greater than 30°C that is adherent to the external surface but is capable of being abraded during use.}
\]

The external surface of the detergent article may comprise one or more layers made of one or more materials.

The external surface of the detergent article preferably comprises one or more material chosen from natural or synthetic or modified polymeric materials and/or waxes that are substantially water insoluble with a melting point greater than 30°C that is adherent to the external surface, but is capable of being abraded during use.
The external surface of the detergent article preferably comprises one or more material chosen from synthetic or modified polymeric materials whose molecular weight is more than 1600 daltons that is substantially water insoluble with a melting point greater than 30°C that is adherent to the external surface, but is capable of being abraded during use.

It preferred that the water vapour permeability coefficient of the polymers is less than $5000 \times 10^{-13} \frac{[Cm^3]}{[Cm^2 s Pa]}$ and more preferably less than $2000 \times 10^{-13} \frac{[Cm^3]}{[Cm^2 s Pa]}$. where $[Cm^3]$ is $= Cm^3 (273,15 K; 1,013 \times 10^5 Pa)$.

The material forming the external surface of the detergent article is preferably in the form of a film whose thickness is maintained in the range 5-1000 microns, more preferably 10-100 microns and particularly 30 to 60 microns.

According to another preferred aspect of the present invention there is provided a shaped detergent composition comprising
- 60-95 % by weight detergent active, and
- 0-90 % by weight inorganic particulates and/or other conventional ingredients,

wherein the external surface of the said shaped detergent article comprises mixture of one or more polymers and film forming diluent selected from one or more of natural and
synthetic waxes, polysacharides, water insoluble salts of fatty acids whose melting point greater than 30°C.

Thus, according to one preferred embodiment of the invention the coated detergent bars contain 60-95 % wt of detergent active, more preferably, 60-90 %.

Detergent bars according to the invention will generally contain at least 5 %wt of water and preferably at least 10 % or even 15 % or more.

The detergent composition useful for fabric or hard surface cleaning or personal washing may suitably be formulated in the form of a bar which form includes a tablet or compact or a cake. This composition is essentially covered with one or more water resistant materials preferably having a melting point greater than 30°C and preferably forming a not less than 5 micron thick film that is inherently adhering to the outer surface of the contour of the product. The water resistant film is preferably substantially insoluble in water, even under alkaline conditions. Preferably the bar is extruded.

Accordingly, a further aspect of the present invention subsists in a process for the manufacture of a detergent bar which comprises the steps of:

(a) forming a detergent composition into a detergent bar, and,
(b) coating the bar with a water resistant film.
The bar may be formed by casting, injection moulding or extrusion.

The film is made of suitable material that forms a water resistant film barrier and such that it is inherently adhering to the outer surface of the detergent product. Materials that do not require UV or other radiation curing form the film. The film is preferably at least 5 microns thick and may be as thick as 1000 microns, preferably 10-100 microns, and more preferably 30-60 microns. The water resistant film is preferably substantially insoluble in water, even under alkaline conditions.

The material used as the film has a melting point greater than 30°C, and preferably greater than 45°C. It will be clear that the working surface of the bar need not initially be coated, provided that the non-working surfaces of the bar are so coated.

Suitable film forming materials can be comprised of water insoluble materials such as polymers and combinations thereof, natural and synthetic waxes, polysaccharides and water insoluble salts of fatty acids that form inherent film on the outer surface of the detergent mass, and mixtures thereof. The film can also comprise of any of the organic materials with inorganic materials as diluents/fillers to modify the mechanical properties of the film.

It is possible to select materials which themselves do not form a film on the detergent product but can be made
adherent by using another material that has the ability to bind the detergent product and the water resistant material.

Films can be formulated in a liquid solution or dispersion using a solvent or in a heated melt form consisting of a single or multiple polymeric/organic materials.

The film composition can be prepared using a composition of polymer(s), various waxes and additives known as tackifiers to improve the adhesive properties of the composition. Appropriate combination of these can be arrived at to provide desired workability and mechanical strength. The film can be prepared using a base polymer alone, depending on the properties of the coating required. The base polymer can ideally be selected from the list below: poly acrylates, poly methylmethacrylate, poly styrenes, poly (ethylene-co-vinyl acetate), poly (ethylene-co-acrylates), poly (ethylene-co-methacrylates), poly (styrene-co-acrylates), poly olefins, atactic α-olefins, poly ethylene, poly propylene, amorphous poly α-olefins, poly imides, nylon, poly vinyl chloride, poly ethylene terephthalate, poly urethanes, epoxy resins.

The natural and synthetic waxes are optionally added to composition to provide application viscosity control in molten state and act towards obtaining less dry tack and erodability. Such waxes can ideally be selected from polyethylene waxes, Fischer Tropsch waxes, microcrystalline waxes, paraffin waxes.
Tackifiers and adhesion promoting agents may optionally be added to the composition to increase the cohesive and binding characteristics of the film. These materials can ideally be chosen from the following list: hydrocarbon resins, petroleum C5-C9 resins, hydrogenated petroleum resins, aliphatic petroleum resins, alicyclic petroleum resins, coumarine petroleum resins, terpene based resins, styrene resins, phenol based resins, ester gums, rosins such as gum rosin and wood rosin.

Antioxidants are optionally added to the composition to prevent degradation in the molten state. These antioxidants can be chosen from the following list: phenol base anioxidants such as 2,6-di-tert-butyl-p-cresol, 2,2′-methylenebis(4-methyl-6-tert-butylphenol), 4,4′-butylenebis(3-methyl-6-tert-butylphenol), 4,4′-thiobis(3-methyl-6-tert-butylphenol), 2,2′-thiobis(4-methyl-6-tert-butylphenol), stearyl-β-(3,5-di-tert-butyl-4-hydroxyphenol)propionate, tetrakis(methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)methane, triethylene glycol, bis(3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionate, 1,3,5-triethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene and 1,1,3-tris(2-methyl-5-tert-butylphenol)-butane; amine base antioxidants such as phenyl-α-naphthylamine, phenyl-β-naphthylamine, N-phenyl-N′-cyclohexyl-p-phenylenediamine and N-isopropyl-N′-phenyl-phenylenediamine; phosphorous base antioxidants such as triisodecyl phosphite and 2,2′-methylenebis(4,6-di-tert-butylphenyl)ocyl phosphite; sulfur- base antioxidants such as 2,2′-thiobis(4-methyl-6-tert-butylphenol); and
hydroquinone antioxidants such as 2,5-di-tert-amylhydroquinone.

The film forming material can also comprise of gloss enhancing compounds, inorganic materials such as talc, silica, china clay, oxides, carbonates and chlorides of alkali or alkaline earth metals or transition metals and preferably they are salts of calcium or magnesium or zinc.

The detergent composition is provided with the water resistant film material by any of the following methods. The shaped detergent article may be first prepared and then the surface is coated with the water resistant material by using any of the conventional processes such as coating using the material in molten condition, as a solution of the material dissolved in appropriate solvents, coating using an intermediate when the water resistant material does not adhere to the product or by co-extruding the material.

The composition according to the invention will preferably comprise detergent actives that may be soap or non-soap surfactants and generally chosen from both anionic, nonionic, cationic, zwitterionic detergent actives or mixtures thereof. Suitable examples of detergent-active compounds are compounds commonly used as surface-active agents given in the well-known textbooks "Surface Active Agents", Volume I by Schwartz and Perry and "Surface Active Agents and Detergents", Volume II by Schwartz, Perry and Berch.
The total amount of detergent active compound to be employed in the detergent composition of the invention will preferably be from 5-30% by weight of the composition.

For bars intended for personal cleansing the total amount of detergent active may usefully be up to 85% and may comprise a large proportion, or even consist exclusively, of fatty acid soap.

Suitable abrasives can be selected from particulate zeolites, calcites, dolomites, feldspar, silicas, silicates, other carbonates, aluminas, bicarbonates, borates, sulphates and polymeric materials such as polyethylene. There can be an abrasive system with more than a single type of abrasive to achieve a balanced abrasive property. For example, studies show that combination of abrasives of different hardness in a formulation provide significant benefits in some of the user properties. Abrasive may be included in the coating to assist in its initial removal.

The detergency builders/alkaline buffer salts used in the formulation are preferably inorganic and suitable builders include, for example, alkali metal aluminosilicates (zeolites), sodium carbonate, sodium tripolyphosphate (STPP), tetrasodium pyrophosphate (TSPP), and combinations of these. Builders/ alkaline buffer salts are suitably used in an amount ranging from 2 % to 15 % by wt, preferably from 5 % to 10 % by wt.
Other ingredients such as fillers, solvents, amines, perfumes, colouring agents, flourescers, enzymes can also be used in the formulation, for example, in an amount up to 10 wt%.

The invention will now be illustrated with respect to the following non-limiting examples.

Examples

A detergent composition useful for personal washing, having a formulation as described in Table 1 was used for testing the rate of wear by the following method. The bar was not covered with any water resistant material (Example 1), and in Example 2 the bars were covered respectively with a film about 20 microns thick made of polystyrene. The polymer was applied on to one face of personal wash bar whose composition is given in Table 1, using appropriate solvent. The rate of wear of the bars were determined and the results are presented in Table 2.

Table 1

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>% wt.</th>
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<td>Soap</td>
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<td>Polyl</td>
<td>6</td>
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<td>Minor ingredients</td>
<td>1.5</td>
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<tr>
<td>Water</td>
<td>to 100</td>
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Table 2

<table>
<thead>
<tr>
<th>Example</th>
<th>% loss in weight</th>
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<tr>
<td>Example 1</td>
<td>25.3</td>
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<td>13.4</td>
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The data presented in Table 2 show that there is significant reduction in rate of wear by providing the bar with the polymer coating according to the invention.

This will add to the economy in use as the bar will last for a longer time. The bar also had other in use benefits such as retention of bar integrity, convenience to hold till the end, perfume retention without affecting in use properties.
Claims

1. A detergent bar composition comprising:
   a. more than 60 % to 95 % by weight detergent active;
   and
   b. 0 to less than 40 % by weight inorganic
      particulates and/or other conventional ingredients;

wherein the external surface of the shaped detergent
composition comprises a polymer coating comprising at
least one polymer layer, at least one of the polymer
layers being a non radiation-curable material and having
a water vapour permeability coefficient for water less
than

\[ 5000 \times 10^{-13} \frac{Cm^3}{Cm^2 s Pa} \],

which polymer coating is
substantially water insoluble and has a melting
point greater than 30°C but is abradable in use.

2. The detergent bar of Claim 1 wherein the film has a
   thickness of 5 to 1000 microns.

3. The detergent bar of Claim 1 or Claim 2 wherein the
   polymer film layer is selected from natural, synthetic
   or modified polymeric materials and/or waxes.

4. The detergent bar of any preceding claim wherein the
   polymer coating material is selected from synthetic or
   modified polymeric materials whose molecular weight is
   greater than 1600 Daltons.
5. The detergent bar of any of preceding claim wherein the water vapour permeability coefficient for the polymer coating material is less than

\[ 2000 \times 10^{-13} \cdot \frac{[Cm^{3}][Cm]}{[Cm^2][s][Pa]} \]

where \([Cm^3] = Cm^3(273,15K; 1,103 X 10^5Pa)\).

6. The detergent bar of any of preceding claim wherein the polymer coating material is a film of thickness 30 - 60 microns.

7. The detergent bar of any of preceding claim wherein the polymer coating material has a melting point greater than 45°C.

8. The detergent bar of any of the preceding claims wherein the external surface polymer coating material comprises one or more polymers and film forming diluent selected from one or more natural and synthetic waxes, polysaccharides and water insoluble salts of fatty acids, the melting point of which is greater than 30°C.

9. The detergent bar of any preceding claim wherein the detergent active is 60-90 % by weight of the composition.

10. The detergent bar of any preceding claim wherein water comprises at least 5 % by weight of the composition.

11. The detergent bar of any preceding claim wherein the polymer coating contains a base polymer which is selected
from a polyacrylates, a polymethylmethacrylate, a polystyrene, a poly (ethylene-co-vinyl acetate); a poly (ethylene-co-acrylate), a poly (ethylene-co-methacrylate), a poly (styrene-co-acrylate), a polyolefin, an atactic --olefin, a polyethylene, a polypropylene, an amorphous poly --olefin, a polyimide, nylon, polyvinyl chloride, polyethylene terephthalate, a polyurethane or an epoxoy resin, or mixtures thereof.

10 12. A process for the manufacture of the detergent bar according to any preceding claim comprising the steps of:

a. forming a detergent composition into a detergent bar; and

b. coating the bar with the polymer coating.
A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D17/00

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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</table>
| P,X      | WO 03 046119 A (UNILEVER PLC)  
5 June 2003 (2003-06-05)  
cited in the application  
example 1, table 2  
extample 2 | 1, 3, 8-12 |
| A        | EP 1 188 820 A (HENKEL KGAA)  
20 March 2002 (2002-03-20)  
claims  
page 16, line 15 - line 19 | 1-8, 10-12 |
| A        | US 5 510 050 A (BEERSE PETER W ET AL)  
23 April 1996 (1996-04-23)  
claims  
examples 1,2,5 | 1,9,10 |

Further documents are listed in the continuation of box C. Patient family members are listed in annex.

Date of actual completion of the international search  
12 February 2004

Date of mailing of the international search report  
19/02/2004

Authorized officer  
Neys, P
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| A        | DE 195 44 453 A (HENKEL KGAA)  
5 June 1997 (1997-06-05)  
claims  
examples | 1-9                                |
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