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ENZYMATIC DETERGENT BAR
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ABSTRACT OF THE DISCLOSURE

An enzymatic detergent bar, especially useful for washing laundry and removing stains therefrom, comprises: a synthetic organic detergent, e.g., linear higher alkyl aryl sulfonate; an enzyme, e.g., a protease; a builder or filter salt, e.g., alkali metal carbonate, alkali metal sulfate; a binder, e.g., corn starch; and water, in such proportions as result in production of a form-retaining, hard, non-tacky, readily soluble and effectively cleaning bar.

Also disclosed are methods for making and using the described detergent bar.

SUBJECT OF THE INVENTION

This invention relates to a detergent bar intended primarily for use in laundering applications. More particularly, the invention is of a detergent bar containing an enzyme or a mixture of enzymes useful to chemically convert hard-to-remove stains on natural or artificial fabric materials to a more readily removable form, so that they can be washed out in a laundering operation.

Also within the invention are processes for manufacturing such enzyme-containing detergent bars and methods for using them to wash stained laundry.

BACKGROUND OF THE INVENTION

The production of synthetic detergents in the last forty years has increased sharply and such materials have been developed to a point where they wash exceptionally well, so that now soap is becoming outmoded or is rarely used for heavy duty laundering of clothing and other soiled articles. However, it has been found that the synthetic detergents, even in highly built formulations containing various additives such as peptizing agents, anti-redeposition compounds and strongly alkaline builders, do not completely remove various stains which "set" into the fabrics of the laundered items. Accordingly, solvents, oxidizing and reducing agents, and more recently, enzymes have been included in built synthetic detergent powders and it has been found that in the wash water the enzymes chemically attack various stains, breaking them down into more easily removable compounds. The effectiveness of enzymes in performing this function is evidenced by the large number of commercial detergent powders and pre-soak compositions which now contain them and the acceptances of such products by consumers.

The high activities of enzymes, which act as catalysts for various biological or chemical reactions, are shown in the use of enzyme-containing built synthetic detergent powders in automatic washing machines. In such machines, which generally hold from 9 to 18 gallons of wash water, the weight of washing powder employed is usually from one to eight ounces or from about 30 to 225 grams. Thus, the concentration of enzyme in wash water, even at a 1% concentration in the detergent powder, would be on the order of 0.001 to 0.004% and of course, for the lesser quantities of enzyme often employed, the concentration is even lower. Similarly, the concentrations of active cleaning agents in such dilute washing solutions are low, although usually many times as great as the enzyme concentration.

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Although enzymes have significant stain-removing properties, they also possess certain disadvantageous characteristics which have hitherto limited their use in various products where they could be functionally important. For example, in the presence of moisture and/or other materials with which the enzymes may be reactive, it has been found that malodorous by-products are produced. The enzymes themselves are often of an aesthetically unpleasant odor and therefore, they are limited in their applications in cosmetics and other products intended for application to the human body or even for handling during use. They also lose their activity on storage in the presence of moisture or reactive materials.

Detergent bars, usually containing a synthetic organic detergent and an inorganic builder or filler salt, have been produced for use as laundry bars and in some cases, have been employed as "toilet soaps," for use with sea water or other extremely hard waters. Among the inorganic salts used in such bars have been the alkali metal silicates, phosphates, carbonates and sulfates and among the synthetic detergents have been the anionic alkyl benzene sulfonates. Gums and gelling agents have been employed as binders in detergent bars and starches have been added as binders or fillers.

DESCRIPTION OF THE INVENTION

Although the various components of the presently invented bars are known ingredients of different detergent compositions and products, they had previously not been combined in a detergent bar like that of the present invention and the special advantages of such bar and its use had not previously been obtained.

In accordance with the present invention there is provided an enzyme-containing detergent bar which comprises effective proportions of an enzyme for chemically converting hard to remove soil and stains to a more readily removable form, a synthetic organic detergent, a builder salt or a filler salt for said detergent, a binding agent for maintaining the detergent, builder or filler salt and enzyme in cohesive bar form, and water, all homogeneously combined in a form retaining, hard, non-tacky, readily soluble, effective cleaning bar. Preferably, this bar is based on a linear higher alkyl aryl sulfonate detergent, alkali metal carbonate, corn starch, protease and moisture, each within the ranges of proportions described later herein. Also within the invention is a method of manufacturing such detergent bars in which the various components are mixed together at an elevated temperature, which may be obtained from a reaction of some of the ingredients, the enzyme is admixed with the rest of the composition at a lower temperature and the total mixture is milled, plodded and pressed into bars. Also claimed as part of this invention are novel processes for use of enzymatic detergent bars wherein wet laundry is rubbed with the detergent bars at dirty or stained spots, soaked in wash water containing dissolved materials from the bar and subsequently agitated in such wash water or other detergent solution.

The invented detergent bars are sufficiently hard so as to be maintained in a solid form resembling soap, and yet, despite the inclusion of very soluble components, do not dissolve too readily and do not become soft or mushy after use, due to gelation with water. The enzyme component, although in the presence of a significant proportion of water in the bar, which helps to maintain the component in homogeneous form and prevents crystallizing out into hard kernels of the less soluble ingredients, does not decompose, and useful enzymatic action is obtained even after lengthy storage periods and after storage at high temperatures and high humidities. The enzymes used do not discolor the bar objectionably on storage and do not become malodorous. In fact, they even seem to improve the bouquets of perfumes employed. Such results are attributed in part, at least, to the binder employed, especially corn starch, which seems to have a stabilizing effect upon the enzymes, in addition to its water-holding, binding, filling and slip-improving effects on the bar product. When significant amounts of fluorescent brighteners are present, they additionally help to improve the appearance of the washed previously stained laundry, by brightening it and thereby making the effects of any small amount of staining material still present after laundering less noticeable. Of course, the detergent, builder and filler constituents all perform their desired functions in the presence of the other ingredients. Of the detergents, it is preferred to employ linear alkyl aryl sulfonates, which wash very well in the presence of the other constituents and also are relatively easily biodegradable. Although phosphates are excellent builders, for water pollution control purposes it may be desirable to replace them with the carbonates, bicarbonates and silicates, as is done in the preferred formulas illustrated herein.

The invented detergent bars are easily manufactured with conventional equipment and may be made directly from detergent acid and soda ash (to form the active detergent ingredient), with addition of the various other constituents, followed by conventional milling, plodding and pressing operations. In use, the products are preferably employed in such a manner that advantage is taken of soaking the soiled and/or stained laundry in a solution of the detergent bar materials, so as to take advantage of then enzymatic action.

The synthetic organic detergent employed may be any suitable such material, including anionic, nonionic or amphoteric detergents and in some cases, cationics may also be employed, although they will usually be avoided when anionics are present. Of the detergents, it is preferred to employ those which are anionic and of these the sulfonated and sulfated (sulf(on)ated) detergents, preferably having an alkyl group of from 8 to 22 carbon atoms, have been found to be best for a desired combination of cleaning effect and best physical characteristics.

The sulfonic or sulfuric group of the anionic sulf(on)ated detergents may be joined directly or indirectly to a hydrophobic organic group, which usually contains the mentioned higher alkyl. Among the water soluble anionic sulfonated detergents the higher alkyl aryl sulfonates having about 8 to 18, preferably 10 to 16 carbon atoms in the alkyl group are particularly effective. It is preferred to use the higher alkyl benzene sulfonate detergents, although analogous materials containing mononuclear aryl groups such as xylene, toluene or phenol, may be employed instead of the benzene nucleus. The higher alkyl substituent may be either straight-chained or branched to produce the desired products. The straight-chained materials include those in which the alkyl groups are n-decyl, n-dodecyl, n-tetradecyl and n-hexadecyl, which formerly were derived exclusively from natural fatty material but now may also be obtained from petroleum. The straight chained or linear alkyl benzene sulfonates are comparatively easily biodegradable, whereas branched chain materials are more difficult to degrade biologically and will often be avoided where water pollution is a problem. However, where branched chain alkyl aryl sulfonates and other detergents containing branched lipophilic groups are usable, they perform very satisfactorily in the present detergent bars, being excellent cleaning agents and possessing the desired physical characteristics for making a good bar. Even in this respect, however, it has been found that the detergents containing linear higher alkyl substituents are generally firmer and make a more satisfactory detergent bar of good physical characteristics. In addition to the alkyl aryl sulfonates, the other anionic sulf(on)ated detergents may be employed, such as the higher alkane sulfonates (higher=8 to 22 carbon atoms in the alkyl group), the higher alkyl sulfates, the higher alkene sulfonates, higher alkene sulfates, the higher alkyl sulfonates wherein the alkyl group is linked to sulfonic acid group through a —COOR group (R being a lower alkyl or a substituted lower alkyl group of 2 to 3 carbon atoms), and analogous types of compounds wherein the linking is through a —CONHR— group or other suitable intermediate radical. The useful sulfates include the alkyl oxyethylene sulfates, the monoglyceride sulfates, the sulfated higher alkyl phenyl oxyethylene ethanols or -polyoxyethylene ethanols and the sulfated polyoxyethylene ethanols or sulfated poly-lower oxyalkylene lower alkanols. These are only a few of the anionic detergents known in the art to be useful solid or solidifiable cleaning agents and which can be incorporated as the principal synthetic organic detergents in the present compositions. Similarly, phosphorus analogues of the above compounds are useful in at least partial replacement of the sulf(on)ated materials.

Among the nonionics, as with the anionic compounds, it is preferred to employ those detergents which are normally solid and water soluble. Included within this group are higher alkyl aryl phenol polyoxy-lower alkylene lower alkanols, polyoxylower alkylene alkanols, higher fatty alcohol ethers of polyoxy-lower alkanols, block copolymers of different polyoxy-lower alkylene alkanols, and the heterocyclic mixed polyoxy-lower alkylene alkanols. In such compounds, the lower alkylenes are usually of 2 to 4 carbon atoms. The alkanol portion of the molecule, in some cases, may be terminated with a lower alkoxy group, instead of a free hydroxyl.

The amphoteric or ampholytic detergents, although not preferred major constituents of the present synthetic detergent component, are useful mainly as partial replacements or supplements for anionic and nonionic detergents. These include the betaines, sulfobetaines, Miranols, amidobetaines, and amidosulfobetaines. The cationic compounds include principally the quarternary ammonium halides but analogous phosphorus compounds may also be employed. Substituents on the nitrogen will normally be lower alkyl, higher alkyl, benzyl or aryl, in various combinations.

The synthetic detergents of the anionic type will usually be employed as their water soluble salts, with the salt-forming ion preferably being an alkali metal, e.g., sodium, potassium. However, other salt forming ions may also be employed, such as ammonium, lower alkanolamine and lower alkylamine. For the cationics, the salt-forming ion will usually be halide, e.g., chloride, bromide or iodide.

Some specific examples of useful detergents which may be used as cleaning agents in the present bars are sodium n-dodecyl benzene sulfonate; sodium n-tridecyl benzene sulfonate; potassium n-hexadecyl benzene sulfonate; sodium n-dodecyl toluene sulfonate; sodium propylene tetramer benzene sulfonate; sodium propylene pentamer benzene sulfonate; sodium tridecyl benzene sulfonate, wherein the tridecyl is a mixture of propylene pentamer and propylene tetramer; sodium butylene trimer benzene sulfonate; potassium tridecyl benzene sulfonate; sodium lauryl sulfate; sodium lauryl sulfonate; ammonium coconut oil fatty acids monoglyceride sulfate; triethanolamine n-hexyl sulfonate; sodium N-lauroyl sarcosine; sodium oleoyl isethionate; sodium lauroyl N-methyl tauride; dodecyl glycerol ether sulfonate; sodium lauryl tri(oxyethylene) sulfate; nonyl phenol hexa(oxyethylene) sulfate; lauryl deca(oxyethylene) ethanol; block copolymers of ethylene oxide and propylene oxide, having a molecular weight of about 3,000 (Pluronics®); various Miranol® detergents, described at pp. 142–144 of Detergents and Emulsifiers (McCutcheon), 1969 Annual; benzothonium chloride; dimethyl dibenzyl ammonium chloride and cetyl trimethyl ammonium bromide. Descriptions of other such detergents are found in the text Synthetic Detergents by Schwartz, Perry and Berch, published in 1958 by Interscience Publishers, New York, pp. 25–143.

The builder salts which are useful in making the present bars include the conventional builders for synthetic organic detergents but of these, it is preferred to employ, at least in part, the alkali metal carbonates and/or bicarbonates. The use of such builder(s) facilitates an economical manufacturing process wherein an anionic detergent acid is neutralized in situ. However, in addition to the carbonates and bicarbonates, there may be employed various boron-containing builders, e.g., borax; silicates, such as those having an $Na_2O:SiO_2$ ratio of from 1:1 to 1:3, preferably from 1:1.6 to 1:2.35; and phosphates, especially the polyphosphates e.g., pentasodium tripolyphosphate and tetrapotassium pyrophosphate. Also useful are the organic builders, which are usually employed to a lesser extent than the inorganic builders. Exemplary of these are NTA (trisodium nitrilotriacetate monohydrate) and EDTA (ethylene diamine tetraacetic acid, usually used as the tetrasodium, tetrapotassium or trisodium salt).

Filler salts, generally water soluble inorganic salts which add bulk to the detergent bar and sometimes desirably modify its solubility and physical characteristics, include the water soluble inorganic sulfates and bisulfates, plus other suitable water soluble salts which may be employed on occasion, e.g., sodium chloride. The filler and builder salts may be anhydrous or hydrates. The fillers will often be present as byproducts from the manufacture of anionic detergents, etc.

Binding agents for holding the bar together in a cohesive, yet desirably soluble form, include the natural and synthetic starches, gums and thickeners and derivatives thereof. Thus various starches such as corn starch, potato starch, yucca starch, tapioca starch and starches derived from cellulose are useful binders, as are the components and derivatives thereof, such as amylose, amylopectin and partially hydrolyzed starches. The starch may be at least partially replaced by cereal flours which contain large proportions of it, such as wheat or potato flours. Gums include alginates, agar agar, guar and mucilages. Some binder compounds also possess soil-suspending properties and help to maintain the removed dirt in finely divided suspension in the wash water to prevent it from re-adhering to the laundered material. Among such materials are polyvinyl alcohol and sodium carboxymethyl cellulose. Although corn starch does not have as significant an effect as the PVA or CMC, as previously mentioned, it is the most preferred binder in the present bars, principally because it forms a bar with desired tactile properties, low density (compared to other detergent bars containing inorganic salts), desired solubility and smoothness, and, most important, it aids in stabilizing the enzymes, preventing their degradation and consequent inactivation and the development of malodorous byproducts. Various corn starches appear to have this desired property, over a variety of amylopectin:amylose content ratios.

The enzyme constituent of the detergent bar is most preferably a proteolytic enzyme. Such enzymes are active on proteinaceous materials and catalyze digestion or degradation of such matter when it is present in the form of a stain on a fabric. The degradation by a hydrolysis mechanism, for example, results in the production of a more soluble material which is removable by the built synthetic detergent solution. The various enzymes employed are generally effective at pH ranges regulated by the content of builder salt in the detergent bar. Such a range may be from about 4 to 12 and is preferably about 8 to 11. The proteolytic enzymes, although subject to some degradation by heat, may be employed in washing solutions at temperatures up to about 80° C. and are also effective at low temperatures, down to about 10° C. Among the proteolytic enzymes may be mentioned pepsin, trypsin, chymostrypsin, papain, bromelain, collagenase, keratinase, carboxylase, amino peptidase, elastase, subtilisin and aspergillopepidases A and B. Preferred enzymes are subtilisin enzymes manufactured and cultivated from special strains of spore forming bacteria, particularly *Bacillus subtilis.*

Proteolytic enzymes such as Alcalase, Maxatase, Protease AP, Protease ATP 40, Protease ATP 120, Protease L–252 and Protease L–423 are among those enzymes derived from strains of spore forming bacilli, such as *Bacillus subtilis.* Different proteolytic enzymes have different degrees of effectiveness in aiding in the removal of stains from textiles and linen. Particularly preferred as stain removing enzymes are subtilisin enzymes. Metalloproteases which contain divalent ions such as calcium, magnesium or zinc bound to their protein chains are of interest. The manufacture of proteolytic enzyme concentrates is described in German Offenlegenschrift 1,800,508 and Dutch patent application 6815944.

Instead of or in partial replacement of the proteolytic enzyme, other enzymes may also be used, usually for specific purposes. Thus, an amylase may be employed, e.g., bacterial amylase of the alpha type such as is obtained by fermentation of *Bacillus subtilis.* Among the other enzymes that may be used are those characterized as hydrolytic, lipolytic, oxidizing, reducing and glycolytic. Such include catalase, lipase, maltase and phosphatase. The mentioned enzymes and classes thereof, while considered to be most useful, are not the only effective ones in the present bars. Virtually any enzymes that contribute to loosening of the bond by which soils or stains are held to fibrious materials may be used in the bar formulas. Guides to such use may be found in Principles of Biochemistry by White, Handler, Smith and Stetten (1954).

The contents of particular enzymes are often measured by their activities in standard tests. Thus, the activities of proteolytic enzymes may be measured by Anson units and that of amylase by Novo alpha-amylase units. The number of Anson units of a highly preferable, commercially available subtilisin enzyme, such as Alcalase, produced by Novo Industri A/S, Copenhagen, Denmark, is 1–4/g. and Anson ratings of starting materials up to about 8/g. are possible. Such enzymes, generally in the form of finely divided powders, beads or prills, may be distributed on a carrier or may be substantially salt-free. When employed, the carrier will often be calcium phosphate, sodium sulfate, sodium chloride or other suitable soluble or insoluble salt or other material, often depending on the product in which the enzyme is to be incorporated. Of course, as with other components of the present detergent bars, mixtures may be used to obtain most desired results.

The water which is a part of the final bar product is obtainable as a solvent with various constituents or as water of hydration accompanying them. If more water is needed to make the product sufficiently plastic to be worked, it may be supplied as an additional ingredient, in which case it is preferred to utilize deionized water. Nevertheless, in some instances, as when the detergent employed foams and washes better in the presence of hardness ions, harder waters, up to about 300 parts per million but usually of a hardness no greater than about 150 parts per million and preferably less than 60 p.p.m., as calcium carbonate, may be used.

The perfumes employed in the present bars may be selected from a wide variety of perfume materials previously found useful in soaps and detergents. They include aromatic, sweet, citric, floral, fragrant, ethereal, esteric, resinous, camphoric and heavy perfumes. Representative perfumes of such types include lemon oil, oil of citronella, citral, pine oil, non-aldehyde, oil of Bergamot, rose hip oil, lemongrass oil, terpineol, menthol, coumarin, eugenol, oil of pepermint, etc., and various fixatives which may be employed with these. It appears that the presence of the enzyme helps to improve the stability of the perfumes, possibly by causing the destruction of proteinaceous and other materials which could otherwise catalyze reactions of the perfumes. This stabilization effect is particularly pronounced with respect to citrus oils, oil of citronella, and proteolytic enzymes.

The fluorescent brighteners which greatly improve the appearance of washed, previously stained laundry items, may be any of the wide variety of such materials, also known as optical bleaches, optical brighteners and fluorescent whiteners. included among these are brighteners specifically useful for whitening cotton, such as the CC/DAS brighteners which are derived from the reaction product of cyanuric chloride and the disodium salt of diaminostilbene disulfonic acid. Various such cotton brighteners differ from each other with respect to substituents on the triazine and aromatic rings. In addition to the cotton brighteners, bleach-stable brighteners, resistant to the action of chlorine-containing bleaches, are usually benzidine sulfone disulfonic acids or may be naphthotriazolylstilbene sulfonic acid or a benzimidazolyl derivative. Polyamide brighteners are generally either aminocoumarins or diphenyl pyrazoline derivatives. Polyester brighteners, also useful in whitening polyamides (nylons), may be naphthotriazolylstilbenes. The brighteners are normally present as their soluble salts but may be utilized as the corresponding acids, subsequently to be converted to salt form. They may be used essentially pure or on carriers. Cotton brighteners will usually comprise a major proportion of the brightener system employed and such system will generally also include an amide-polyester brightener. Among the brighteners usable in the present bars are Calcofluor White ALF (American Cyanamid); ALF-N (American Cyanamid); SOF A-2001 (Ciba); CWD (Hilton-Davis); Phorwite RKH (Verona); CSL, powder, acid (American Cyanamid); CSL, liquid, monoethanolamine salt (American Cyanamid); FB 766 (Verona); Blancophor PD (GAF) UNPA (Geigy); Tinopal RBS (Geigy); and RBS 200 (Geigy). A good description of the optical brighteners is found in Optical Brighteners and Their Evaluation, by Per S. Stensby, a reprint of articles published in Soap and Chemical Specialties in April, May, July, August and September 1967, especially at pp. 3–5 thereof.

In addition to the required constituents of these bars, various adjuvants may be present to give them additional desired properties, either of functional or aesthetic nature. Thus, there may be included in the bars pH adjusting agents, e.g., sodium hydroxide, triethanolamine, sulfuric acid; buffering agents, e.g., sodium borate, sodium bisulfate; foam improvers, e.g., lauric myristic diethanolamide, lauryl dimethylamine oxide; bactericides, e.g., tetrachlorosalicylanilides, hexachlorophene; fungicides; dyes; pigments (water dispersible); preservatives; ultraviolet absorbers; fabric softeners, and bleaches, e.g., sodium perborate. Of course, in the selections of the adjuvants to be employed, they will be chosen so as to be compatible with the main constituents of the bars.

The proportions of the components of the detergent bar are maintained so as to produce an effective cleaning or laundry bar with good enzymatic action and of desired physical properties. Thus, within the description in the specification and the proportions mentioned herein, adjustments will be made depending on the particular characteristics most desired in the product.

The synthetic organic detergent will be from 10 to 40% of the bar in almost all situations and will preferably be from 20 to 40% thereof, the most preferable concentration being about 25 to 35% of the final product. It has been found that such proportions result in effective cleaning and often help to maintain the homogeneity of the bar product, in conjunction with the binder and water constituents. As has been mentioned, the preferred alkyl benzene sulfonate detergent is usually a major proportion of the detergent constituent. Preferably, it comprises from 70 to 100% thereof. With it may be included other anionic, nonionic or ampholytic detergents, and sometimes, even cationic materials. The alkyl benzene sulfonate may be completely replaced, in some instances, by other anionic or nonionic detergents and may be replaced in minor proportion by the ordinary higher fatty acid soaps which, strictly speaking, are not synthetic organic detergents within the usual meaning of that term.

The builder and filler salts will ordinarily be from 20 to 60% of the bar and preferably, a major proportion of the total of filler and builder will be builder. Depending on the types of builders and fillers employed, the contents thereof in the products may be near the bottom or top of this range. Thus, a preferred range is from 25 to 55% of builder salt, with any remaining materials being filler. Of the builders, it is generally desirable to have from about 5 to 25% of sodium carbonate, from about 5 to 40% of sodium bicarbonate, and 0 to 10% of sodium silicate, with 0 to 3% of sodium sulfate and from 0 to 2% of pentasodium tripolyphosphate or tetrasodium pyrophosphate also being present.

Usually, at least about 0.5% of each of the builders or fillers will be present, it they are employed, because lesser amounts appear to have no useful activity.

The binder constituent will generally comprise from 5 to 40% of the detergent bar, preferably from 10 to 35% thereof. This will usually include a major proportion of starch, preferably from 70 to 100% thereof and most preferably, it will be entirely corn starch. Other binders of the types previously mentioned may be employed to supplement the effects of the starch in the product.

The enzyme, as a concentrated commercial form thereof, may be from 0.05 to 5% of the bar. However, because of cost and functional considerations, this proportion will normally be 0.1 or 0.2 to 1% of the product, which proportion has been found to be commercially competitive and yet, sufficiently active to improve the stain-removing properties of the bar significantly. Preferably, the entire proportion of the enzyme concentration will be protease or other useful proteolytic enzyme, because the proteinaceous stains appear to be those which are more common and most difficult to remove. Thus, of the enzyme charge, a major proportion, preferably from 70 to 100%, will be proteolytic enzyme or protease. If the enzyme is present on a carrier, the percentage will be adjusted accordingly. In terms of Anson units, the proportion of enzyme in the detergent bar will be such as to result in from about 0.001 to 0.1 Anson unit per gram of bar.

The moisture content of the milled, plodded and pressed detergent bars will usually be within the range of from 5 to 25% thereof. Such a wide range of moisture contents is useful because some of the builder and filler salts are hydratable and moisture is taken up by the corn starch or other binder. Normally, the moisture content will be within the 8 to 22% range and preferably it is from 10 or 12 to 17%. Such a moisture content allows the bar to be processed easily, gives it desired solubility characteristics and promotes homogeneity in manufacture.

The fluorescent brightener content usually will be from about 0.05 to 2% of the bar and will preferably be from about 0.1 to 0.5% thereof. A major proportion of the fluorescent brightener content will often be cotton brightening compound, with a minor proportion thereof being useful in brightening nylons and polyesters.

The content of perfume, while also minor, is very important to the aesthetic acceptance of a detergent bar. It will usually be from 0.1 to 2% of the bar, preferably 0.1 to 1% thereof and in some preferred enzymatic bars a major proportion of the perfume will be a citrus oil or oil of citronella. Stabilizer materials in the products, pigments, soluble or insoluble; dyes; foaming agents; solvents; buffers; and any other adjuvants which may be employed, will usually be limited to 10% of the bar, preferably 5% and most preferably 3% thereof. Individual additive constituents will normally not exceed 5% of the bar and will generally be maintained at a level less than 1% thereof.

The detergent bar produced will usually be comparatively light, when judged against other inorganic salt-built competitive products. Thus, the density will ordinarily range from about 1.2 to 1.5 grams per cubic centimeter. The pH of a 1% solution of the bar will usually be in the range of from 7 to 11 and is preferably from 8 to 10. In wash water or soaking solution, the pH may drop about one unit. It will usually be desired to maintain the pH at a range at which the particular enzyme and detergents employed are most effective.

To manufacture the detergent bars the various constituents may be admixed in any suitable order. A sigma blade mixer is a suitable medium, especially where a subsequent drying operation is desirably avoided, as in the case of heat-sensitive enzymes. To avoid such need for heating the final composition, a "dry" process of manufacture is found to be most efficient, especially when anionic synthetic organic detergent salts are employed. For example, in the case of alkyl benzene sulfonates, there may be used the corresponding detergent acid, usually in aqueous solution, and it may be dry neutralized with sodium carbonate or sodium bicarbonate powder or sodium hydroxide or other suitable agent. Preferably, the neutralizing agent, e.g., sodium carbonate, is employed in excess, so that some of it will be converted to the bicarbonate and some will not be consumed in the neutralization reaction, thereby serving as the desired builder salt in the composition. Heat is generated in the neutralization reaction, even when a cooling jacket is employed, and the temperature often rises to about 50° C. and sometimes, above 55° C. Such temperatures are harmful to many enzymes and other heat sensitive ingredients of the composition, so the mixture of the neutralized detergent salt, binder, builder and/or filler and water is cooled to a temperature of 45° C. or below, preferably to below 35° C., at which temperatures the enzyme and other heat sensitive materials, such as perfumes and dyes, are added. The proportions of the various ingredients were previously given and will not be repeated here. After good mixing in the sigma blade mixer or other equivalent apparatus, the mix is dropped to a conventional soap line, wherein it is milled to chip, usually from 0.002 to 0.015 inch thick, which is plodded in a standard ploddler with heat on the nozzle plate, to produce a bar which is then cut to length and pressed in a conventional soap press, usually at a pressure of from 25 to 500 lbs./sq. in. In a modification of this procedure, to produce attractively colored or speckled bars, colored material, i.e., dyed pentasodium tripolyphosphate granules or beads, may be blended in with the composition paste or with milled chips. This is done so as to prevent complete distribution of the color throughout the bar and leave it with a speckled or marbelized appearance. Generally, in such procedure, the weight of colored particles added to the paste will be from 0.2 to 5% thereof, preferably from 0.5 to 2%. It is considered that the main area of manufacturing process novelty in the invention resides in the use of the dry neutralization process in the making of an enzymatic detergent bar, with cooling to protect the enzyme. Consequently, since the various other steps in the method involve conventional equipment and processing conditions (milling, plodding and pressing), these are not recited in detail here. Of course, it is clear that orders of additions of materials may be varied, other adjuvants may be included, constituents may be added as solids, suspensions or solutions, etc., without departing from the procedures of the invention.

Enzymatic detergent bars are especially useful for removing stains and deeply worked-in dirt from clothing and other items of laundry. Of course, the particular detergent bar formula that will be employed may have the enzyme chosen so as to have greatest activity at the pH employed and against the stains encountered. Thus, with respect to dye stains, oxidative or reductive enzymes may be used whereas with fruit stains, which may be carbohydrate-based, enzymes which attack the larger carbohydrate molecules may be most successful. However, although it is known to vary the enzyme employed with the type of stain being removed, it has been found that with the present bars the proteolytic enzymes seem to be effective against a wide variety of staining materials, perhaps due to a proteinaceous link in the affixation mechanism by which the stain is held to a substrate, whether that substrate be cotton or synthetic, such as polyester or nylon. In further discussion, for simplicity, reference will be made mostly to proteolytic enzymatic bars.

The laundry is initially moistened or wet, preferably by immersion in a tub of water, after which it is drained and the bar is rubbed by hand against the most badly soiled areas, e.g., shirt collars, cuffs, trouser knees, and on stained surfaces. The stains to which the bar may be applied are, for example, food stains such as chocolate, cherry, blueberry, grape, blood, gravy, ketchup, mustard, wine and grease, but also removed are grass stains, inks, etc. Normally the stains will not have to be rubbed for more than seconds and rarely is this necessary for more than one minute. After rubbing of all the stains of a particular item of laundry, it may be left in that wet condition to enable the enzyme to work on the stain or, if desired, the laundry may be placed in a tub with more water, allowing the dissolved detergent bar constituents to contact the entire area of the laundry, although in a more dilute state. Generally, the concentration of detergent bar materials in the "soak" water will be from 0.05 to about 1.0% and the soaking period will be from about ½ hour to 10 hours but it may be as long as 24 hours or even more. Normally, the enzymes are effective for only about 2 to 10 hours, but even so, additional soaking allows the combination of detergent and builder better to loosen the partially broken down stain. The temperature of the soak water will usually be about room temperature or slightly higher although temperatures within the range of 20–60° C. are useful. Normally, however, the temperature will be from 20° C. to 40° C. At the temperatures and over the times indicated, the binder or corn starch component of the enzymatic bar performs a useful function in tending to coat the item being soaked when the laundry is not placed into a dilute bath, preventing it from drying out excessively, which could inactivate the enzyme.

After completion of the soaking period, a dilute solution of the applied detergent bar materials may be formed and washing of the laundry may be conducted in this solution, generally at an elevated temperature of from 50 to 90° C. although preferably at a temperature of 50 to 80° C. In some cases, colder water, at a temperature as low as 15° C., can be employed. If the enzyme has become inactivated, additional detergent bar or other enzymatic and detergent materials may be added to the wash water. The subsequent washing may be in an automatic washing machine for a period of from five minutes to one hour or may be by hand and may take a similar or shorter time. After completion of washing, the laundry is rinsed, wrung out and dried. If, after washing is finished, any stains are still noted on the laundry, they may be rubbed with the detergent bar and, if desirable, may be soaked again.

The results of the washing procedures described are surprisingly good. Despite the fact that the detergent bar may have withstood lengthy periods of storage, up to six months and such storage may have been at a high temperature and under high humidity, with the bar containing a substantial proportion of moisture, the enzyme is still active and the bar color is good. Furthermore, the perfume is truer than in bars without enzyme. Thus, by the present invention, there is produced a product which is needed in the laundry to supplement the granular enzymatic materials now available and to perform a function for which the granular products are not suited. The invention is a surprising one because the expectedly incompatible constituents of the product do not destroy each other and, on the contrary, result in the creation of a highly useful and hitherto unavailable detergent product and an effective washing and stain-removing process. Such products are useful where washing machines are not available and hand washing is standard practice but they are also employable in conjunction with machine washing to improve washing and stain removal.

The following examples illustrate the invention. Unless otherwise specified, all parts given are by weight and all temperatures are in degrees centigrade.

EXAMPLE 1

	Percent
Bleached higher alkyl benzene sulfonic acid (95% aqueous solution, higher alkyl-tetrapropylene)	33.3
Soda ash, finely divided (90% passes through a 140 mesh sieve, U.S. Standard Sieve Series)	27.3
Corn starch	29.6
Water	8.1
Sodium bisulfite, powder	0.6
Protease Alcalase enzyme (Novo Industries, 1.5 Anson units per gram minimum activity)	0.6
Titanium dioxide, anatase	0.3
Perfume, Rondelia detergent type	0.2

In a sigma blade mixer the detergent acid is admixed with soda ash in the presence of a sufficient small proportion of water to aid in the neutralization reaction. Although a cooling jacket is employed, the heat of reaction raises the temperature to about 65° C. After substantial completion of neutralization, the corn starch, titanium dioxide, sodium bisulfite, water and perfume are added with continued mixing. The neutralization occurs over a period of about ten minutes and the mixing with other materials lasts for an additional five minutes. At the end of the mixing, the temperature of the paste resulting is about 55° C. Because this temperature is considered too high at which to add heat-sensitive enzyme to the formulation, the paste is removed from the sigma blade mixer and is cooled, utilizing a heat exchanger, to a temperature of about 40° C., after which it is returned to the sigma blade mixer and the Protease Alcalase enzyme is added. If desired, such addition may be in the presence of some of the water of the formula, to promote better dispersion.

After complete mixing of the formula ingredients, which takes about an additional five minutes, the paste is discharged to a mill, wherein it is milled to a chip or ribbon about 0.18 mm. thick. The milled detergent composition is then fed to a plodder, equipped with a vacuum connection to prevent entrapment of air in the bar, and, using a nozzle plate at a temperature of about 60° C., composition is plodded at a pressure of about 14 kg./sq. cm. into a continuous bar of rounded rectangular cross-section. The bar is cut to lengths and is pressed in a conventional four pocket automatic soap press at a pressure of about 21 kg./sq. cm., after which the detergent bars are wrapped and packed, ready for shipment to warehouses or retail stores.

The enzymatic detergent bars produced contain about 31% of the sodium alkyl aryl sulfonate detergent, 17.5% of sodium carbonate, 7.5% of sodium bicarbonate, 26.4% of corn starch, 13.9% of moisture, 1% of sodium sulfate and 1% of free acid. The bars produced are of a desirable light color and of good perfume aroma. They are hard enough so that they can be handled and shipped without distortion and yet, dissolve in water at a satisfactory rate, neither so fast as to smear and become gelatinous nor so slow as to be difficult to employ in the treatment of stained or dirty sections of laundry to be washed.

The detergent bars are tested for useful washing and stain-removing activity by actual use tests on stained and dirty laundry and by other tests on intentionally stained cloths. In the laundry tests, the dirty or stained laundry items are first wet with warm water, at about 40° C., which is then drained or wrung out to leave the laundry damp. Then, dirty or stained sections are rubbed with the enzymatic detergent bar, producing a rather concentrated detergent and enzyme deposit in contact with the dirt or stain. Yet, there is sufficient water to promote the working of the enzyme on the proteinaceous or other organic bonding agent which holds the dirt or stain to the textile. After about a minute's rubbing of the detergent bar constituents on the stains or dirty sections, they are left in this condition, with the concentration of bar constituents being about 5% on the average over the period of standing. Alternatively, more water may be added and a more dilute soak, at a concentration from about 0.05 to about 1%, may be used. Soaking lasts for about 6 to 24 hours, after which the laundry is washed, using, if desired, more detergent bar constituents plus the previous wash water. Such washing takes place at about 70° C. and is effected in an automatic washing machine, wherein the concentration of the enzymatic detergent composition is about 0.2% and the pH is about 9.

The washed laundry is noticeably cleaner and stains are removed to a significantly better extent than when a similar laundry is washed in the same manner, utilizing a bar containing no enzyme additive. Also, it is noted that the perfume and color of the enzymatic detergent bar are very good, despite storage under high temperature and high humidity conditions for periods as long as six months. In this respect, the enzyme appears to stabilize the perfume better in the "experimental" bar than in the "control" bar. Similar results are obtained when the experimentally stained cloths are washed by the same techniques. The stains are either completely or substantially removed.

Additional enzymatic detergent bars are made wherein minor proportions, 0.05 to 1.0% of optical brighteners of the cotton and amide-polyester brightener classes, previously described in the specification, are included in the formula in place of a similar proportion of corn starch. Such products, when used according to the washing techniques described previously, remove stains and dirt and also brighten the laundry so as to make any small signs of stains still present less apparent. In other experiments, pentasodium tripolyphosphate granules, colored with blue and green dyes, are mixed in with the milled enzymatic detergent composition before plodding and, using a total proportion of about 0.7% of such granules (which also contain minor proportions of dextrose). A speckled and somewhat marbleized detergent bar appearance is obtained, which distinctively identifies the enzymatic product to a consumer.

In similar manner, other synthetic or organic detergents are employed instead of the one described above and in preferred compositions, the synthetic organic detergent is a linear tridecyl benzene sulfonate, sodium salt. Nevertheless, instead of or in addition to such anionic detergents, there may be used others, such as sodium monoglyceride sulfate, sodium lauryl alcohol sulfate, ammonium higher olefin sulfonates, Pluronics® and Miranols.® With respect to the builder salts, pentasodium tripolyphosphate, tetrasodium pyrophosphate and NTA can be added to or substituted for the carbonate or bicarbonate. Similarly, instead of corn starch or part thereof there may be used amylopectin, potato starch, amylose or similar binder, and amylases, glycolase, hydrolases, oxidases, reductases may be substituted for the proteolytic enzyme. The antioxidant, sodium bisulfite, may be omitted or other adjuvants with similar properties may be used. The variations in the bar formulas and changes in proportions within the ranges previously given result in enzymatic detergent bars having similar good washing and stain-removing properties, providing that the materials employed and the proportions thereof present are within the scopes of the previous descriptions. Also, in such formulas, it is highly preferred that corn starch be the binder used, with protease being the enzyme.

EXAMPLE 2

	Percent
Dodecyl benzene sulfonic acid, bleached	29.0
Soda ash, dense, fine	42.4
Corn starch	12.2
Sodium silicate, 49.5° Bé. (Na_2O:SiO_2=1:2.0)	10.0
Proteolytic enzyme (Protease Alcalase)	0.6
Water, deionized	5.6
Perfume, citronella	0.2

Following the manner of Example 1, as modified for the different ingredients, the sulfonic acid is neutralized with the soda ash, in the presence of the sodium silicate and water, corn starch and perfume are added, after which the mix is cooled and the enzyme is added. The product comprises about 27.5% of active detergent, 35.0% sodium bicarbonate, 6.6% of sodium carbonate, 11.1% of corn starch, 4.5% of sodium silicate and 14.7% water.

When tested in the washing of laundry and in stain removal from cotton cloths, even after months of storage, the enzyme is noticeably active and the enzymatic detergent bar removes stains noticeably better than a control bar containing no enzyme. When brighteners such as Tinopal LCS, Uvitex S2R and Uvitex SFC are employed, to the extent of a total as small as 0.1% or 0.2%, the combined cleaning and brightening effects are significant improvements over similar bars not containing such ingredients. Also noted is the improved stability of the perfume of the bar, apparently due to the presence of the enzyme and/or the combination of enzyme and corn starch in the formula. The color of the bar is good and it is not darkened or otherwise degraded by the presence of enzymes, corn starch and water therein. The bar density is about 1.3 g./cc., desirably light in weight, and it is non-tacky.

Similar bars may be made containing more or less moisture and different proportions of the enzymes, binders and builder salts and the desired advantages are still obtainable. Among the enzymes which may be included are those commercially supplied as Protease Alcalase, Novo Industri (1.5 Anson units per gram minimum activity); Alcaline Protease, Wallerstein Company, Division of Travenol Laboratories, Inc. (180,000 PCA units per gram minimum activity); Maxatase 330,000, Charles Pfizer and Company, Inc., Chemical Division (330,000 Delft. units per gram minimum activity); and Chase Protease M–223, Chase Chemical Company (1.5 Anson units per gram minimum activity).

Although the washing methods described in Example 1 are preferred means of effecting the best stain removal, since they utilize an extensive soaking period in contact with the enzymatic detergent bar, it is also found that ordinary rubbing and washing of stained and soiled laundry with the bar is effective, even when no extensive soaking period is employed intermediate the initial rubbing and the final washing steps.

EXAMPLE 3

The procedure of Example 1 is repeated with the exception that the anionic detergent is charged to the mixer as a neutral salt, together with a proportion of water equivalent to that obtained in he neutralization reaction. By utilizing the neutralized detergent, mixing can be effected at a lower temperature, even at room temperature, although it is preferred to mix at about 40° C. to improve the plasticity of the product during processing, so that it can be milled, plodded and pressed easily.

When tested against specific stains, such as coffee, chocolate, blood, mustard, wine, ketchup and grass stains, on cotton, rayon, nylon and polyester-nylon blends, such detergent bars are good cleaning and stain-removing agents. In modifications thereof, the proteolytic enzyme is replaced by amylase, oxidases, reductases, and esterases and each of these is also found to have good stain-removing action. It is notable that the enzymes are not degraded by the presence of the corn starch, moisture, perfume detergent and builder components and in fact the presence of the binder appears to stabilize the enzyme.

The invention has been described with respect to various illustrations and examples thereof but is not to be considered as specifically limited by them because it is apparent that equivalents may be substituted to produce composition, products, methods and uses within the spirit and scope of the invention.

What is claimed is:

1. A detergent bar which consists essentially of 0.5 to 5% of an enzyme selected from the group consisting of proteolytic enzyme, amylase, catalase, lipase, maltase, phosphatase and mixtures thereof, the major proportion of which is proteolytic enzyme, in an effective proportion for chemically converting hard to remove soils and stains on laundry to a more readily removable form, 10 to 40% of synthetic organic detergent, 20 to 60% of a salt selected from the group consisting of alkali metal carbonate, alkali metal bicarbonate, borax, alkali metal silicate, alkali metal phosphate, trisodium nitrilotriacetate, tetrasodium ethylene diamine tetraacetate, tetrapotassium ethylene diamine tetraacetate and trisodium ethylene diamine tetraacetate builder salts and water soluble inorganic sulfate, bisulfate and sodium chloride filler salts, 5 to 40% of a binding agent selected from the group consisting of starch, amylose, amylopectin, partially hydrolyzed starch, alginates, agar, guar gum, polyvinyl alcohol and sodium carboxymethyl cellulose and 12 to 25% of water, all homogeneously combined in a form-retaining, hard, non-tacky, readily soluble, effectively cleaning bar.

2. A detergent bar according to claim 1 in which the enzyme content is from 0.1 to 1% and from 70 to 100% thereof is proteolytic enzyme so that the detergent bar contains from 0.001 to 0.1 Anson unit/gram, 20 to 60% of a builder or a mixture of builders is present and the binding agent is from 10 to 35% of the bar, with from 70 to 100% thereof being starch.

3. A detergent bar according to claim 1 in which the synthetic detergent is an anionic synthetic organic detergent, builder salt is present and the binding agent includes a major proportion of starch.

4. A detergent bar according to claim 3 in which the enzyme content is from 0.1 to 1% and from 70 to 100% thereof is proteolytic enzyme so that the detergent bar contains from 0.001 to 0.1 Anson unit per gram, the anionic synthetic organic detergent is selected from the group consisting of sulfated and sulfonated detergents having an alkyl group of 8 to 22 carbon atoms, the builder and filler salts are inorganic sodium salts and the binding agent is from 10 to 35% of the bar and 70 to 100% thereof is starch.

5. A detergent bar according to claim 4 wherein the enzyme is a proteolytic enzyme or mixture thereof, the anionic synthetic organic detergent is higher alkyl benzene sulfonate of 8 to 18 carbon atoms in the alkyl group, the builder salt is from 25 to 55% of the bar and the binding agent is starch.

6. A detergent bar according to claim 5 wherein the enzyme is subtilisin enzyme of 1–8 Anson units/gram and from 0.2 to 1% thereof is present, the anionic synthetic organic detergent is sodium higher alkyl benzene sulfonate wherein the higher alkyl is of 10 to 16 carbon atoms, the builder salt includes sodium carbonate and sodium bicarbonate and the binding agent is corn starch.

7. A detergent bar according to claim 6 which is milled and plodded and in which the moisture content is from 12 to 17%.

8. A detergent bar according to claim 7 which contains about 28% of sodium higher alkyl benzene sulfonate, 35% sodium bicarbonate, 7% sodium carbonate, 11% corn starch, 5% sodium silicate, 15% water and 0.6% proteolytic enzyme.

9. A detergent bar according to claim **7** which contains about 31% of sodium alkyl benzene sulfonate detergent, 18% sodium carbonate, 8% sodium bicarbonate, 26% of corn starch, 14% of moisture and at least 0.009 Anson unit/gram of protease.

10. A detergent bar according to claim **9** which contains from 0.5 to 1% of optical brightener and sufficient proportion of coloring material to give the bar a distinct speckled appearance to identify it to a consumer as an enzymatic detergent bar.

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