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(54) **Flexible multiple compartment pouch**

(57) The present invention relates to a flexible multiple compartment pouch, preferably capable of being used, when comprising compositions, to refill a multiple compartment durable container. In a preferred embodiment, the multiple compartment pouch comprises a gripping means. In another preferred embodiment, the multiple compartment pouch comprises at least one gusset. In yet another preferred embodiment, the multiple compartment pouch comprises at least a first and second compartment wherein the first compartment comprises a first composition and the second compartment comprises a second composition and wherein the first and second compositions are incompatible.

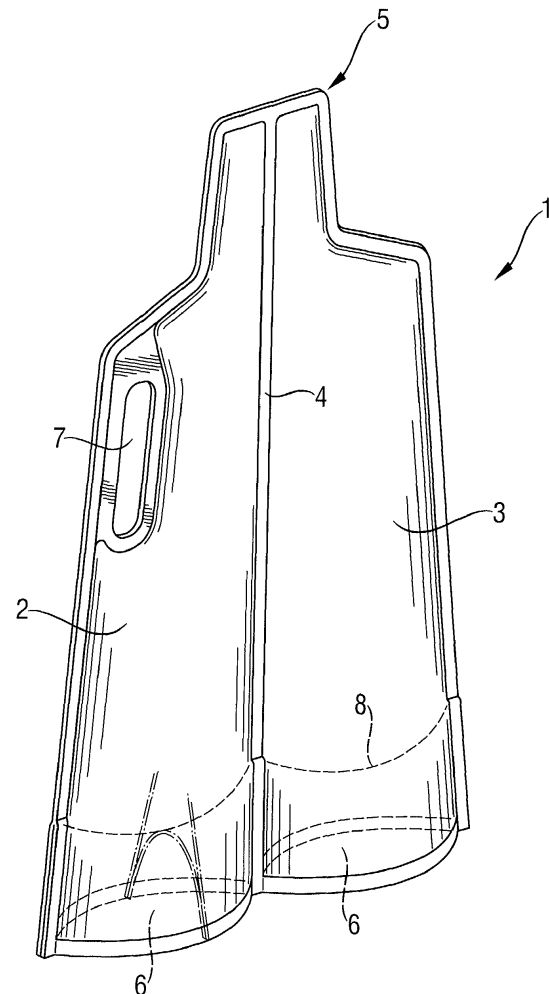


Fig. 1

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Description**Technical field**

5 **[0001]** The present invention relates to flexible multiple compartment pouches, preferably used for storing incompatible liquids and refilling multiple compartment durable containers.

Background

10 **[0002]** Many free flowing consumer products, for example cleaning products, are sold in relatively rigid plastic bottles which are durable and generally designed to be thrown away after use. Such durable bottles, usually containing one free flowing composition, are well known in the art. However, consumer products have increased in complexity and there has been considerable interest in durable containers that comprise two or more separate compositions. WO 00/61712 discloses multiple component cleaning compositions and a multiple compartment durable container suitable for storing and dispensing said separate compositions. Frequently, the two or more compositions are incompatible with one another and must be kept separate during storage in order to prevent decomposition or loss of performance. One such multiple compartment durable container capable of comprising two or more free flowing compositions is the subject of our co-pending European patent application number 00870095.7. Said multiple compartment durable containers can be used to deliver products for a wide range of applications including toilet bowl and laundry cleaning compositions.

15 **[0003]** For clarity of description, we shall refer to containers that are capable of being refilled as 'durable'. Each separate area within the durable container capable of containing a composition will be referred to as a 'compartment'. In the present application, two or more compositions can be considered 'incompatible' if the mixing of these compositions prior to dispensing from the durable container would result in a loss of activity for the final application of the mixture. Loss of activity could be loss of cleaning efficiency, loss of consumer appeal or loss of fabric care activity.

20 **[0004]** As consumers have become more environmentally aware, the need to minimise the amount of waste packaging has arisen. This need has been satisfied by providing the consumer with a flexible and disposable container, comprising the desired composition, which can be used to refill the original durable container. Flexible single compartment pouches, suitable for refilling single compartment durable containers, that can be easily discarded after use and that result in minimum waste packaging are described in EP 0626319.

25 **[0005]** Although not problem free, refilling a single compartment durable container with a single compartment pouch is a straightforward process wherein the consumer usually cuts the corner off the pouch and pours the contents into the durable container. However, if the consumer wants to refill each individual compartment of a multiple compartment durable container using single compartment pouches then there are a number of problems.

30 **[0006]** One disadvantage of using single compartment pouches is that the consumer must select and purchase two or more different pouches containing the correct types of composition. Consumers must also consider the relative volumes of each compartment of the durable container since uneven refilling may result in an undesired ratio of products being dispensed from said durable container. During the refilling process, the consumer must be extremely careful and accurate so as not to allow any of the incompatible compositions to enter the incorrect compartment of the durable container. If such contamination occurs, the performance of the final composition may be substantially reduced due to undesirable reactions or decomposition of the active components of the compositions. Moreover, multiple compartment containers may dispense aesthetically pleasing coloured compositions therefore any mixing prior to dispensing would lessen this effect. Said contamination may occur by spillage while transferring the contents of the flexible single compartment pouch to the compartments of the durable container, or by mistakenly adding the compositions to the wrong compartments.

35 **[0007]** The consumer's use of single compartment pouches to refill multiple compartment durable containers also inconveniences the retailer because he must stock two or more different pouches to satisfy the need for different compositions.

40 **[0008]** A further disadvantage of using said flexible pouches is that they are difficult to hold and control during the refilling process especially when there is the possibility of slippery compositions, such as detergent, or water on the surface of the pouch. This difficulty of handling is also due to the constantly changing shape of the pouch due to composition moving inside the pouch. An additional reason for the difficulty of handling is that during the refilling process the volume of composition in the pouch decreases and the shape of the pouch changes. To compensate for this changing volume and shape, the consumer must constantly change their grip. Spillage of the composition is wasteful and should be avoided as it results in consumer dissatisfaction and may cause cross contamination in the compartments of the durable container. The compositions contained within pouches according to the present invention are usually intended for use in a certain ratio. If this ratio is upset by spilling one composition more than another then a reduction in performance of the final composition may result. In addition, it is extremely undesirable to have spillages that result in contact of the composition with the consumer since it may be unsafe and again may result in consumer dissatisfaction.

[0009] Yet another disadvantage with said pouches is that their flexibility and lack of rigidity often renders them inconvenient for consumers to store and use. In addition to the problems with storage, retailers and advertisers are faced with the difficulty of displaying the pouch in an aesthetically pleasing manner. They are not able to stack and display the pouch with maximum visual effect because they cannot predict what shape and orientation the pouch will adopt once placed on the shelf.

[0010] It is an object of the present invention to provide a flexible multiple compartment pouch capable of containing incompatible liquids which allows the manufacturer to select the appropriate type and volume of compositions so the consumer buys only one refill pouch with the correct types of composition and the correct relative volumes of each compartment.

It is an object of the present invention to provide a flexible multiple compartment pouch capable of standing upright unassisted for greater ease of storage use by the consumer as well as easier and more aesthetically pleasing displaying in the retail premises.

It is an object of the present invention to provide a flexible multiple compartment pouch comprising at least one gripping means to assist the consumer in handling and controlling said pouch before, during and after the refilling process.

Summary of the invention

[0011] According to the present invention there is provided a flexible multiple compartment pouch comprising at least a first and second compartment and at least one gusset.

According to a second aspect of the present invention there is provided a flexible multiple compartment pouch comprising at least a first and second compartment wherein the first compartment comprises a first composition and the second compartment comprises a second composition and wherein the first and second compositions are incompatible. According to a third aspect of the present invention there is provided a flexible multiple compartment pouch comprising at least a first and second compartment and at least one gripping means.

According to a fourth aspect of the present invention there is provided a method of refilling a multiple compartment durable container with a multiple compartment pouch comprising the steps of:

- a. preparing the durable container for receipt of composition;
- b. preparing the outlets of the multiple compartment pouch, and then
- c. adding the compositions to the compartments of the durable container

Detailed description of the invention

[0012] The invention will now be described by way of example and with reference to the accompanying diagram:

Fig 1: A perspective view of a gusseted based, side by side multiple compartment pouch with a handle as a gripping means.

Fig 2: A perspective view of a gusseted based, side by side multiple compartment pouch with no gripping means.

Fig 3: A perspective view of a gusseted based, side by side multiple compartment pouch with a gripping means made of rubbery material.

Fig 4: A perspective view of a gusseted based, side by side multiple compartment pouch with handles as gripping means and an off-centered edge.

Fig 5: A perspective view of a gusseted based, side by side multiple compartment pouch with a gripping means made of rubbery material and a handle located in the center of the pouch.

Fig 6: A perspective view of a gusseted based, multiple compartment pouch wherein one compartment is located inside the other compartment and with 2 handles as gripping means located at the bottom of the gusset.

Fig 7: A perspective view of a gusseted based, side by side multiple compartment pouch with handles as gripping means, one located on the side and another located at the bottom of the pouch.

Fig 8: A perspective view of a side by side multiple compartments pouch with a handle as gripping means.

[0013] The present invention provides a flexible multiple compartment pouch 1, comprising at least as many com-

partments 2, 3 as the number of compositions contained therein, preferably to provide the consumer with a means of refilling a multiple compartment durable container with maximum convenience and minimum waste packaging. The flexible multiple compartment pouch according to the present invention preferably comprises from one to ten compartments, more preferably two, three, four or five compartments.

5 **[0014]** In a preferred embodiment, the pouch 1 comprises adjacent compartments 2 and 3 separated by a permanent seal 4 (See figures 1 to 5, 7 and 8). By 'permanent' it is meant herein a seal that is no more easily ruptured than the other seals around the perimeter of the pouch. This embodiment can be made by superimposing two sheets of film, sealing the edges to form one large compartment followed by sealing further divisions in order to form said adjacent compartments.

10 **[0015]** The flexible multiple compartment pouch 1, of the present invention can be made from any suitable material. More preferably the compartments 2 and 3 of the pouch are made from sealable films. Preferred sealable films include those made from plastics, polymers, laminated materials and mixtures thereof. A sealable material as described herein is a material which is capable of adhering to the same or another material through a sealing process. Sealing may be using any suitable technique known in the art, more preferably heat sealing, ultrasonic sealing, glue sealing, pressure sealing, induction sealing and mixtures thereof. Heat sealing encompasses heating the films to the point where they both melt and form a connection and then allow to cool. Induction sealing is a similar technique to heat sealing but requires the film to contain a metal layer e.g. aluminium. The metal layer is heated by applying a strong magnetic field, which then causes the sealing film to melt and form a connection as before. Ultrasonic sealing requires localised high frequency vibration of the two films to create heat which then melts the films a before. Glue sealing is simply where glue is added to the film to stick the two sheets of film together. Importantly, the material from which the pouch is made and the seals described above should be impermeable and stable with regards to the compositions stored in the compartment. With regards to the latter point, it may be preferable to use a laminated film including a barrier layer. A barrier layer is defined as a sheet of material which protects the physical or chemical stability of the composition stored in the compartment. Examples of suitable layer materials may be selected from anything that prevents or reduces for example the ingress of external elements e.g. water, gases, the egress of internal compounds (e.g. the composition), light. Preferred examples of such barrier layers include aluminium, ethyl vinyl alcohol, nylon and mixtures thereof.

20 **[0016]** In a preferred aspect the sealable film is 20 to 500 microns thick, more preferably 70 to 300 microns and most preferably 90 to 150 microns thick. More preferably the pouch is made from plastic, more preferably plastics selected from the group consisting of polyethylene, polypropylene, polyethylene terephthalate, ethyl vinyl alcohol and mixtures thereof.

25 **[0017]** In another preferred embodiment the pouch may comprise an aesthetic layer, which for example may trap inks and thus would be suitable for displaying usage instructions and other trade dress features, for examples brand names. Alternatively the sealable or barrier layer may provide this function and the aesthetic layer, where present, may be a transparent layer suitable for protecting the sealable layer. Preferably the aesthetic layer is made from polyethylene terephthalate. Most preferably the sealable film of the compartments of the pouch is made from polyethylene and the aesthetic layer is made from polyethylene terephthalate. More preferably the polyethylene film is 50-130 microns thick and the polyethylene terephthalate film is 6-20 microns thick.

30 **[0018]** A preferred embodiment has at least one compartment substantially enclosed within an outer compartment (See figure 6). Said embodiment can be made by placing one or more compartments substantially within an outer compartment and sealing around the perimeter of the outer most compartment.

35 **[0019]** It is also envisaged that pouches according to the present invention may comprise a plurality of separate flexible compartments which are held together by an internal means or an external means. Said internal means could be adhesive applied between the compartments in order to connect them at least one point, for example the outlets. An example of an external means could be an adhesive sleeve which is substantially wrapped around said compartments in order to hold them together.

40 **[0020]** In a highly preferred embodiment each compartment of the pouch may be provided with an outlet allowing the compositions to flow from the pouch into the corresponding compartments of the durable container without mixing. See figures 1-8 and especially figure 4 wherein the outlet is off-centered.

45 In a preferred embodiment, the outlet from each compartment will converge to a connection device which, by virtue of its configuration, bridges between the pouch and durable container, and allows each composition to flow into the correct compartment without mixing.

In a further preferred embodiment, the outlet from each compartment may be made by cutting away a section of the edge of the pouch 5. A tearing line or a cutting line (9) can be indicated on the pouch (see figures 4, 6 and 7)

50 In another preferred embodiment, said section 5 to be cut away will comprise the edges of all the individual compartments therefore one cut will expose outlets from all compartments (see figures 1 to 8).

55 **[0021]** In yet another preferred embodiment the multiple compartment pouch comprises preferably two compartments 2, 3 separated by a permanent seal 4 which runs substantially vertically from the gusseted base 6 (See figures 1 to 7) to the upper edge of the pouch. The intersection of the upper edge of the pouch with the permanent seal may comprise

outlets from each compartment or it may be an edge capable of being cut so as to form said outlets. Said pouch is capable of standing upright and comprises an upper and a lower section. While in a standing position, the lower section contains the majority of the free flowing composition. In said standing position, the upper section is substantially empty of composition and is flexible. The combined height of said lower section and flexible upper section is preferably sufficiently great that the consumer may place the pouch in the proximity of the multiple compartment durable container, open the outlets from the pouch, position said outlets in or near the compartments of the durable container then lift the lower section of the pouch allowing the compositions to flow into the compartments of the durable container.

[0022] In all of the above preferred embodiments, the compartments of the pouch may be emptied via the outlets by applying pressure to the exterior of the pouch by, for example, squeezing. Alternatively, the pouch can be raised above the durable container and aligned so that the outlets are at the lowest point of the pouch and the compositions allowed to drain into the compartments of the durable container under the force of gravity. Regardless of which method is used, the outlets for each composition will preferably dispense the separate compositions in close proximity to one another without any mixing occurring prior to exiting the multiple compartment pouch. The consumer may pour the streams of composition from the outlets directly into the compartments of the durable container or the consumer may use a funnel device that directs the flow of composition into the desired compartment. Multiple compartment pouches comprising connection devices as outlined above are the subject of a copending patent application.

[0023] A further highly preferred embodiment of the present invention comprises at least one gusset 6 (see figures 1 to 7 and in particular figures 1, 2 and 7 wherein the gusset fold (8) is pictured). Said gusseted multiple compartment pouches are more convenient to store in the home and to display in the retail premises. Said gussets may be situated anywhere in the flexible multiple compartment pouch. Preferably, a gusset is incorporated into the edge furthest from the outlets, therefore forming a base on which the pouch can sit. A pouch according to the present invention comprising a gusset at the base can stand upright when substantially full of liquid so that the label and contents information can be clearly displayed and storage is more convenient. The weight of the composition in the pouch forces the material comprising the gusset into contact with the surface upon which it is resting therefore increasing the contact area of the base and adding stability. Preferably, while the pouch is standing upright, the top of the pouch or part of the pouch can be folded over, for example to fit the height of the shelf. See the pouch folding line in figures 4 and 7. An example of said pouch can be made by superimposing two sheets of film, folding an additional sheet of film, 'the gusset', in half and inserting the folded edge between the two superimposed sheets. The two superimposed sheets are then sealed to one another around the edges except where the gusset prevents said sheets from meeting. In these areas the superimposed sheets are sealed to the edge of the gusset with which they are in contact. Sealing methods that are common knowledge to those skilled in the art are heat sealing, ultrasonic sealing, pressure sealing or induction sealing.

[0024] A yet further highly preferred embodiment of the present invention comprises a gripping means 7. It is also an object of the present invention to provide consumers with a convenient means of handling the flexible multiple compartment pouch before and during the refilling process. The addition of at least one 'gripping means' to a pouch according to the present invention will provide the consumer with a more secure grip even if the surface of the pouch become contaminated with slippery substances such as a cleaning composition. By a 'gripping means' it is meant herein a device which helps the consumer to gain control of the pouch. Examples of a 'gripping means' include handles (See figures 1 and 4 to 8), areas of high friction material, rigid sections (See figures 3 and 5) and any feature that increases the consumers grip on the pouch. Said gripping means may be positioned anywhere on the surface of the pouch, preferably on an edge, most preferably on the edge of the pouch furthest from the outlets. In a preferred embodiment, the pouch will comprise two handles, one close to the gusseted base of the pouch and the other close to the outlets at the top of the pouch (See figures 4 and 7). In a preferred embodiment the gripping means is made by sealing an approximately circular ring into the pouch and removing the center of said ring to form a hole into which the consumer can place their fingers and gain an improved grip (See figures 1 and 4 to 8). Alternatively, the flexible pouch may comprise a gripping means made from different materials (See figures 3 and 5) and may be attached by any methods including adhesive and heat bonding.

[0025] In dual compartment pouches according to the present invention, the addition of a handle 7 is especially useful to the consumer (See figures 1 and 4 to 8). As we have already seen, single compartment pouches are difficult to grip and to accurately use to refill durable containers. This is due to the movement of composition within the pouches and the constantly changing volume of composition within the pouch during the refilling process. In multiple compartment containers these problems are even greater due to the presence of two compartment which move independently of each other and may change volume at different rates. In addition, the consumer may have to simultaneously control two streams of free flowing composition while avoiding mixing or spillage.

[0026] The volume of the separate compartments of the pouch will clearly depend on the volume of each compartment in the durable container to be refilled. Pouches according to the present invention may comprise compartments of identical volumes (See figures 1, 2 and 8), of similar volumes and of substantially different volumes (See figures 3 to 7). A preferred embodiment according to the present invention comprises at least a first and second compartment comprising a first and a second composition whereby the ratio of volumes of the first and second compositions are

preferably between 1:1 and 1:20, more preferably between 1:1 and 1:10 and most preferably between 1:1 and 1:4. In domestic applications, for reasons of convenience and ease of handling, the total volume of all the compartments of the pouch will generally be between 0.1 - 5 liters. For industrial applications the total volume of the compartments of the refill may be up to 100 liters.

[0027] The containers as described above are designed to store free flowing compositions. The free flowing compositions stored in the first and second compartments may be incompatible. The incompatible compositions differ in that at least one compound of the first composition stored in the first compartment, is not present in the second composition stored in the second compartment, or vice versa. The free flowing compositions may be in particulate, gel or paste form, but is preferably a liquid. In one embodiment of the present invention, the free flowing composition stored in the first and second compartments have different rheological properties, for example the free flowing compositions may have different viscosities, densities, flow properties etc.

[0028] In a preferred embodiment a first compartment 2 contains an aqueous liquid detergent composition and a second compartment 3 contains a bleaching composition.

[0029] In another preferred embodiment a first compartment 2 contains an aqueous liquid detergent composition and a second compartment 3 contains a fabric care composition, or the cleaning agents and fabric care actives can be divided between the compartments 2 and 3.

[0030] In a further preferred embodiment, the composition contained in the first and second compartments comprise components that effervesce when mixed. The components of said effervescent system, the liquid detergent composition, the fabric care composition and bleaching composition are described in detail below.

Aqueous liquid detergent composition

[0031] The aqueous liquid detergent compositions of the present invention preferably comprise an effervescent component, one or more surfactants and one or more suitable cleaning adjunct materials. When the aqueous liquid detergent compositions of the present invention is associated with a bleaching composition, it may as well comprise fabric care adjunct materials as described below.

[0032] The term "cleaning adjunct materials", as used herein, means any liquid, solid or gaseous material selected for aqueous liquid detergent compositions, preferably compatible with the other ingredients present in the aqueous liquid detergent compositions of the present invention. Incompatible cleaning adjunct materials may be physically separated in the different compartments of the pouch according to the present invention.

Examples of suitable cleaning adjunct materials include, but are not limited to, surfactants, builders, bleaches, bleach activators, bleach catalysts, enzymes, enzyme stabilizing systems, chelants, optical brighteners, soil release polymers, dye transfer inhibiting agents, dispersants, suds suppressors, dyes, perfumes, colorants, filler salts, hydrotropes, photoactivators, fluorescers, fabric conditioners, fabric softening agents, hydrolyzable surfactants, preservatives, anti-oxidants, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, alkalinity sources, solubilizing agents, carriers, processing aids, pigments and pH control agents as described in U.S. Patent Nos. 5,705,464, 5,710,115, 5,698,504, 5,695,679, 5,686,014 and 5,646,101. Specific cleaning adjunct materials are exemplified in detail hereinafter.

Also suitable cleaning adjunct materials are : Brighteners, also known as fluorescent whitening agents (FWAs), are described in detail in WO 00/24851 pages 92-93; Dye transfer inhibiting agents are described in detail in WO 00/24851 pages 100-101. Dispersants are described in detail in WO 00/24851 pages 105-107 and Suds suppressors and aqueous carriers are described in detail in WO 00/24851 pages 113-114.

[0033] When the aqueous liquid detergent compositions of the present invention are formulated as compositions suitable for use in a laundry machine washing method, the compositions of the present invention preferably contain both a surfactant and a builder compound and additionally one or more cleaning adjunct materials preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional cleaning adjunct materials.

Surfactants

[0034] Preferably, the aqueous liquid detergent compositions of the present invention will comprise a surfactant system wherein the surfactant can be selected from cationic, nonionic and/or conventional anionic and/or mixtures thereof. Also suitable are ampholytic and/or zwitterionic and/or semi-polar surfactants. The surfactant system is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of laundry detergent compositions in accord with the invention.

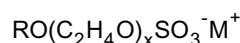
i. Anionic Surfactant

[0035] Anionic surfactants include C₁₁-C₁₈ alkyl benzene sulfonates (LAS) and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates (AS), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺) CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺) CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-18 glycerol ethers sulfate, the C₁₀-C₁₈ alkyl sulfate polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters.

Generally speaking, anionic surfactants useful herein are disclosed in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981, and in U.S. Patent No. 3,919,678, Laughlin et al, issued December 30, 1975.

Other useful anionic surfactants herein include the water-soluble salts of esters of a-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and b-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Particularly preferred anionic surfactants herein are the alkyl sulfates, in particular, the alkyl polyethoxylate sulfates of the formula:



wherein R is an alkyl chain having from about 10 to about 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and x averages from about 1 to about 15, and the non-ethoxylated C₁₂₋₁₅ primary and secondary alkyl sulfates. Under cold water washing conditions, i.e., less than about 65°F (18.3°C), it is preferred that there be a mixture of such ethoxylated and non-ethoxylated alkyl sulfates.

The fatty acids useful in the present invention as anionic surfactants include saturated and/or unsaturated fatty acids obtained from natural sources or synthetically prepared. Examples of suitable fatty acids include, but are not limited to, capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinoleic acid.

Also suitable as anionic surfactants are the biodegradably branched and/or crystallinity disrupted and/or mid-chain branched surfactants or surfactant mixtures. These surfactants are more fully disclosed in WO98/23712 A published 06/04/98; WO97/38957 A published 10/23/97; WO97/38956 A published 10/23/97; WO97/39091 A published 10/23/97; WO97/39089 A published 10/23/97; WO97/39088 A published 10/23/97; WO97/39087 A1 published 10/23/97; WO97/38972 A published 10/23/97; WO 98/23566 A Shell, published 06/04/98; technical bulletins of Sasol; and the following pending patent applications assigned to Procter & Gamble: U.S. Patent Application Serial Nos. 09/170,711 and 09/170,694.

ii. Nonionic surfactants

[0036] If nonionic surfactants are used, the compositions of the present invention will preferably contain up to about 20%, preferably from 7% to about 18%, more preferably from 9% to about 12%, by weight of a nonionic surfactant. Preferred are the ethoxylated alcohols and ethoxylated alkyl phenols of the formula R(OC₂H₄)_nOH, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of n is from about 5 to about 15. These surfactants are more fully described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981. Particularly preferred are ethoxylated alcohols having an average of from about 10 to about 15 carbon atoms in the alcohol and an average degree of ethoxylation of from about 6 to about 12 moles of ethylene oxide per mole of alcohol.

Other nonionic surfactants for use herein include, but are not limited to:

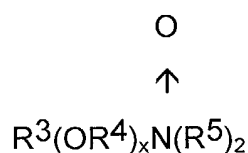
The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation; and Triton® X-45, X-114, X-100, and X-102, all marketed

by the Rohm & Haas Company. These compounds are commonly referred to as alkyl phenol alkoxylates, (e.g., alkyl phenol ethoxylates).

The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol® 15-S-9 (the condensation product of C₁₁-C₁₅ linear secondary alcohol with 9 moles ethylene oxide), Tergitol® 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), Neodol® 23-6.5 (the condensation product of C₁₂-C₁₃ linear alcohol with 6.5 moles of ethylene oxide), Neodol® 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), Neodol® 45-4 (the condensation product of C₁₄-C₁₅ linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro® EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. Other commercially available nonionic surfactants include Dobanol 91-8® marketed by Shell Chemical Co. and Genapol UD-080® marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl ethoxylates."

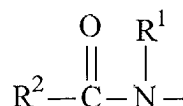
Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula:



wherein R³ is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R⁴ is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R⁵ groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

[0037] These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides. Also suitable as nonionic surfactant are the polyhydroxy fatty acid amide surfactant. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:



wherein: R¹ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R² is a C₅-C₃₁ hydrocarbyl, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₅ alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glyceryl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from

the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

[0038] R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

$\text{R}^2-\text{CO}-\text{N}<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

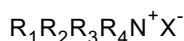
Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

iii. Cationic Surfactant

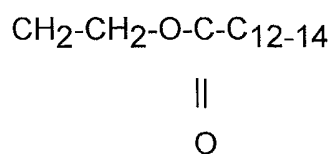
[0039] Cationic deterative surfactants suitable for use in the compositions of the present invention are those having one long-chain hydrocarbonyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula: $[\text{R}^2(\text{OR}^3)_y][\text{R}^4(\text{OR}^3)_z]\text{R}^5\text{N}^+\text{X}^-$ wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}(\text{CH}_3)-$, $-\text{CH}_2\text{CH}(\text{CH}_2\text{OH})-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-\text{CH}_2\text{CHOH}-\text{CHOHCOR}^6\text{CHOHCH}_2\text{OH}$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula (i):



wherein R_1 is C_8-C_{16} alkyl, each of R_2 , R_3 and R_4 is independently C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and $-(\text{C}_2\text{H}_4)_x\text{H}$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2 , R_3 or R_4 should be benzyl. The preferred alkyl chain length for R_1 is $\text{C}_{12}-\text{C}_{15}$ particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulfate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are include, but are not limited to: coconut trimethyl ammonium chloride or bromide; coconut methyl dihydroxyethyl ammonium chloride or bromide; decyl triethyl ammonium chloride; decyl dimethyl hydroxyethyl ammonium chloride or bromide; C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide; coconut dimethyl hydroxyethyl ammonium chloride or bromide; myristyl trimethyl ammonium methyl sulphate; lauryl dimethyl benzyl ammonium chloride or bromide; lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide; choline esters (compounds of formula (i) wherein R_1 is



alkyl and $\text{R}_2\text{R}_3\text{R}_4$ are methyl); and di-alkyl imidazolines [(i)].

[0040] Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

When included therein, the compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 25%, preferably to about 8% by weight of such cationic surfactants.

5 iv. Zwitterionic Surfactant - Zwitterionic surfactants, examples of which are described in U.S. Patent No. 3,929,678, are also suitable for use in the compositions of the present invention.

When included therein, the compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such zwitterionic surfactants.

10 Effervescent system

[0041] Preferred flexible multiple compartment pouches according to the present invention comprise effervescent systems. Said effervescent systems preferably comprise two components contained in separate compartments of the pouch. Suitable effervescent systems are described in WO01/00765 to Procter & Gamble, on pages 4 to 7.

15 [0042] In a preferred embodiment the effervescent system comprises an acidic component and an effervescent base. In another preferred embodiment the effervescent system comprises a peroxide reducing enzyme and a source of peroxide.

[0043] In a highly preferred embodiment the first compartment comprises an aqueous liquid detergent and the second comprises a fabric care composition wherein the aqueous liquid detergent comprises an acidic component and the fabric care composition comprises an effervescent base.

20 [0044] In another highly preferred embodiment the first compartment comprises an aqueous liquid detergent and the second comprises a fabric care composition wherein the aqueous liquid detergent comprises an effervescent base and the fabric care composition comprises an acidic component.

[0045] In a further highly preferred embodiment the first compartment comprises an aqueous liquid detergent and the second comprises a bleaching composition wherein the aqueous liquid detergent comprises an effervescent base and the bleaching composition comprises an acidic component.

25 [0046] Also encompassed is the present invention, is the embodiment wherein the first compartment comprises an aqueous liquid detergent and the second comprises a bleaching composition wherein the aqueous liquid detergent comprises an acidic component and the bleaching composition comprises an effervescent base.

30 [0047] In yet another highly preferred embodiment the first compartment comprises an aqueous liquid detergent and the second comprises a bleaching composition wherein the aqueous liquid detergent comprises a peroxide reducing enzyme and the bleaching composition comprises a source of peroxide.

[0048] Also encompassed is the present invention, is the embodiment wherein the first compartment comprises an aqueous liquid detergent and the second comprises a bleaching composition wherein the aqueous liquid detergent comprises a source of peroxide and the bleaching composition comprises a peroxide reducing enzyme.

35 [0049] Said effervescent base is preferably selected from carbonates, bicarbonates, sesquicarbonates and mixtures thereof. More preferably, the effervescent base is selected from the group consisting of sodium bicarbonate, monoethanolammonium bicarbonate and mixtures thereof. Said bases are preferably present at a level of from about 1% to about 10%, more preferably from about 2% to about 5% by weight of the compositions of the present invention.

40 [0050] Said peroxide reducing enzyme is preferably selected from peroxidase, laccase, dioxygenase and/or catalase enzyme, preferably catalase enzyme, preferably present at a level of from about 0.001% to about 10%, more preferably, from about 0.01% to about 5%, even more preferably from about 0.1% to about 1%, most preferably from about 0.1% to about 0.3% by weight of the compositions of the present invention. Catalase enzyme is commercially available from Biozyme Laboratories under the trade name Cat-1A, which is a bovine liver derived catalase enzyme; from Genencor International under the trade name Oxy-Gone 400, which is a bacterial derived catalase enzyme; and from Novo Nordisk under the trade name Terminox Ultra 50L.

[0051] Any suitable acidic component known to those skilled in the art can be used in the present invention so long as the acidic component's pH, when physically separated from the effervescent agent-containing component, is about 7 or less, preferably from about 0 to about 6, more preferably from about 3 to about 4.

50 Preferably, the acid agent-containing component comprises an acid, preferably present at a level of from about 1% to about 20%, more preferably from about 3% to about 10% by weight of the compositions of the present invention.

Suitable acids for use in the effervescent agent-containing component include acids that have a pKa of 7 or less, preferably from about 3 to about 7.

55 Nonlimiting examples of suitable acids for use in the present invention include inorganic acids, organic acids and mixtures thereof. Preferably, the inorganic acids are selected from the group consisting of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, sulfamic acid and mixtures thereof. Preferably, the organic acids are selected from the group consisting of formic acid, acetic acid, C₁₂-C₁₈ fatty acids, malic acid, maleic acid, malonic acid, succinic acid, tartaric acid, lactic acid, glutaric acid, fumaric acid, benzoic acid, phthalic acid, citric acid and mixtures thereof. Organic

acids are preferred, most preferred are citric acid and/or succinic acid.

[0052] Said source of peroxide, preferably hydrogen peroxide, may be any suitable source of peroxide and present at any level, such as fully described in U.S. Patent No. 5,576,282, preferably present at levels of from about 0.001% to about 15%, more preferably present at levels of from about 0.01% to about 10%, most preferably present at levels

of from about 0.1% to about 6% by weight of the composition. Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

OPTIONAL ADJUNCT CLEANING MATERIALS

Enzymes

[0053] Detergent compositions of the present invention may further comprise one or more enzymes which provide cleaning performance benefits. Suitable enzymes include enzymes selected from peroxidases, proteases, gluco-amy-lases, amylases, xylanases, cellulases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, re-ductases, oxidases, phenoloxidasases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, dextranase, transferase, laccase, mannanase, xyloglu- canases, or mixtures thereof. Detergent compositions generally comprise a cocktail of conventional applicable enzymes like protease, amylase, cellulase, lipase.

[0054] Enzymes are generally incorporated in detergent compositions at a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

[0055] Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis*, *B. licheniformis* and *B. amyloliquefaciens* (*subtilisin BPN* and *BPN'*), *B. alcalophilus* and *B. lentus*. Suitable *Bacillus* protease is Espe- rease® with maximum activity at pH 8-12, sold by Novozymes and described with its analogues in GB 1,243,784. Other suitable proteases include Alcalase®, Everlase® and Savinase® from Novozymes. Proteolytic enzymes also encom- pass modified bacterial serine proteases, such as those described in EP 251 446 (particularly pages 17, 24 and 98), referred to as "Protease B", and in EP 199 404 which refers to a modified enzyme referred to as "Protease A". Also suitable is the enzyme called "Protease C", which is a variant of an alkaline serine protease from *Bacillus* (WO 91/06637). A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, described in WO95/10591 and WO95/10592. Preferred proteases are multiply-substi- tuted protease variants comprising a substitution of an amino acid residue at positions corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one or more amino acid residue positions other than

amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens subtilisin*. WO 99/20723, WO99/20726, WO99/20727, WO99/20769, WO99/20770 and WO99/20771 describe also suitable proteases, wherein preferred variants have the amino acid substitution set 101/103/104/159/232/236/245/248/252, more preferably 101 G/103A/104I/159D/232V/ 236H/245R/248D/252K according to the BPN' numbering.

[0056] Amylases (α and/or β) can be included for removal of carbohydrate-based stains. Suitable amylases are described in WO94/02597 and WO95/10603 (both Novozymes). WO95/26397 describes other suitable amylases: α - amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α -amylase activity assay. Suitable variants of the above enzymes are described in WO96/23873 (Novozymes). Preferred variants therein are those with increased thermostability described on p16 of WO96/23873, and especially the D183* + G184*. Examples of commercial α -amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban®, Funga- myl® and Duramyl®, all available from Novozymes.

[0057] Suitable cellulases include both bacterial or fungal cellulases, preferably with a pH optimum of between 5 and 12. Examples are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), partic- ularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a preferred en- doglucanase component has the amino acid sequence disclosed in WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* (WO94/21801, Genencor). Especially suitable cellulases are the

cellulases having color care benefits such as described in EP 495 257. Celluzyme® commercially available from Novozymes is especially useful. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 WO95/24471, WO91/17244 and WO91/21801.

[0058] Suitable lipases include those produced by the *Pseudomonas* group, such as *P. stutzeri* ATCC 19.154 (GB1,372,034). Suitable lipases include those showing a positive immunological cross-reaction with the antibody of the *Pseudomonas fluorescent* lipase AM 1057 available from Amano Pharmaceutical Co. Ltd Japan, under the trade name "Lipase P Amano". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands; and lipases ex *Pseudomonas gladioli*. Especially suitable are the lipases produced by *Pseudomonas pseudoalcaligenes* (EP 218 272) or variants thereof (WO9425578) previously supplied by Gist-Brocades as M1 Lipase^R and Lipomax^R. Preferred lipases are the Lipolase^R and Lipolase Ultra^R from Novozymes. Also suitable are the enzymes described in EP 258 068, EP 943678, WO 92/05249, WO 95/22615, WO 9942566, WO 200060063 (all by Novozymes) and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] being considered as lipases which do not require interfacial activation. Suitable cutinases are described in WO88/09367 (Genencor); WO 90/09446 (Plant Genetic System); WO94/14963 and WO94/14964 (Unilever) and WO00/344560 (Novozymes).

[0059] Also suitable are bleaching enzymes, the following starch degrading enzymes:

Cyclomaltodextrin glucanotransferase "CGTase" (E.C. 2.4.1.19), maltogenic alpha amylase (EC 3.2.1.133) and amyloglucosidase (EC 3.2.1.3); and the following carbohydrases : Mannanase (E.C. 3.2.1.78), protopectinase, polygalacturonase, pectin lyase, pectin esterase, pectate lyase and Xyloglucanase.

Bleaching System

[0060] The aqueous liquid detergent compositions of the present invention may comprise a bleaching system. Such aqueous liquid detergent composition which comprises a bleaching system in a first compartment can be further associated with a fabric care composition or bleaching composition in a second compartment as described hereinafter. Bleaching systems typically comprise a "bleaching agent" (source of hydrogen peroxide) and an "initiator" or "catalyst". When present, bleaching agents will typically be at levels of from about 1%, preferably from about 5% to about 30%, preferably to about 20% by weight of the composition. If present, the amount of bleach activator will typically be from about 0.1%, preferably from about 0.5% to about 60%, preferably to about 40% by weight, of the bleaching composition comprising the bleaching agent-plus-bleach activator.

Bleaching Agents -

[0061] Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Compositions of the present invention may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC"). However, chlorine-type bleaches are less preferred for compositions which comprise enzymes.

(a) Bleach Activators -

[0062] Preferably, the peroxygen bleach component in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01%, preferably from about 0.5%, more preferably from about

1% to about 15%, preferably to about 10%, more preferably to about 8%, by weight of the composition. Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C₁₀-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C₈-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred hydrophobic bleach activators include, but are not limited to, nonanoyloxybenzenesulphonate (NOBS), 4-[N-(nonaoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS) an example of which is described in U.S. Patent No. 5,523,434, dodecanoyloxybenzenesulphonate (LOBS or C₁₂-OBS), 10-undecenoyloxybenzenesulphonate (UDOBS or C₁₁-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA).

Preferred bleach activators are those described in U.S. 5,698,504 Christie et al., issued December 16, 1997; U.S. 5,695,679 Christie et al. issued December 9, 1997; U.S. 5,686,401 Willey et al., issued November 11, 1997; U.S. 5,686,014 Hartshorn et al., issued November 11, 1997; U.S. 5,405,412 Willey et al., issued April 11, 1995; U.S. 5,405,413 Willey et al., issued April 11, 1995; U.S. 5,130,045 Mitchel et al., issued July 14, 1992; and U.S. 4,412,934 Chung et al., issued November 1, 1983, and copending patent applications U. S. Serial Nos. 08/709,072, 08/064,564, all of which are incorporated herein by reference.

The mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1, more preferably from about 10:1 to about 1:1, preferably to about 3:1.

Quaternary substituted bleach activators may also be included. The present laundry compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in U.S. 5,686,015 Willey et al., issued November 11, 1997; U.S. 5,654,421 Taylor et al., issued August 5, 1997; U.S. 5,460,747 Gosselink et al., issued October 24, 1995; U.S. 5,584,888 Miracle et al., issued December 17, 1996; and U.S. 5,578,136 Taylor et al., issued November 26, 1996; all of which are incorporated herein by reference.

Highly preferred bleach activators useful herein are amide-substituted as described in U.S. 5,698,504, U.S. 5,695,679, and U.S. 5,686,014 each of which are cited herein above. Preferred examples of such bleach activators include: (6-oc-tanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl) oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate and mixtures thereof.

Other useful activators, disclosed in U.S. 5,698,504, U.S. 5,695,679, U.S. 5,686,014 each of which is cited herein above and U.S. 4,966,723 Hodge et al., issued October 30, 1990, include benzoxazin-type activators, such as a C₆H₄ ring to which is fused in the 1,2-positions a moiety --C(O)OC(R¹)=N-. Depending on the activator and precise application, good bleaching results can be obtained from bleaching systems having with in-use pH of from about 6 to about 13, preferably from about 9.0 to about 10.5. Typically, for example, activators with electron-withdrawing moieties are used for near-neutral or sub-neutral pH ranges. Alkalis and buffering agents can be used to secure such pH.

Acyl lactam activators, as described in U.S. 5,698,504, U.S. 5,695,679 and U.S. 5,686,014, each of which is cited herein above, are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A) and acyl valerolactams (see U.S. 5,503,639 Willey et al., issued April 2, 1996 incorporated herein by reference).

(b) Organic Peroxides, especially Diacyl Peroxides -

[0063] These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming.

(c) Metal-containing Bleach Catalysts -

[0064] The present invention compositions and methods may utilize metal-containing bleach catalysts that are effective for use in bleaching compositions. Preferred are manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequester having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U. S. 4,430,243 Bragg, issued February 2, 1982.

Manganese Metal Complexes -

[0065] If desired, the compositions herein can be catalyzed by means of a manganese compound. Such compounds and levels of use are well known in the art and include, for example, the manganese-based catalysts disclosed in U. S. Patent Nos. 5,576,282; 5,246,621; 5,244,594; 5,194,416; and 5,114,606; and European Pat. App. Pub. Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1; Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})\text{-}(\text{OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Patent Nos. 4,430,243 and U.S. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following: U.S. Patent Nos. 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Cobalt Metal Complexes -

[0066] Cobalt bleach catalysts useful herein are known, and are described, for example, in U.S. Patent Nos. 5,597,936; 5,595,967; and 5,703,030; and M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[\text{Co}(\text{NH}_3)_5\text{OAc}] \text{T}_y$, wherein "OAc" represents an acetate moiety and "T_y" is an anion, and especially cobalt pentaamine acetate chloride, $[\text{Co}(\text{NH}_3)_5\text{OAc}]\text{Cl}_2$; as well as $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{OAc})_2$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{PF}_6)_2$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{SO}_4)$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{BF}_4)_2$; and $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{NO}_3)_2$ (herein "PAC"). These cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. Patent Nos. 5,597,936; 5,595,967; and 5,703,030; in the Tobe article and the references cited therein; and in U.S. Patent 4,810,410; J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

Transition Metal Complexes of Macropolycyclic Rigid Ligands -

[0067] Compositions herein may also suitably include as bleach catalyst a transition metal complex of a macropolycyclic rigid ligand. The phrase "macropolycyclic rigid ligand" is sometimes abbreviated as "MRL" in discussion below. The amount used is a catalytically effective amount, suitably about 1 ppb or more, for example up to about 99.9%, more typically about 0.001 ppm or more, preferably from about 0.05 ppm to about 500 ppm (wherein "ppb" denotes parts per billion by weight and "ppm" denotes parts per million by weight).

Suitable transition metals e.g., Mn are illustrated hereinafter. "Macropolycyclic" means a MRL is both a macrocycle and is polycyclic. "Polycyclic" means at least bicyclic. The term "rigid" as used herein includes "having a superstructure" and "cross-bridged". "Rigid" has been defined as the constrained converse of flexibility: see D.H. Busch., Chemical Reviews, (1993), 93, 847-860, incorporated by reference. More particularly, "rigid" as used herein means that the MRL must be determinably more rigid than a macrocycle ("parent macrocycle") which is otherwise identical (having the same ring size and type and number of atoms in the main ring) but lacking a superstructure (especially linking moieties or, preferably cross-bridging moieties) found in the MRL's. In determining the comparative rigidity of macrocycles with and without superstructures, the practitioner will use the free form (not the metal-bound form) of the macrocycles. Rigidity is well-known to be useful in comparing macrocycles; suitable tools for determining, measuring or comparing rigidity include computational methods (see, for example, Zimmer, Chemical Reviews, (1995), 95(38), 2629-2648 or Hancock et al., Inorganica Chimica Acta, (1989), 164, 73-84.

Preferred MRL's herein are a special type of ultra-rigid ligand which is cross-bridged. A "cross-bridge" is nonlimitingly illustrated in 1.11 hereinbelow. In 1.11, the cross-bridge is a $-\text{CH}_2\text{CH}_2-$ moiety. It bridges N¹ and N⁸ in the illustrative structure. By comparison, a "same-side" bridge, for example if one were to be introduced across N¹ and N¹² in 1.11, would not be sufficient to constitute a "cross-bridge" and accordingly would not be preferred.

Suitable metals in the rigid ligand complexes include Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cu(III), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(V), W(VI), Pd(II), Ru(II), Ru(III), and Ru(IV). Preferred transition-metals in the instant transition-metal bleach catalyst include manganese, iron and chromium.

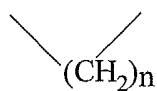
More generally, the MRL's (and the corresponding transition-metal catalysts) herein suitably comprise:

- (a) at least one macrocycle main ring comprising four or more heteroatoms; and
- (b) a covalently connected non-metal superstructure capable of increasing the rigidity of the macrocycle, preferably selected from

- (i) a bridging superstructure, such as a linking moiety;
- (ii) a cross-bridging superstructure, such as a cross-bridging linking moiety; and
- (iii) combinations thereof.

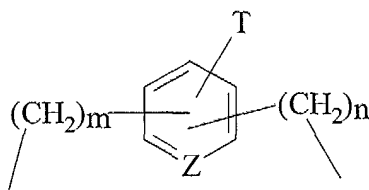
5 The term "superstructure" is used herein as defined in the literature by Busch et al., see, for example, articles by Busch in "Chemical Reviews".

Preferred superstructures herein not only enhance the rigidity of the parent macrocycle, but also favor folding of the macrocycle so that it co-ordinates to a metal in a cleft. Suitable superstructures can be remarkably simple, for example a linking moiety such as any of those illustrated in Fig. 1 and Fig. 2 below, can be used.



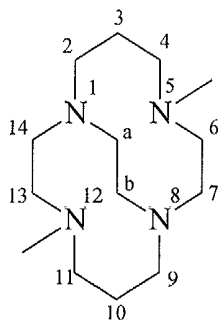
15 Fig. 1

wherein n is an integer, for example from 2 to 8, preferably less than 6, typically 2 to 4, or



25 Fig. 2

30 wherein m and n are integers from about 1 to 8, more preferably from 1 to 3; Z is N or CH; and T is a compatible substituent, for example H, alkyl, trialkylammonium, halogen, nitro, sulfonate, or the like. The aromatic ring in 1.10 can be replaced by a saturated ring, in which the atom in Z connecting into the ring can contain N, O, S or C. Suitable MRL's are further nonlimitingly illustrated by the following compound:



45 Fig. 3

50 This is a MRL in accordance with the invention which is a highly preferred, cross-bridged, methyl-substituted (all nitrogen atoms tertiary) derivative of cyclam. Formally, this ligand is named 5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane using the extended von Baeyer system. See "A Guide to IUPAC Nomenclature of Organic Compounds: Recommendations 1993", R. Panico, W.H. Powell and J-C Richer (Eds.), Blackwell Scientific Publications, Boston, 1993; see especially section R-2.4.2.1.

55 Transition-metal bleach catalysts of Macrocyclic Rigid Ligands which are suitable for use in the invention compositions can in general include known compounds where they conform with the definition herein, as well as, more preferably, any of a large number of novel compounds expressly designed for the present laundry or laundry uses, and non-limitingly illustrated by any of the following:

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)
 Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(II)Hexafluorophosphate
 Aquo-hydroxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(III) Hexafluorophosphate
 Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(II) Tetrafluoroborate
 5 Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneManganese(III) Hexafluorophosphate
 Dichloro-5,12-di-n-butyl-1,5,8,12-tetraaza bicyclo[6.6.2]hexadecane Manganese(II)
 Dichloro-5,12-dibenzyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)
 Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II)
 Dichloro-5-n-octyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II)
 10 Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II).

As a practical matter, and not by way of limitation, the compositions and laundry processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic washing process, typical compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the bleaching compositions.

20 (d) Other Bleach Catalysts -

[0068] The compositions herein may comprise one or more other bleach catalysts. Preferred bleach catalysts are zwitterionic bleach catalysts, which are described in U.S. Patent Nos. 5,576,282 (especially 3-(3,4-dihydroisoquinolinium) propane sulfonate) and 5,817,614. Other bleach catalysts include cationic bleach catalysts are described in U.S. Patent Nos. 5,360,569, 5,442,066, 5,478,357, 5,370,826, 5,482,515, 5,550,256, and WO 95/13351, WO 95/13352, and WO 95/13353.

Builders

30 **[0069]** The detergent and laundry compositions described herein preferably comprise one or more detergent builders or builder systems. When present, the compositions will typically comprise at least about 1% builder, preferably from about 5%, more preferably from about 10% to about 80%, preferably to about 50%, more preferably to about 30% by weight, of detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Preferred builders for use in the detergent and laundry compositions, particularly dishwashing compositions, described herein include, but are not limited to, water-soluble builder compounds, (for example polycarboxylates) as described 35 in U.S. Patent Nos. 5,695,679, 5,705,464 and 5,710,115.

[0070] Other suitable polycarboxylates are disclosed in U.S. Patent Nos. 4,144,226, 3,308,067 and 3,723,322. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly titrates.

40 Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates (see, for example, U.S. Patent Nos. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137), phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates.

45 However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

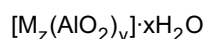
Suitable silicates include the water-soluble sodium silicates with an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of from about 1.0 to 2.8, with ratios of from about 1.6 to 2.4 being preferred, and about 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.0 is the most preferred. Silicates, when present, are preferably present in the detergent and laundry compositions described herein at a level of from about 5% to about 50% by weight of the composition, more preferably from about 10% to about 40% by weight. Partially soluble or insoluble builder compounds, which are suitable for use in the detergent and laundry compositions, particularly granular detergent compositions, include, but are not limited to, crystalline layered silicates, preferably crystalline layered sodium silicates (partially water-soluble) as described in U.S. Patent No. 4,664,839, and sodium aluminosilicates (water-insoluble). When present in detergent and laundry compositions, these builders are typically present at a level of from about 1% to 80% by weight, preferably from about 10% to 70% by weight, most preferably from about 20% to 60% by weight of the composition.

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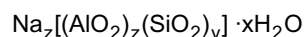
Crystalline layered sodium silicates having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from about 1.9 to about 4, preferably from about 2 to about 4, most preferably 2, and y is a number from about 0 to about 20, preferably 0 can be used in the compositions described herein. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. The most preferred material is delta- Na_2SiO_5 , available from Hoechst AG as NaSKS-6 (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. SKS-6 is a highly preferred layered silicate for use in the compositions described herein herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used in the compositions described herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionizable material. The solid, water-soluble ionizable material is preferably selected from organic acids, organic and inorganic acid salts and mixtures thereof.

[0071] Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders have the empirical formula:

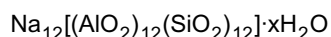


wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264. Preferably, the aluminosilicate builder is an aluminosilicate zeolite having the unit cell formula:



wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably 7.5 to 276, more preferably from 10 to 264. The aluminosilicate builders are preferably in hydrated form and are preferably crystalline, containing from about 10% to about 28%, more preferably from about 18% to about 22% water in bound form.

These aluminosilicate ion exchange materials can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite MAP and Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter. Zeolite X has the formula:



Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions described herein are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984. Useful succinic acid builders include the C_5 - C_{20} alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate

(preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

FABRIC CARE COMPOSITION

[0072] The fabric care composition herein will comprise at least one fabric care active selected from the group consisting of (I) fabric softeners, (II) textile color care agents, (III) textile property modifiers, from which textile odor modifiers are specifically excluded, (IV) textile odor modifiers, (V) fabric care actives other than (I)-(IV), and (VI) mixtures thereof. The fabric care active is preferably present at a level of from about 0.001% to about 80%, more preferably from about 0.1% to about 40% by weight of the fabric care composition.

[0073] Preferably the fabric care composition comprises at least one of said fabric softeners (I), and wherein said fabric softeners are selected from the group consisting of: (A) organic fabric softeners, (B) inorganic fabric softeners, e.g., clays, preferably hectorite clays, and (C) mixtures thereof and/or hybrid organic-inorganic fabric softeners. When present in one or more compositions of the articles of the present invention, fabric softeners are used in an amount between about 1% and about 30% by weight of the compositions.

One preferred group of fabric softeners for use as the fabric care active are organic fabric softeners (A), and wherein said organic fabric softener is selected from the group consisting of: (i) quaternary nitrogen-containing organic fabric softeners free from ester and/or amide moieties such as are disclosed in WO 00/24851 beginning on page 61; (ii) quaternary nitrogen-containing organic fabric softeners comprising ester and/or amide and/or olefinically unsaturated moieties, preferably quaternary nitrogen-containing organic fabric softeners comprising ester moieties, such as are described in WO 00/24851 beginning on page 62; (iii) quaternary-nitrogen-free organic fabric softeners, such as are described in WO 00/24851, beginning on page 74; and (iv) mixtures thereof. Notably, the type (ii) organic fabric softeners described above are generally preferred over the type (i) organic fabric softeners.

Preferred inorganic fabric softeners for use in the articles of the present invention are clays, preferably hectorite clays, and the inorganic fabric softeners disclosed in WO 97/04065 beginning on page 5. Hybrid organic-inorganic fabric softeners, such as organo-modified clays, that may be used to advantage in the articles of the present invention include organosilicones softeners amongst other materials.

[0074] A preferred group of fabric care actives are textile color care agents (II) selected from the group consisting of dye fixatives, dye transfer inhibitors, color maintenance agents, whiteness enhancers, anti-fading agents including bleach scavengers and/or antioxidants, color appearance restoration agents of non-chelant types (e.g., Carezyme® being a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity commercially available from Novozyme, DK), brightness restoration agents e.g., antiencrustation agents, UV protection agents for fabrics, sun fade inhibitors, anti-fading agents, and mixtures thereof. Such materials are well known to those skilled in the art and descriptions thereof are common in the patent literature such as found in U.S. Patent Nos. 6,107,270 and 6,020,302, which are commonly assigned to The Procter and Gamble Company. "Textile color care agents" as used herein refers to materials that provide a color care benefit to laundered fabrics primarily by preserving the existing fabric colors and preventing their degradation. "Textile color care agents" should not be understood to refer to optical brighteners or other cleaning agents as described above. Textile color care agents are not intended to provide a general detergent effect such as is typical of bleaches and surfactants. Suitable are the following polymeric dye transfer inhibiting agents: polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof such as described in for example EP-A-262,897; EP-A-256,696; EP 635 565, EP 635 567; US 5,804,543 and US 5,912,221. When present in one or more compositions of the articles of the present invention, textile color care agents are used in an amount between about 0.1% and about 10% by weight of the compositions.

[0075] Another preferred group of fabric care actives are textile property modifiers (III) selected from the group consisting of fabric bodying agents, fabric drape and form control agents, fabric smoothness agents, static control agents other than fabric softeners inherently possessing static control ability, fabric wrinkle control and/or ironing aid agents, fabric integrity agents, fabric anti-abrasion agents, fabric anti-wear agents, humectants and/or lubricants, pill removal agents, insect repellents, mite control agents, non-bleaching fabric sanitizers, e.g., fabric substantive antibacterials and/or antiviral agents and/or antifungals, flame retardants and mixtures thereof. "Textile property modifiers" specifically excludes odor modifiers which are treated separately herein. When present in one or more compositions of the articles of the present invention, textile property modifiers are used in an amount between about 0.1% and about 10% by weight of the compositions. Preferred are silicone polymers, especially polydimethylsiloxanes and their functionalised derivatives as described in WO97/31997, WO97/31998, WO00/71806, WO00/71807 and WO97/32917 and the cationic siloxane polymers such as the polydimethylsiloxane polymers comprising at least one quaternised nitrogen atom as

described in WO99/32539. Preferred class of cationic silicone polymers are those comprising one or more polysiloxane units, preferably polydimethylsiloxane units of formula $-(\text{CH}_3)_2\text{SiO})_n$ - having a degree of polymerization, n, of from 50 to 200 and organosilicon-free units comprising at least one diquatary unit as described on pages 10-17 of co-pending patent application US serial No. SN60/268174, filed on February 12, 2001 by The Procter & Gamble Company. Preferred cationic silicone is those of Structure 2b on pages 13, line 22 to page 15 line 18 in such patent application US serial No. SN60/268174 as filed. More preferred is the cationic silicone described in example 1 having Structure 2, R¹=methyl, R² = (CH₂)₃, X = CH₂CHOHCH₂, cationic divalent moiety ii(a) with R⁴, R⁵, R⁶, R⁷ all methyl and Z¹ is (CH₂)₆. A = 50% acetate, 50% laurate, weight basis; polyalkyleneoxide moiety (iii) of Structure 2 is NHCH(CH₃)CH₂O (C₂H₄O)₃₈(C₃H₆O)₆CH₂CH(CH₃)NH; cationic monovalent moiety iv(a) of Structure 2 has R¹², R¹³ and R¹⁴ all methyl; a = 0; b = 1; c = 150; d = 0; m = 2. Also preferred are polyamide-polyamine materials that comprise epichlorohydrin adduct of polamide-polyamines which are the reaction products of diethylentriamine and adipic acid (WO98/29530).

[0076] Other preferred fabric care actives are textile odor modifiers (IV) selected from the group consisting of perfumes, (preferably pro-perfumes - A preferred pro-perfume useful herein is described in columns 7-14 of US 5,378,468 and in US 5,652, - and/or substantive perfumes and/or perfumes combined with perfume carriers), odor enhancers, malodor control agents as cyclodextrins (as described on pages on pages 9 to 12 of WO96/04940) and mixtures thereof. When present in one or more compositions of the articles of the present invention, textile odor modifiers are used in an amount between about 0.1% and about 10% by weight of the compositions.

[0077] Specific examples of fabric care actives are the preferred anti-shrinkage agents, anti-wrinkle agents, soil release polymers, fabric softening agents and fabric conditioning agents selected from the group consisting of oligosaccharides, especially mixtures of oligosaccharides, especially isomaltooligosaccharides (IMO) (including mixtures, the individual components of said mixtures, substituted versions thereof, derivatised versions thereof, and mixtures thereof. Further examples can be found in WO 00/24851 especially on pages 8-9. Especially preferred for fabric softening, and anti wrinkle are diester quaternary ammonium compounds such as 1,2-di(acyloxy)-3-trimethylammonio propane chloride. Further examples are provided in WO 00/24851 pages 61-75.

[0078] The fabric care compositions according to the present invention preferably comprise an effervescent component. More preferably an acid or peroxide as previously described in the effervescent system.

Dual- or poly- functional agents or adjuncts

[0079] The present compositions can additionally comprise at least about 0.0001%, when present, of a dual-functional agent having both cleaning and fabric care activity. For example, certain polymers can be useful to suspend soil and to provide a fabric care effect.

Optional Components

[0080] The following optional components may be found in either the cleaning, the bleaching or the fabric care compositions of the articles of the present invention. These optional ingredients can include, solvents, stabilizers, aesthetic adjuncts, e.g., colorants; pH adjusting agents, fillers, soil release agents, stain resistance agents, can be optionally present in any of the inventive compositions. Optional components, when present, are at levels of from about 0.001% to about 80% of the composition. Water and/or solvents can in general be present or absent from any of the compositions; however water and/or solvents are usually present at levels of at least about 0.01% to about 80%, or higher, in any of the compositions.

BLEACHING COMPOSITION

[0081] The bleaching compositions of the present invention can comprise a bleaching system as described above. Preferably, the bleaching composition will comprise a pre-formed peroxy carboxylic acid, a suspending agent, a chelant and an effervescent component. The effervescent component is preferably an acid or peroxide as previously described in the effervescent system.

Pre-formed Peroxy Carboxylic acid

[0082] The bleaching compositions of the present invention preferably comprise a pre-formed peroxy carboxylic acid (hereinafter referred to as a "peracid"). Any suitable peracid compound known in the art can be used herein.

The preformed peracid compound as used herein is any convenient compound which is stable and which under consumer use conditions provides an effective amount of peracid anion. The preformed peracid compound preferably is selected from the group consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxy monosulfuric acids and salts, and mixtures thereof.

One class of suitable organic peroxycarboxylic acids have the general formula:



wherein R is an alkylene or substituted alkylene group containing from 1 to about 22 carbon atoms or a phenylene or substituted phenylene group, and Y is hydrogen, halogen, alkyl, aryl, -C(O)OH or -C(O)OOH.

10 Organic peroxyacids suitable for use in the present invention can contain either one or two peroxy groups and can be either aliphatic or aromatic. When the organic peroxycarboxylic acid is aliphatic, the unsubstituted acid has the general formula:



20 where Y can be, for example, H, CH₃, CH₂Cl, C(O)OH, or C(O)OOH; and n is an integer from 1 to 20. When the organic peroxycarboxylic acid is aromatic, the unsubstituted acid has the general formula:



wherein Y can be, for example, hydrogen, alkyl, alkylhalogen, halogen, C(O)OH or C(O)OOH.

Typical monoperoxy acids useful herein include alkyl and aryl peroxyacids such as:

- 30 (i) peroxybenzoic acid and ring-substituted peroxybenzoic acid, e.g. peroxy-a-naphthoic acid, monoperoxyphthalic acid (magnesium salt hexahydrate), and o-carboxybenzamidoperoxyhexanoic acid (sodium salt);
- (ii) aliphatic, substituted aliphatic and arylalkyl monoperoxy acids, e.g. peroxyauric acid, peroxysearic acid, N-nonylamino-peroxycaproic acid (NAPCA), N,N-(3-octylsuccinoyl)aminoperoxyacaproic acid (SAPA) and N,N-phthaloylamidoperoxyacaproic acid (PAP);
- 35 (iii) amidoperoxyacids, e.g. monononylamide of either peroxysuccinic acid (NAPSA) or of peroxyadipic acid (NAPAA).

[0083] Typical diperoxyacids useful herein include alkyl diperoxyacids and aryldiperoxyacids, such as:

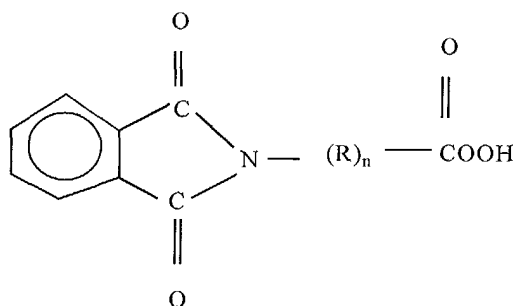
- 40 (iv) 1,12-diperoxydodecanedioic acid;
- (v) 1,9-diperoxyazelaic acid;
- (vi) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (vii) 2-decyldiperoxybutane-1,4-dioic acid;
- 45 (viii) 4,4'-sulfonylbis(oxo)peroxybenzoic acid.

[0084] Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent 4,634,551 to Burns et al., European Patent Application 0,133,354, Banks et al. published February 20, 1985, and U.S. Patent 4,412,934, Chung et al. issued November 1, 1983. Sources also include 6-nonylamino-6-oxoperoxy-

50 caproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al. Persulfate compounds such as for example OXONE, manufactured commercially by E.I. DuPont de Nemours of Wilmington, DE can also be employed as a suitable source of peroxymonosulfuric acid.

Particularly preferred peracid compounds are those having the formula:

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wherein R is C₁₋₄ alkyl and n is an integer of from 1 to 5. A particularly preferred peracid has the formula where R is CH₂ and n is 5 i.e., phthaloylamino peroxy caproic acid (PAP) as described in U.S. Patent Nos. 5,487,818, 5,310,934, 5,246,620, 5,279,757 and 5,132,431. PAP is available from Ausimont SpA under the tradename Euroco.

The peracids used herein preferably have a solubility in aqueous liquid compositions measured at 20 °C of from about 10 ppm to about 1500 ppm, more preferably from about 50 ppm to about 1000 ppm, most preferably from about 50 ppm to about 800 ppm solubility is measured at 20 °C.

In a particularly preferred embodiment of the present invention the peracid has mean average particle size of less than 100 microns, more preferably less than 80 microns, even more preferably less than 60 microns. Most preferably, when the peracid is PAP, it has a mean average particle size of between about 20 and about 50 microns.

The peracid is preferably present at a level of from about 0.1% to about 25%, more preferably from about 0.1% to about 20%, even more preferably from about 1% to about 10%, most preferably from about 2% to about 4%. Alternatively, the peracid may be present at a much higher level of for example 10% to 40%, more preferably from 15% to 30%, most preferably from 15% to 25%.

Suspending Agents

[0085] The composition of the present invention may preferably comprise, especially when the composition contains a solid particulate such as a peracid, a suspending agent. A suspending agent is an ingredient which is specifically added to the composition of the present invention to suspend a solid particulate ingredient of the composition.

Suitable suspending agents are those known in the art. Examples of suspending agents include gum-type polymers (e.g. xanthan gum), polyvinyl alcohol and derivatives thereof, cellulose and derivatives thereof and polycarboxylate polymers including, but not limited to, : tamarind gum (preferably consisting of xyloglucan polymers), guar gum, locust bean gum (preferably consisting of galactomannan polymers), and other industrial gums and polymers, which include, but are not limited to, Tara, Fenugreek, Aloe, Chia, Flaxseed, Psyllium seed, quince seed, xanthan, gellan, welan, rhamosan, dextran, curdlan, pullulan, scleroglucan, schizophyllan, chitin, hydroxyalkyl cellulose, arabinan (preferably from sugar beets), de-branched arabinan (preferably from sugar beets), arabinoxylan (preferably from rye and wheat flour), galactan (preferably from lupin and potatoes), pectic galactan (preferably from potatoes), galactomannan (preferably from carob, and including both low and high viscosities), glucomannan, lichenan (preferably from icelandic moss), mannan (preferably from ivory nuts), pachyman, rhamnogalacturonan, acacia gum, agar, alginates, carrageenan, chitosan, clavan, hyaluronic acid, heparin, inulin, cellodextrins, carboxymethylcellulose (CMC), dextrans, dextrans, ethylhydroxyethylcellulose (EHEC), guar, hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), hydroxybutylcellulose (HBC), karaya, larch, methylcellulose (MC), tamarind, scleroglucan, xanthan, carboxymethylhydroxyethylcellulose (CMHEC), methoxypropyl methyl cellulose (MPMC), hexylcarboxymethyl cellulose, C₁₂ - C₂₀ alkyl carboxymethylcellulose, methylhydroxyethylcellulose (MHEC), methylhydroxypropylcellulose (MHPC), hydroxyethylmethylcellulose (HEMC), hydroxypropylmethylcellulose (HPMC), hydroxybutylmethylcellulose (HBMC) and mixtures thereof

In a particularly preferred embodiment of the present invention, the suspending agent is selected from a gum-type polymer or a polycarboxylate polymer.

Chelants

[0086] Chelants are preferably formulated within the bleaching composition but can be as well formulated within the aqueous liquid detergent, both aqueous liquid and bleaching compositions or the fabric care composition. Suitable are one or more copper and/or nickel chelating agents ("chelators"), such as diethylenetriaminepentaacetic acid (DTPA) or ethylenediamine-N,N'-disuccinic acid (EDDS). Water-soluble chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and

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mixtures thereof, all as hereinafter defined and all preferably in their acidic form. Amino carboxylates useful as chelating agents herein include ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates (NTA), ethylenediamine tetrapropionates, ethylenediamine-N,N'-diglutamates, 2-hydroxypropylenediamine-N,N'-disuccinates, triethylenetetraaminehexacetates, di-ethylenetriaminepenta acetates (DTPA) and ethanoldiglycines, including their water-soluble salts such as the alkali metal, ammonium, and substituted ammonium salts thereof and mixtures thereof. Amino phosphonates are also suitable and can include ethylenediaminetetrakis (methylenephosphonates), diethylenetriamine-N,N,N',N",N"-pentakis(methane phosphonate) (DTMP) and 1-hydroxyethane-1,1-diphosphonate (HEDP). Preferred chelating agents useful herein include those described in U.S. 5,686,376 to Rusche, et al., issued November 11, 1997 included herein by reference in its entirety. Chelants are usually present at a range of from about 0.001% to about 10% by weight of the composition. Preferably in the bleaching composition, the chelant is present at a level of from 1% to 10%, more preferably from 5%-8% by weight of the composition. Chelants may also be used to advantage in the fabric care compositions of the present invention as well.

Example A

[0087] A dual compartment pouch having at least a first and a second compartment which may separately comprise an aqueous liquid detergent composition and a bleaching composition as follows.

<u>Compartment 1</u>	% By Weight
C13-15 2.5-Ethoxy Alkyl sulphate	14.2
HLAS	4.37
C12-14 Alkyl dimethylamine oxide	1.10
C13-15 Alkyl alcohol 9-ethoxylated	2.18
Citric acid	2.80
C12-18 fatty acid	5.00
Protease	1.20
Amylase	0.18
Catalase	0.25
Boric acid	2.28
CaCl ₂	0.068
Ethoxylatedtetraethylenepentimine	0.55
Ethoxylated polyethyleneimine	1.09
Diethylene triamine peracetic acid	0.27
FWA-49	0.125
Ethanol	4.00
1,2-propanediol/Glycerine	6.73
Monoethanolamine	0.40
NaOH	3.80
Silicone suds suppressor	0.06
Perfume	0.66
Water	Balance
<u>Compartment 2</u>	
PAP (70% Slurry)	17.30
Citric acid	2.00
Xanthan gum	0.46

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(continued)

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Compartment 2	
Sulphonated ethoxylated polyterphtalic	0.80
Hydrogen Peroxide	2.00
Trimethyl benzoic acid	0.20
NaOH	0.47
Water	Balance

Example B

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[0088] A dual compartment pouch having at least a first and a second compartment which may separately comprise 2 compositions with fabric care actives and cleaning agents divided over the 2 compartments for better chemical and physical stability.

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Compartment 1	
C45 alcohol 7-ethoxylate	17,0
C12-alkyl dimethylamine N-oxide	2.5
Hydroxyethane diphosphonic acid	0.3
Triethanolamine dicanoyl ester, quaternized, methylsulfate salt	11,0
Hydrogen peroxide	2.7
Cyclohexanedimethanol	9.5
Sulfuric acid	to pH 3.0
Perfume / minors	0.1
Water	balance

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Compartment 2	
C45 alcohol 7-ethoxylate	14
C12-alkyl dimethylamine N-oxide	3.5
Citric acid	3.0
Polyethylenimine (MW 600), 20 ethoxylate	1.2
Ethoxylated tetraethylene pentamine	0.6
Catalase enzyme	0.6
Amylase enzyme	0.12
Protease enzyme	0.03
Cyclohexanedimethanol	2.0
Boric acid	2.0
Propandiol	7.2
Hydrogenated castor oil	0.75
Monoethanolamine	To pH 8.0
Perfume / minors	2.5
Water	balance

Claims

1. A flexible multiple compartment pouch (1) comprising at least a first (2) and second (3) compartment and at least one gusset (6).
2. A flexible multiple compartment pouch according to claim 1 comprising at least a first and second compartment wherein the first compartment comprises a first composition and the second compartment comprises a second composition and wherein the first and second compositions are incompatible.
3. A flexible multiple compartment pouch according to any preceding claim comprising at least one gripping means (7).
4. A flexible multiple compartment pouch comprising at least a first and second compartment wherein the first compartment comprises a first composition and the second compartment comprises a second composition and wherein the first and second compositions are incompatible.
5. A flexible multiple compartment pouch according to claim 4 comprising at least one gripping means.
6. A flexible multiple compartment pouch according to claim 4 or 5 comprising at least one gusset.
7. A flexible multiple compartment pouch comprising at least a first and second compartment and at least one gripping means.
8. A flexible multiple compartment pouch according to claim 7 comprising at least one gusset.
9. A flexible multiple compartment pouch according to claim 7 or 8 wherein the first compartment comprises a first composition and the second compartment comprises a second composition and wherein the first and second compositions are incompatible.
10. A flexible multiple compartment pouch according to any preceding claims where the second and optionally additional compartments are substantially enclosed within the first.
11. A flexible multiple compartment pouch according to claim 1 to 9 where the separate compartments (2), (3) are adjacent to one another and separated by a permanent seal (4).
12. A flexible multiple compartment pouch according to any preceding claims where each separate compartment is provided with an outlet and said outlets converge at a single outlet device without allowing the mixing of compositions contained therein.
13. A flexible multiple compartment pouch according to claim 1 to 11 where each separate compartment is provided with an outlet and said outlets are adjacent to one another.
14. A flexible multiple compartment pouch according to any preceding claims wherein the outlet from each compartment will converge to a connection device which bridges between the pouch and durable container
15. A flexible multiple compartment pouch according to any preceding claims wherein the gripping means comprises a handle.
16. A flexible multiple compartment pouch according any preceding claims wherein a gripping means is at the opposite edge of the pouch to the outlets.
17. A flexible multiple compartment pouch according to claim 1 to 16 wherein a gusset is situated at the opposite edge of the pouch to the outlets.
18. A flexible multiple compartment pouch according to any preceding claims wherein the first compartment comprises an aqueous liquid detergent and the second comprises a fabric care composition.
19. A flexible multiple compartment pouch according to any preceding claims wherein the first compartment comprises an aqueous liquid detergent and the second comprises a bleaching composition.

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20. A flexible multiple compartment pouch according to any preceding claims comprising a sealable film and an aesthetic layer.

5 **21.** A method of refilling a multiple compartment durable container with a multiple compartment pouch according to any of the preceding claims, comprising the steps:

- a. preparing the durable container for receipt of composition, and
- b. preparing the outlets from the multiple compartment pouch, then
- c. adding the compositions to the compartments of the durable container

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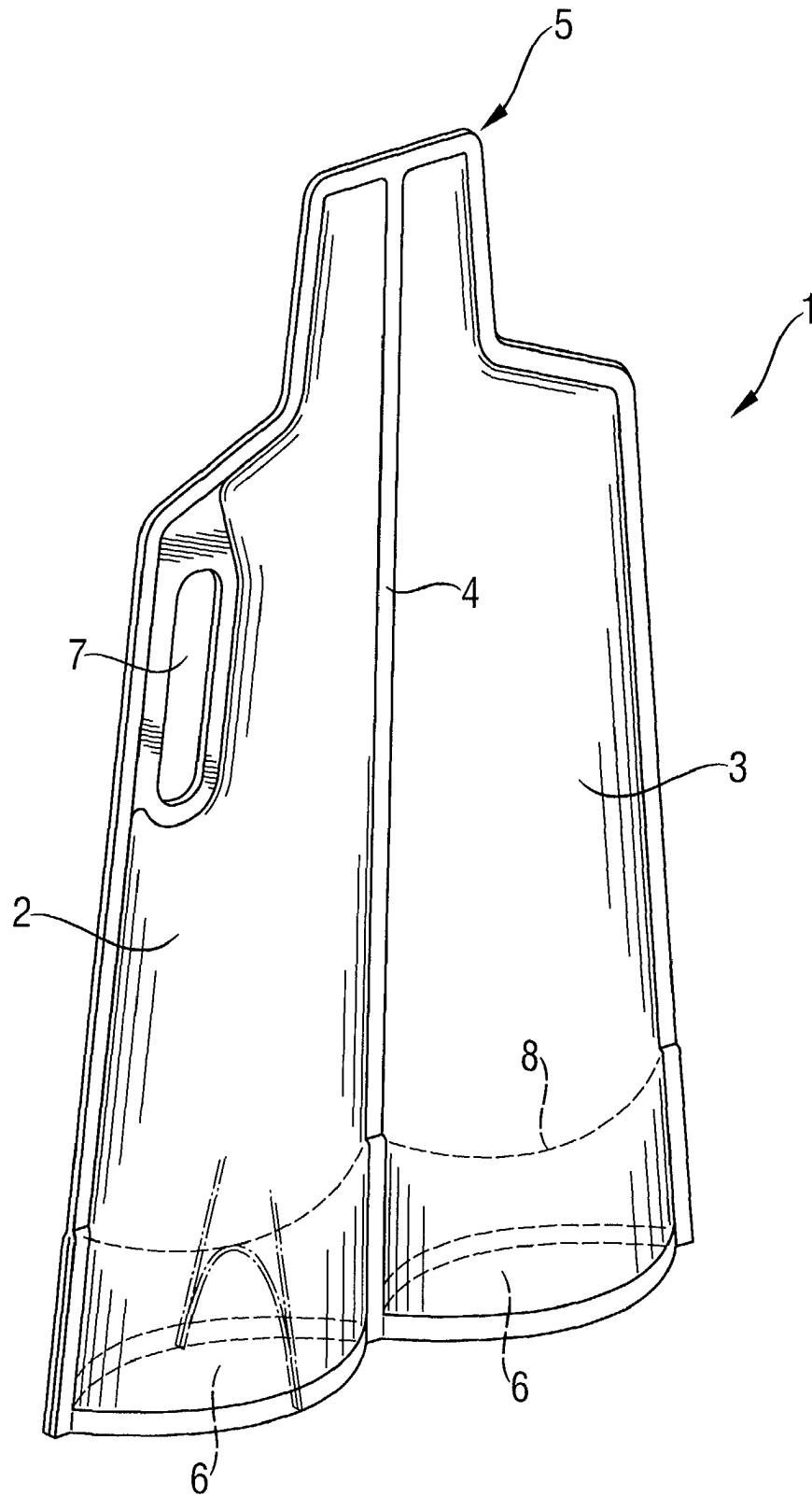


Fig. 1

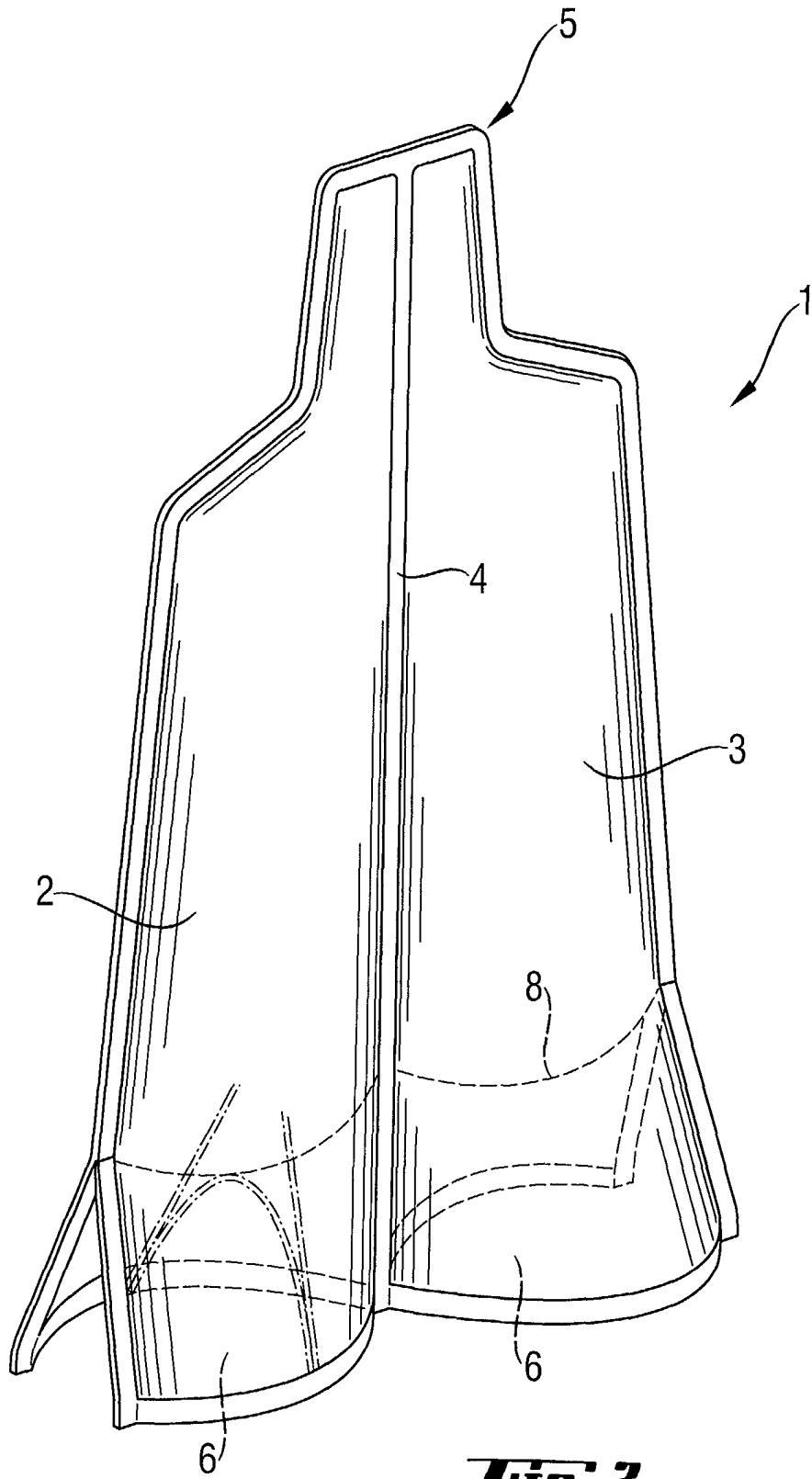


Fig. 2

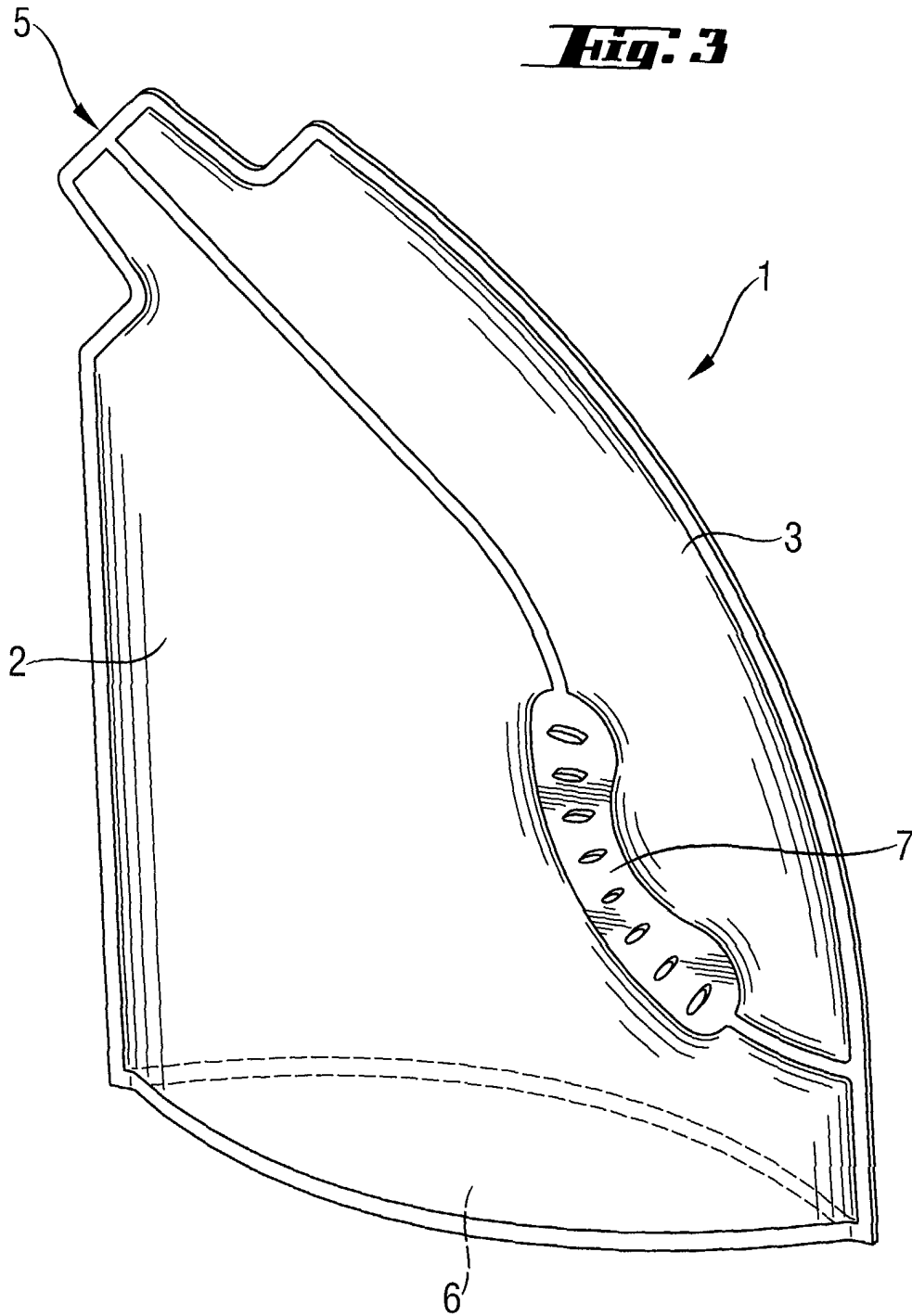


Fig. 4

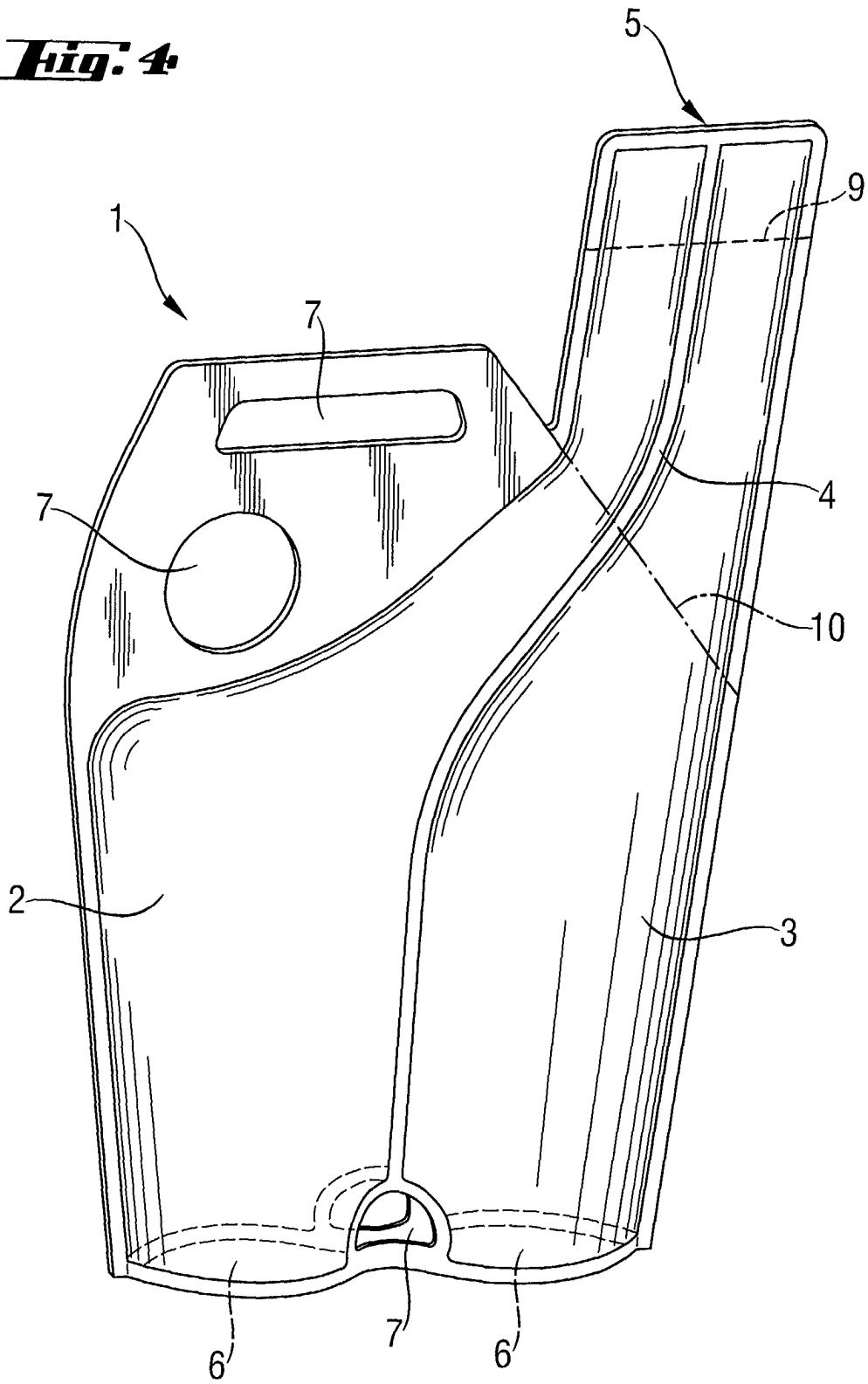
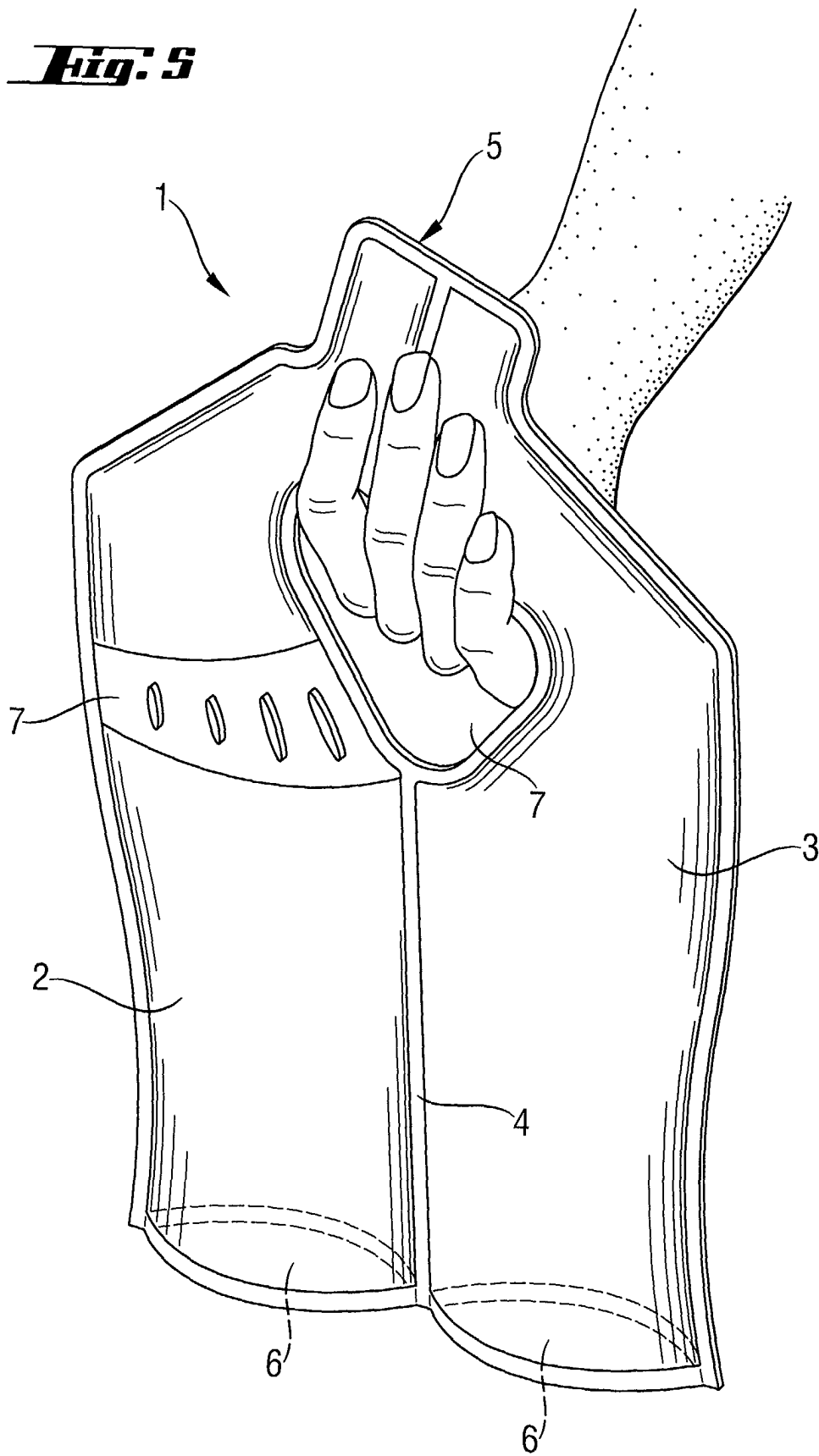
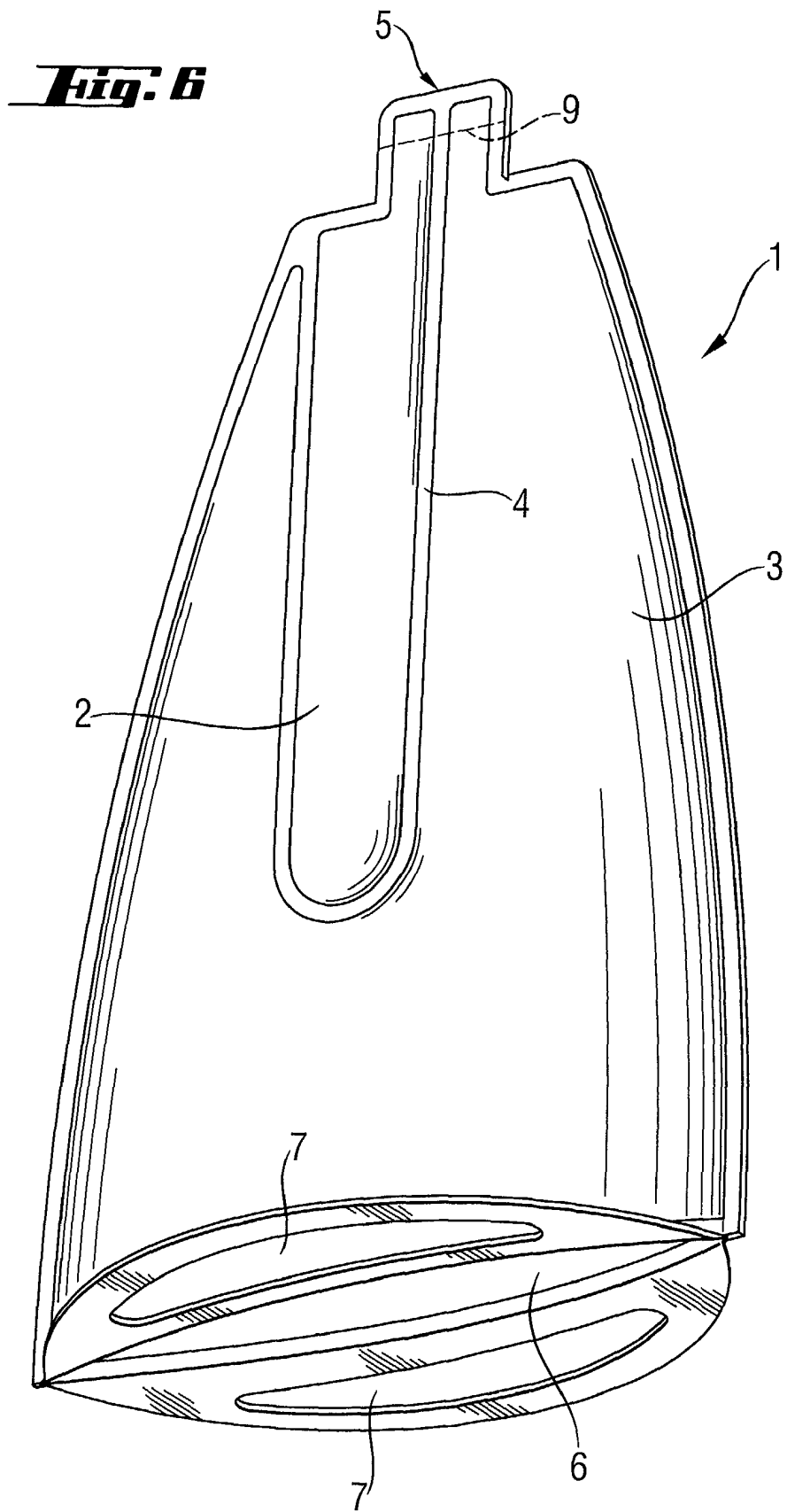


Fig. 5





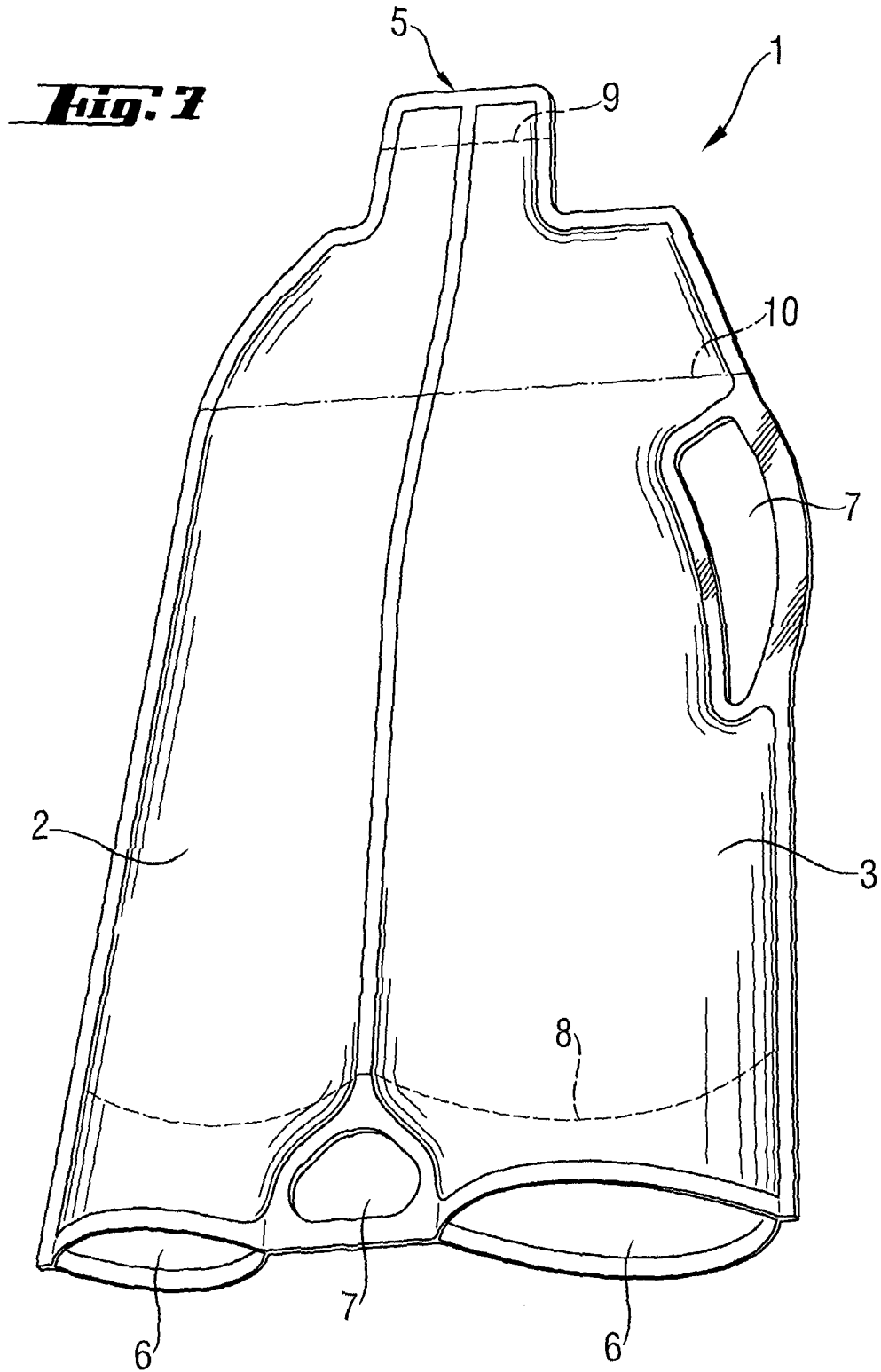


Fig. 8

