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(54) Title: LAUNDRY DETERGENT COMPOSITION

(57) Abstract: The present invention relates to a laundry detergent composition which provides a visual cue once an effective product dosing in an aqueous medium is attained. Also to a process for handwashing with the composition and to use of the composition as a sufficiency of dosage indicator. The laundry composition comprises : a) a deterative surfactant; b) a colour change indicator system comprising: i) an indicator dye capable of binding to divalent metal cations; ii) one or more other complexing agents for divalent metal cations, said complexing agent having a greater binding capacity than the indicator dye for said divalent metal cations at the pH of use, and c) optionally carriers and adjuncts to 100 wt. %.

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LAUNDRY DETERGENT COMPOSITION**Technical Field of the Invention**

5

The present invention relates to a laundry detergent composition that incorporates a dosage indicator to indicate to the consumer when a sufficient amount of laundry detergent is present in a wash liquor.

10

Background of the Invention

For the purposes of washing textile fabrics the hand wash method remains by far the most widely used washing technique. Within the broad definition of 'handwash' exist a multitude of different washing techniques; though in most cases water is added to a wash bowl container and then a detergent product is added to make the wash liquor. The amount of product added by consumers tends to be based on previous experience, or routine. However, consumer self dosing can lead to the use of the wrong amount of the detergent product. If the product is underdosed, then a less than satisfactory cleaning performance is seen, if however the product is overdosed, i.e. excess detergent product, then this is unnecessarily wasteful, both financially for the consumer and environmentally due to the use of a higher weight of chemical product per wash than is strictly required. A follow on effect of the use of excessive product is the need for excess water to rinse the excess detergent off the clothes. Such problems of wastage

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are becoming increasingly important in our more environmentally concerned world.

To remedy the excessive use of product, one possibility
5 would be to introduce so called 'unit dose' products to
handwash markets. Unit dose products are self contained
doses of detergent product, such that the same amount of
product can be delivered to each wash. This has found
success in many machine-wash based markets. However, such
10 an approach requires that a constant amount of water is
present in each and every wash, to enable the concentration
of actives in the wash liquor to be the same for each wash.
This fails to consider one of the problems associated with
laundry handwash, namely that the amount of wash liquor
15 varies greatly for different consumers, and generally
follows the size of the 'wash bowl container' available to
the consumer. Unit dose in handwash is therefore not a
promising solution to fix the concentration of detergent
ingredients in the wash liquor regardless of the 'wash bowl
20 container' used by the consumer. Similarly, the provision
of a dosing cup, or similar, is also limited via a similar
argument.

Historically, sufficiency of detergent dosage has been
25 judged via cues associated with either product appearance,
for example, product volume, or else generated by the
product on contact with the wash medium. As an example,
foam generation has been used for many years as a consumer
cue for sufficiency of dosage - once a certain level of foam
30 is achieved, the consumer takes this as a cue that there is
an effective level of detergent present. However, this

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learned cue has imposed a serious limitation on handwash product formulators in that they are now often forced to incorporate foam producing elements in their formulations.

- 5 The adoption of such cues by consumers significantly restricts the choice of ingredients and processing options available to the formulator.

10 In addition to the problems caused by the variation of the amount of water used by the laundry handwash detergent consumer when laundering; variable water hardness for the same volume of water also presents another problem to the handwash detergent formulator. In these situations, as the ratio of metal ion chelating agent to detergent is fixed in
15 a product, harder water requires more product to be added, leading to more detergent being dosed. Many handwash detergents have instructions to dose detergent product according to the water hardness. This is a problem because many consumers are not sure what water hardness they have in
20 the water being used.

The deliberate introduction of visual cues to indicate product performance has precedent. A visual consumer cue is disclosed in WO 2004/078896 (Unilever). The visual cue is a
25 fabric pre-treatment cleaning method, whereby a textile is treated with a liquid detergent in the form of a foam and wherein the visual cue is a colour change to said foam. The colour change is provided by a pH dependent chromophore and as such the reagent cannot then be buffered or else it could
30 not change pH and so would not be able to work.

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Another pH based indicator system is disclosed in CH313346. The specific pH indicator disclosed is Alizarine Yellow R which changes colour from yellow to orange red as the solution pH rises from 10.1 to 12.1. As mentioned above,
5 for a buffered laundry composition with a typical pH of 10.5 such an indicator system would be unsuitable to indicate sufficiency of dosage.

Another indicator product is disclosed in GB 2 349 895 (The
10 Robert McBride Group). The indicator product comprises a substrate and a colour indicator component distributed on or in the substrate, and has a barrier present to isolate the colour indicator from the surrounding environment. This product (in particular a tumble dryer sheet) alerts the
15 consumer that it has exhausted its capacity for releasing active material.

A method for softening water in a washing machine is disclosed in WO 2005/005329 (Reckitt Benckiser), wherein
20 hard water is contacted with a water insoluble product added to the washing machine, wherein the product has a different appearance after being contacted with the hard water.

An indicator for calcium and magnesium is disclosed in WO
25 02/084278 (Reckitt Benckiser). Disclosed is a product, preferably a fibre product, having immobilised onto it an indicator dye, which can be used to detect metal ions in a liquid.

30 EP 0 597 900 B1 (SEBA DIAGNOSTICS) discloses a method for the colorimetric determination of magnesium ions in a fluid,

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particularly biological fluids such as blood serum, blood plasma and the like. The method comprises contacting said fluid with a reagent comprising a metallochromic dye substance 2-(4,5-dihydroxy-2,7-disulpho-3-

5 naphthylazo)benzene-arsonic acid [Arsenoaza I], together with a selective complexing agent, and determinating the formation of a magnesium-dye complex.

EP 0 513 564 B1 discloses a buffered reagent for determining
10 the ionic strength and/or the specific weight of an aqueous liquid (urine) with the aid of a colour indicator, the reagent contains at least one detergent and one pH indicator.

15 Buffered laundry detergent compositions containing dyes that may change colour in response to certain cations are disclosed in WO 2006/041739. These compositions are stated to be for use to mask a red discolouration in the water. The compositions are not concentrated laundry powders. The
20 problem of sufficiency of dosage is not addressed.

Summary of the Invention

The invention provides a sufficiency of dosage indicator for
25 laundry main wash, preferably in the field of handwash. The composition, when added to an aqueous medium provides a visual cue that signifies when an effective dosing of a laundry detergent composition is attained. The visual cue of the present invention is provided by a colour change
30 indicator system. The colour desirably reverses during rinsing.

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A first aspect of the present invention provides a laundry detergent composition comprising:-

- a) detersive surfactant;
- 5 b) a colour change indicator system comprising:-
 - i) an indicator dye capable of binding to divalent metal cations; and,
 - ii) one or more other complexing agents for divalent metal cations, said complexing agent
 - 10 having a greater binding capacity than the indicator dye for said divalent metal cations at the pH of use; and,
- c) optionally carriers and adjuncts to 100 wt.%.

15 The composition when contacted with an aqueous medium causes a colour change to said aqueous medium once an effective product dosing of the composition is attained.

The divalent metal cations are preferably Ca^{++} and/or Mg^{++} .

20 The amount of detersive surfactant in the composition is preferably at least 19.5wt%. The amount of anionic surfactant is also preferably at least 18wt% of the composition. A second aspect of the current invention provides the use of a composition according to the first

25 aspect as a sufficiency of dosage indicator for laundry main wash, preferably in the field of handwash.

The laundry detergent composition is advantageously pH buffered to maintain the pH of the resulting wash liquor at

30 a stable pH level suitable for laundry purposes. This is preferably from between pH 7 and 12, more preferably between

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pH 7.5 to 11.5 even more preferably 9 to 11.2. The pH buffering of the composition can come entirely from the complexing agent, for example if a builder such as sodium tripolyphosphate (STP) is used as whole or part of the
5 complexing agent. An alternative embodiment of the composition of the invention has a separate pH buffer added as an additional component in the composition.

In this case, a preferred embodiment of the composition of
10 the invention is a laundry detergent composition comprising:-

- a) detersive surfactant;
- b) a colour change indicator system comprising:-
 - 15 i) an indicator dye capable of binding to divalent metal cations;
 - ii) one or more complexing agents for divalent metal cations, said complexing agent having a greater binding capacity than the indicator dye for said
20 divalent metal cations at the pH of use; and,
 - iii) pH buffer, which is preferably non-precipitating; and,
- c) optionally carriers and adjuncts to 100 wt.%.

25 Process of Use

The composition of the present invention can advantageously be used to provide a visual cue once an effective product dosing of said laundry detergent composition in an aqueous
30 medium is attained. Preferably this is for the handwash

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field, and the visual cue prompts the end consumer to stop addition of the laundry detergent composition.

For the compositions of the invention, one process of use
5 for handwash comprises the following steps:-

- 10 a) provision of a wash liquor by admixture of a laundry handwash detergent composition according to the invention to an aqueous medium containing hardness ions; and,
- b) optionally addition of one or more subsequent portions of said laundry handwash detergent composition,
- c) washing laundry in the wash liquor; and then
- 15 d) rinsing the laundry by adding further aqueous medium containing hardness ions, thereby reversing the colour change.

wherein addition of the laundry handwash detergent
20 composition is continued until a visual cue is provided by a colour change of the wash liquor. Preferably, the composition contains a buffer in sufficient quantity that the pH of the wash liquor is held constant.

25 The admixture may take place in any usual fashion that brings the composition and the aqueous medium into contact with each other. Preferably, upon admixture, the laundry handwash detergent composition is present in the aqueous medium in a dissolved or dispersed state. The laundry
30 handwash detergent composition can be any suitable form, such as a solid, liquid or paste. Preferably it is a solid,

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particularly a particulate solid such as a powder or granular composition.

The indicator dye in the composition is selected to be non substantive to the laundry. Although the primary field of use of the sufficiency of dosage composition will be as a handwash composition, it may also be adapted for washing machine use. For example, the colour change caused when the detergent dosing level is sufficient can be sensed not only by a human consumer, but also by a washing machine that is equipped with a sensor for detecting a colour change in a wash liquor. Such compositions and uses thereof therefore also fall within the scope of the current invention. Laundry handwash compositions, uses thereof and laundry handwash processes are preferred embodiments.

Laundry detergent compositions according to the present invention that utilise a colour change indicator system to provide a visual cue for the end consumer has one or more of the following associated advantages:-

- a) concentrated products having from 19.5 to 70wt% deterative surfactant can now be used without excess product use and wastage by the consumer; this leads to reductions on the amount of packaging and chemicals in the final product, and hence a lower environmental footprint;
- b) as a lesser amount of detergent composition is used (due to using the correct effective amount and not an excess) then less water is needed to rinse the

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laundered clothes; the visual indication of rinsing may also assist with attainment of this objective.

- c) a wider selection of surfactants can be incorporated, for example, the formulator is not limited by the necessity of incorporating a surfactant that produces a high level of foam, as an alternative visual cue other than foam can be provided; furthermore, foam boosters do not have to be in the formulation.

Detailed Description of the Invention

The visual cue is provided by a colour change indicator system, causing a colour change of the wash liquor due to interaction of the indicator dye, the complexing agents and hardness ions. Although the colour change once an effective product dosing has been attained can conceivably be from colourless to coloured, or from coloured to colourless, preferably the colour change is from one colour to a second different colour. In a preferred embodiment, the laundry detergent composition imparts a colour to the aqueous medium upon contact. For example, if the aqueous medium is water, the composition changes the colour from colourless to coloured upon initial contact, then once an effective dose of the composition is attained, the initial colour changes to a different colour to provide the visual cue to the consumer.

All percentages quoted herein are defined as percentages by weight.

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An effective product dosing of the laundry detergent composition can be considered to mean the provision of a sufficient amount of a laundry detergent system, for example a surfactant system and/or a hardness ion complexing agent, to provide the required fabric cleaning. The amount of the laundry detergent system present will vary depending on the formulation specification, and the region in which it will be sold.

Such terms as 'laundry process' and 'laundry detergent compositions and products' as used herein, should be taken to mean the actual laundering process itself (whether handwash or by machine) and products classed as 'main wash' detergent products. Accordingly, the present invention is not concerned with pre- and post fabric treatments, nor with so-called 'rinse' products.

The aqueous medium is water or predominantly water. Once a laundry detergent product has been added to the aqueous medium, for example water, the resulting medium is commonly known as a 'wash liquor'.

The wash liquor may be at any pH level suitable for laundry wash purposes. This may be, for example, between pH 4 and 12. However preferentially, the pH of the wash liquor is 7 or above, for example, between 7 and 12.

The wash liquor may change pH during the laundry wash. In such a case of varying pH, the indicator dye and complexing agents are chosen such that the colour change occurs independently of pH range. Although the pH of the wash

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liquor may vary during the wash, preferably the pH of the wash liquor is maintained at a stable pH. By incorporation of a component that can act as a pH buffer. This may be achieved, for example, by the complexing agent included in compositions of the invention, by addition of builder or the
5 addition of a separate pH buffer.

For optimum cleaning when the deterative surfactant comprises anionic surfactant, the wash liquor is advantageously
10 maintained at a pH of from 7 to 12, more preferably it is kept stable at a level between pH 7.5 and 11.5, more preferably still at a level between pH 8 and 11, for example between pH 8.5 and 10.5. Preferably the pH is kept stable by incorporating a pH buffer into the composition. Useful
15 pH buffers compatible with laundry main wash and handwash are well known to the skilled formulator.

The Colour Change Indicator System

20 The colour change indicator system is present in the wash liquor to provide a visual cue once an effective level of laundry detergent composition is present. Preferably it is incorporated within the wash liquor in a dissolved or dispersed state, preferably a dissolved state.

25

The colour change indicator system is provided as part of a laundry detergent composition, i.e. incorporated as part of the laundry detergent product.

30 The species that the colour change indicator is responsive to are the hardness ions Ca^{++} and/or Mg^{++} already present in

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the aqueous medium prior to contact with the laundry detergent composition.

The colour change indicator system is pH independent, i.e.
5 the colour change is not mediated by hydrogen or hydronium cations, so that it is not affected by pH within the normal pH ranges used in laundry main wash or handwash.

One skilled in the art will realise that the actual pH of
10 the wash liquor is not important to the working of the invention. The invention can conceivably work at any pH suitable for laundry main wash, with the skilled person able to choose a suitable indicator dye/complexing agent combination for the desired pH, such that the pH level, or
15 variation thereof during the laundry process has no material effect on the colour change of the chosen indicator dye/complexing agent combination.

Preferred, however, is a system that is maintained at a
20 stable pH. So preferably the laundry composition comprises a pH buffer. It is usual for laundry detergents to be buffered to maintain the pH of the wash liquor at a stable level. Preferably this stable level is in the range of from pH 7 to 12, preferably between pH 7.5 and 11.5, more
25 preferably still between pH 8 and 11, for example between pH 8.5 and 10.5. In this way, the pH of the wash liquor is stable, and as such hydrogen ions would be unsuitable to use as the species to which the colour change indicator is responsive.

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The colour change indicator system comprises an indicator dye capable of binding to divalent metal cations and one or more complexing agents for divalent metal cations. The complexing agent (or one complexing agent from a mixture of
5 two or more complexing agents) has a stronger affinity, measured, for example, by binding capacity, for the divalent metal cation to which it is responsive than the indicator dye.

10 Binding capacity is one way of measuring the affinity of one species to another, and can be equated to values for the stability constant of the metal cation(s) with either complexing agent and indicator dye. Preferably the metal-indicator dye complex is less stable than the metal-
15 complexing agent complex. A discussion of the principles behind relative stability of metal-indicator dye and metal-complexing agent can be found in "Vogel's Textbook of Quantitative Chemical Analysis" 6th Edition Revised and Updated by Mendhem, Denney, Barnes and Thomas and published
20 by Prentice Hall (March 28, 2000), at pages 375-376.

A skilled person would understand that it is the relative values of the respective binding capacities for the metal cation with the indicator dye and the metal cation with the
25 complexing agent that are important. The complexing agent should have a greater binding capacity than the indicator dye for the metal cation. Preferably the difference in binding capacities (or other chosen value for affinity) is at least one order of magnitude; with the greater binding
30 capacity belonging to the complexing agent. More preferably the difference is two orders of magnitude.

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Complexing Agents

Suitable complexing agents are chelating agents for metal cations especially divalent metal cations which cause or are associated with hard water. Chelating agents have two or more species capable of co-ordinating to a metal cation. It is well within the ambit of the person skilled in the art to be able to choose suitable chelating agents in combination with textbook knowledge such as that present in "Vogel's Textbook of Quantitative Chemical Analysis" 6th Edition Revised and Updated by Mendhem, Denney, Barnes and Thomas and published by Prentice Hall (March 28, 2000), see especially section 10.65 and 10.66 at pages 375 and 378 respectively.

Useful chelating agents can include any of those known to those skilled in the art such as amino carboxylates, phosphates (such as STP), phosphonates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof.

Suitable phosphonate chelating agents for use herein may include alkali metal ethane 1-hydroxy diphosphonates (HEDP), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino aminotri(methylene phosphonic acid) (ATMP), nitrilo trimethylene phosphonates (NTP), ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates (DTPMP). The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating

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agents to be used herein are diethylene triamine penta
methylene phosphonate (DTPMP) and ethane 1- hydroxy
diphosphonate (HEDP). Such phosphonate chelating agents are
commercially available from Monsanto under the trade name
5 DEQUEST®.

Polyfunctionally-substituted aromatic chelating agents may
also be useful in the compositions herein. See U.S. Pat.
No. 3,812,044, issued May 21, 1974, to Connor et al.
10 Preferred compounds of this type in acid form are
dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-
disulfobenzene.

A preferred biodegradable chelating agent for use herein is
15 ethylene diamine N,N'-disuccinic acid, or alkali metal, or
alkaline earth, ammonium or substitutes ammonium salts
thereof or mixtures thereof. Ethylenediamine N,N'-
disuccinic acids, especially the (S,S) isomer have been
extensively described in U.S. Pat. No. 4,704,233, Nov. 3,
20 1987, to Hartman and Perkins.

Suitable amino carboxylates to be used herein include
ethylene diamine tetra acetates, diethylene triamine
pentaacetates, diethylene triamine pentaacetate (DTPA), N-
25 hydroxyethylethylenediamine triacetates, nitrilotri-
acetates, ethylenediamine tetrapropionates,
triethylenetetraaminehexa-acetates, ethanol-diglycines,
propylene diamine tetracetic acid (PDTA) and methyl glycine
di-acetic acid (MGDA), both in their acid form, or in their
30 alkali metal, ammonium, and substituted ammonium salt forms.
Particularly suitable amino carboxylates to be used herein

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are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS® and methyl glycine di- acetic acid (MGDA).

5

Further carboxylate chelating agents to be used herein include salicylic acid, aspartic acid, glutamic acid, glycine, malonic acid or mixtures thereof.

10 In addition, many common laundry builders can also provide a similar function as these chelating agents, suitable builders are detailed in the optional ingredients section.

pH Buffer

15

When the resulting wash liquor is required to be maintained at a stable pH, then the composition incorporates a material that acts as a pH buffer. Some builder materials, when incorporated in accordance with the present invention as a
20 complexing agent can also provide a pH buffering function to the composition. However, it is preferred that a separate pH buffer is incorporated in the composition, such that it is an additional component other than any dual purpose pH buffering complexing agent/builder. Preferably the pH
25 buffer is non-precipitating.

The pH buffer may also be non-responsive (i.e. a non-divalent cation complexing buffer) to the metal cations to which the colour change system is responsive. For example,
30 the pH buffer should have little or no affinity for Ca^{++} or Mg^{++} . However, the pH buffer may, in certain embodiments of

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the invention also be the complexing agent. For example, many common laundry builders, such as sodium tripolyphosphate (STP), can act as the complexing agent and also provide a pH buffering function.

5

Useful pH buffers will be well known to skilled laundry detergent formulators. In addition to the buffering properties conferred by many of the common laundry builders mentioned above, additional buffering may be achieved by the use of a separate buffering system that is typically based on materials such as carbonate, bicarbonates, protonic acids and/or co-ordinatively unsaturated metals or non metals.

The pH buffer, if added as a separated additional component is preferably present in the pH buffered laundry detergent composition at a level of from 1 to 95 wt.%, more preferably 2 to 85 wt.%.

The weight ratio of the pH buffer to total surfactant in the laundry detergent composition is preferably from 15:1 to 1:50, more preferably from 15:1 to 1:25.

If the pH buffer is a separate component from the complexing agent (i.e. if the complexing agent does not function as a pH buffer, or if additional pH buffer is required), then the weight ratio of the pH buffer to complexing agent in the laundry detergent composition is preferably from 15:1 to 1:15, more preferably from 12:1 to 1:12.

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Indicator Dye

The indicator dye is preferably present in the laundry detergent composition at a level of from 0.001 to 5 wt.%,
5 more preferably 0.01 to 2.5 wt.%, for example from 0.05 to 2 wt.%, alternatively from 0.1 to 1 wt.%. The absolute concentration of dye in solution should be sufficiently high to ensure that the colour change, when it occurs, is sufficiently intense to allow perception by the user.

10

Preferably in the laundry detergent composition the weight ratio of the indicator dye to total surfactant is from 1:1 to 1:500, more preferably from 1:1 to 1:350.

15 The indicator dye is chosen from those that exhibit a colour change in the aqueous medium/wash liquor, between its state when complexed to a divalent metal cation and its non-complexed state. Such a dye may be colourless when complexed to a metal cation, but be coloured when in its
20 free non-complexed state or vice versa. Alternatively, and preferably, the indicator dye exhibits one colour when it is bound to the divalent metal cation, and a second, different colour when it is in its free, non-complexed state.

25 Preferred indicator dyes are those which operate in the pH region of pH 7 to 12. Suitable indicator dyes can be found in "Indicators", by Edmund Bishop, published by Elsevier 1972. Although most indicator dyes will work to some extent over a range of pH values, they generally will have a
30 preferred pH range where the colour change will be particularly sharp. The skilled person can therefore choose

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a suitable dye according to the pH of the final laundry formulation. It is highly preferable that the indicator dye is non substantive to the fabric being laundered.

Optionally the indicator dye can be non-light fast, meaning
5 that the colour produced by the dye fades upon exposure to light, especially U.V. light.

An example of an embodiment of a colour change indicator system is the combination of TRIS buffer, EDTA (a complexing
10 agent) and Calmagite Indicator (an indicator dye).

Without wishing to be bound by theory, it is thought that this and similar embodiments function by being responsive to calcium and/or magnesium cations that are naturally present
15 in water. Although such divalent alkali earth metal ion levels can vary (different water hardness values); they are well known for each country/region, and so the formulation can be tailored to match the local calcium level in water (water hardness). On addition of a small amount of the
20 composition comprising the indicator dye, the aqueous medium turns pink as there is excess divalent metal ion present in the water, enough to bind to both the complexing agent and the indicator dye, which turns pink when complexed to the divalent metal ion. On addition of more of the composition
25 comprising the indicator dye, more complexing agent (and more dye) is added, but the level of divalent metal ions is not changed. The complexing agent preferentially binds the divalent metal ions over the dye, and when the free divalent metal ions in the aqueous medium are all bound, the
30 complexing agent then strips divalent metal ions away from the indicator dye. This produces a blue colour (the colour

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of non-complexed indicator dye) and is the visual cue for the consumer to stop addition of composition because there is enough composition present.

- 5 This system can therefore be used to provide an effective dose of deterative surfactant and other laundry actives.

Addition of more water during the rinse reverses the colour change to provide another visual cue. This can lead to
10 reduction of water used in the rinse.

Surfactants

The laundry detergent compositions of the invention
15 comprises surfactant. This can be a single surfactant or a mixture of two or more surfactants. In general any surfactant may be used, including anionic, non-ionic, cationic, amphoteric and zwitterionic surfactants. Preferably the surfactant is anionic, non-ionic or a mixture
20 of the two. The surfactant incorporated in the laundry detergent composition is deterative surfactant. By this, we mean that the surfactant, or at least one surfactant of any surfactant mixture, provides a deterative, i.e. cleaning effect to textile fabrics treated as part of a laundering
25 process. Other surfactants, which may or may not be deterative surfactants can be used as part of the composition.

When the laundry detergent composition is used in the field
30 of handwash, then the deterative surfactant is suitable of handwash purposes.

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In general, the non-ionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, 5 Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. It is preferred if the surfactant chosen is an anionic surfactant, a non- 10 ionic surfactant or a mixture of one or more anionic surfactants with one or more non-ionic surfactants.

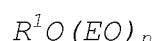
Preferred non-ionic surfactants are detailed below.

15 Non-ionic Surfactant

For the purposes of this disclosure, "non-ionic surfactant" shall be defined as amphiphilic molecules with a molecular weight of less than about 10,000, unless otherwise noted, 20 which are substantially free of any functional groups that exhibit a net charge at the normal wash pH of 6-11.

Any type of non-ionic surfactant may be used, although preferred materials are further discussed below. Highly 25 preferred are fatty acid alkoxyates, especially ethoxyates, having an alkyl chain of from C₈-C₃₅, preferably C₈-C₃₀, more preferably C₁₀-C₂₄, especially C₁₀-C₁₈ carbon atoms.

30 *Fatty Alcohol Ethoxyates*

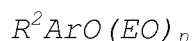


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Wherein R^1 represents an alkyl chain of between 4 and 30 carbon atoms, (EO) represents one unit of ethylene oxide monomer and n has an average value between 0.5 and 20. R^1 may be linear or branched. Such chemicals are generally produced by oligomerizing fatty alcohols with ethylene oxide in the presence of an effective amount catalyst, and are sold in the market as, for example, Neodols from Shell (Houston, Tex.) and Alfonics from Sasol (Austin, Tex.). The fatty alcohol starting materials, which are marketed under trademarks such as Alfol, Lial and Isofol from Sasol (Austin, Tex.) and Neodol, from Shell, may be manufactured by any of a number of processes known to those skilled in the art, and can be derived from natural or synthetic sources or a combination thereof. Commercial alcohol ethoxylates are typically mixtures, comprising varying chain lengths of R^1 and levels of ethoxylation. Often, especially at low levels of ethoxylation, a substantial amount of unethoxylated fatty alcohol remains in the final product, as well.

Because of their excellent cleaning, environmental and stability profiles, fatty alcohol ethoxylates wherein R^1 represents an alkyl chain from 10-18 carbons and n is an average number between 5 and 12 are highly preferred.

Alkylphenol Ethoxylates



Where R^2 represents a linear or branched alkyl chain ranging from 4 to 30 carbons, Ar is a phenyl (C_6H_4) ring and $(EO)_n$ is an oligomer chain comprised of an average of n moles of

- 24 -

ethylene oxide. Preferably, R^2 is comprised of between 8 and 12 carbons, and n is between 4 and 12. Such materials are somewhat interchangeable with alcohol ethoxylates, and serve much the same function. A commercial example of an
5 alkylphenol ethoxylate suitable for use in this invention is Triton X-100, available from Dow Chemical (Midland, Mich.).

Ethylene Oxide / Propylene Oxide Block Polymers



wherein EO represents an ethylene oxide unit, PO represents
15 a propylene oxide unit, and x and y are numbers detailing the average number of moles ethylene oxide and propylene oxide in each mole of product. Such materials tend to have higher molecular weights than most non-ionic surfactants, and as such can range between 1,000 and 30,000 Daltons.
20 BASF (Mount Olive, N.J.) manufactures a suitable set of derivatives and markets them under the Pluronic trademarks.

Other non-ionic surfactants should also be considered within the scope of this invention. These include condensates of
25 alkanolamines with fatty acids, such as cocamide DEA, polyol-fatty acid esters, such as the Span series available from Uniqema (Wilmington, Del.), ethoxylated polyol-fatty acid esters, such as the Tween series available from Uniqema (Wilmington, Del.), Alkylpolyglucosides, such as the APG
30 line available from Cognis (Gulph Mills, Pa.) and n-alkylpyrrolidones, such as the Surfadone series of products

- 25 -

marketed by ISP (Wayne, N.J). Furthermore, non-ionic surfactants not specifically mentioned above, but within the definition, may also be used.

5 Preferred anionic surfactants are outlined below.

Anionic Surfactants

The anionic surfactants used in this invention can be any
10 water soluble anionic surfactant other than soap. "Water soluble" surfactants are, unless otherwise noted, here defined to include surfactants which are soluble or dispersible to at least the extent of 0.01% by weight in distilled water at 25°C. "Anionic surfactants" are defined
15 herein as amphiphilic molecules comprising one or more functional groups that exhibit a net anionic charge when in aqueous solution at the normal wash pH of between 6 and 11. Preferred anionic surfactants are the alkali metal salts of organic sulphur reaction products having in their molecular
20 structure an alkyl radical containing from about 6 to 24 carbon atoms and a radical selected from the group consisting of sulphonic and sulphuric acid ester radicals.

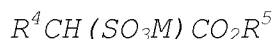
Although any anionic surfactant hereinafter described can be
25 used, highly preferred anionic surfactants are the alkali and alkaline earth metal salts of both fatty alcohol sulphates, preferably primary alkyl sulfates, more preferably they are ethoxylated, for example alkyl ether sulfates, and alkylbenzene sulfonates or mixtures thereof.

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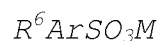
- 26 -

Alkyl Ether Sulphates

where R^3 is a primary alkyl group of 8 to 18 carbon atoms, n
5 has an average value in the range from 1 to 6 and M is a
solubilising cation. The alkyl group R^3 may have a mixture
of chain lengths. It is preferred that at least two-thirds
of the R^3 alkyl groups have a chain length of 8 to 14 carbon
atoms. This will be the case if R^3 is coconut alkyl, for
10 example. Preferably n has an average value of 2 to 5.
Ether sulphates have been found to provide viscosity build
in certain of the formulations of this invention, and thus
are considered a preferred ingredient.

15 *Fatty Acid Ester Sulphonates*

where R^4 is an alkyl group of 6 to 16 atoms, R^5 is an alkyl
group of 1 to 4 carbon atoms and M is a solubilising cation.
20 The group R^4 may have a mixture of chain lengths. Preferably
at least two-thirds of these groups have 6 to 12 carbon
atoms. This will be the case when the moiety $R^4CH(-)CO_2(-)$
is derived from a coconut source, for instance. It is
preferred that R^5 is a straight chain alkyl, notably methyl
25 or ethyl.

Alkyl Benzene Sulphonates

30 where R^6 is an alkyl group of 8 to 18 carbon atoms, Ar is a
benzene ring (C_6H_4) and M is a solubilising cation. The

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group R^6 may be a mixture of chain lengths. A mixture of isomers is typically used, and a number of different grades, such as "high 2-phenyl" and "low 2-phenyl" are commercially available for use depending on formulation needs. A

5 plentitude of commercial suppliers exist for these materials, including Stepan (Northfield, Ill.) and Witco (Greenwich, Conn.) Typically they are produced by the sulphonation of alkylbenzenes, which can be produced by either the HF-catalyzed alkylation of benzene with olefins
10 or an $AlCl_3$ -catalyzed process that alkylates benzene with chlor-paraffins, and are sold by, for example, Petresa (Chicago, Ill.) and Sasol (Austin, Tex.). Straight chains of 11 to 14 carbon atoms are usually preferred.

15 *Paraffin sulphonates* having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, in the alkyl moiety. They are usually produced by the sulfoxidation of petrochemically-derived normal paraffins. These surfactants are commercially available as, for example, Hostapur SAS from
20 Clariant (Charlotte, N.C.).

Olefin sulphonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms. U.S. Patent No. 3,332,880 contains a description of suitable olefin sulphonates, and is
25 incorporated herein by reference. Such materials are sold as, for example, Bio-Terge AS-40, which can be purchased from Stepan (Northfield, Ill.)

Sulphosuccinate esters

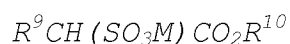
30 $R^7OOCCH_2CH(SO_3^-M^+)COOR^8$

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are also useful in the context of this invention. R^7 and R^8 are alkyl groups with chain lengths of between 2 and 16 carbons, and may be linear or branched, saturated or unsaturated. A preferred sulphosuccinate is sodium bis (2-ethylhexyl) sulphosuccinate, which is commercially available under the tradename Aerosol OT from Cytec Industries (West Paterson, N.J.).

Organic phosphate based anionic surfactants include organic phosphate esters such as complex mono- or diester phosphates of hydroxyl- terminated alkoxide condensates, or salts thereof. Included in the organic phosphate esters are phosphate ester derivatives of polyoxyalkylated alkylaryl phosphate esters, of ethoxylated linear alcohols and ethoxylates of phenol. Also included are non-ionic alkoxyates having a sodium alkylenecarboxylate moiety linked to a terminal hydroxyl group of the non-ionic through an ether bond. Counterions to the salts of all the foregoing may be those of alkali metal, alkaline earth metal, ammonium, alkanolammonium and alkylammonium types.

Other preferred anionic surfactants include the fatty acid ester sulphonates with formula:



where the moiety $R^9CH(-)CO_2(-)$ is derived from a coconut source and R^{10} is either methyl or ethyl; primary alkyl sulphates with the formula:



- 29 -

wherein R^{11} is a primary alkyl group of 10 to 18 carbon atoms and M is a sodium cation; and paraffin sulphonates, preferably with 12 to 16 carbon atoms to the alkyl moiety.

5 Other anionic surfactants preferred for use with this formulation include isothionates, sulphated triglycerides, alcohol sulphates, ligninsulphonates, naphthelene sulphonates and alkyl naphthelene sulphonates and the like. Additional anionic surfactants, falling into the general
10 definition but not specifically mentioned above, should also be considered within the scope of this invention.

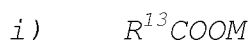
Primary Alkyl Sulphates



15

where R^{12} is a primary alkyl group of 8 to 18 carbon atoms and M is a solubilising cation. The alkyl group R^{12} may have a mixture of chain lengths. It is preferred that at least two-thirds of the R^{12} alkyl groups have a chain length of 8
20 to 14 carbon atoms. This will be the case if R^{12} is coconut alkyl, for example. The solubilising cation may be a range of cations which are in general monovalent and confer water solubility. An alkali metal, notably sodium, is especially envisaged. Other possibilities are ammonium and substituted
25 ammonium ions, such as trialkanolammonium or trialkylammonium.

Carboxylic Acid Salts



30

where R^{13} is a primary or secondary alkyl group of 3 to 29 carbon atoms and M is a solubilising cation. The alkyl

- 30 -

group represented by R^{13} may represent a mixture of chain lengths and may be saturated or unsaturated, although it is preferred that at least two thirds of the R^{13} groups have a chain length of between 7 and 17 carbon atoms. Non-limiting
5 examples of suitable alkyl group sources include the fatty acids derived from coconut oil, tallow, tall oil and palm kernel oil. For the purposes of minimising odour, however, it is often desirable to use primarily saturated carboxylic acids. Such materials are well known to those skilled in
10 the art, and are available from many commercial sources, such as Uniqema (Wilmington, Del.) and Twin Rivers Technologies (Quincy, Mass.). The solubilising cation, M, may be any cation that confers water solubility to the product, although monovalent such moieties are generally
15 preferred. Examples of acceptable solubilising cations for use with this invention include alkali metals such as sodium and potassium, which are particularly preferred, and amines such as triethanolammonium, ammonium and morpholinium. Although, when used, the majority of the fatty acid should
20 be incorporated into the formulation in neutralised salt form, it is often preferable to leave a small amount of free fatty acid in the formulation, as this can aid in the maintenance of product viscosity.

25 Product Form

A product according to the invention may take any suitable form, such as a solid, liquid or paste composition. Preferably it is in a solid form, particularly in a powder
30 or granular form.

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Optional Ingredients

In addition to the essential components detailed in the claims, the formulation may include one or more optional ingredients. While it is not necessary for these elements to be present in order to practice this invention, the use of such materials is often very helpful in rendering the formulation acceptable for consumer use.

Examples of optional components include, but are not limited to: additional nonionic and anionic surfactants, amphoteric and zwitterionic surfactants, cationic surfactants, hydrotropes, fluorescent whitening agents, photobleaches, fibre lubricants, reducing agents, enzymes, enzyme stabilising agents, powder finishing agents, defoamers, builders, bleaches, bleach catalysts, soil release agents, antiredeposition agents, dye transfer inhibitors, buffers, colorants, fragrances, pro-fragrances, rheology modifiers, anti-ashing polymers, preservatives, insect repellents, soil repellents, water-resistance agents, suspending agents, aesthetic agents, structuring agents, sanitisers, solvents, fabric finishing agents, dye fixatives, wrinkle-reducing agents, fabric conditioning agents and deodorizers.

Builders

In addition to the complexing agent used according to one embodiment of the invention, optionally one or more detergency builders may be added. Builders are often added to fabric cleaning compositions to complex and remove alkaline earth metal ions, which can interfere with the

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cleaning performance of a detergent by combining with anionic surfactants and removing them from the wash liquor.

Soluble builders, such as alkali metal carbonates and alkali metal citrates, are particularly preferred, especially for the liquid embodiment of this invention. Other builders, as further detailed below, may also be used, however. Often a mixture of builders, chosen from those described below and others known to those skilled in the art, will be used.

Alkali and Alkaline Earth Metal Carbonates

Alkali and alkaline earth metal carbonates, such as those detailed in German patent application 2,321,001, published Nov. 15, 1973, are suitable for use as builders in the compositions of this invention. They may be supplied and used either in anhydrous form, or including bound water. Particularly useful is sodium carbonate, or soda ash, which both is readily available on the commercial market and has an excellent environmental profile.

The sodium carbonate used in this invention may either be natural or synthetic, and, depending on the needs of the formula, may be used in either dense or light form. Natural soda ash is generally mined as trona and further refined to a degree specified by the needs of the product it is used in. Synthetic ash, on the other hand, is usually produced via the Solvay process or as a coproduct of other manufacturing operations, such as the synthesis of caprolactam. It is sometimes further useful to include a small amount of calcium carbonate in the builder

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formulation, to seed crystal formation and increase building efficacy.

Organic Builders

5

Organic detergent builders can also be used as builders in the present invention. Examples of organic builders include alkali metal citrates, succinates, malonates, sulphamic acid and/or water soluble salts thereof, fatty acid sulphonates, 10 fatty acid carboxylates, nitrilotriacetates, oxydisuccinates, alkyl and alkenyl disuccinates, oxydiacetates, carboxymethyloxy succinates, ethylenediamine tetraacetates, tartrate monosuccinates, tartrate disuccinates, tartrate monoacetates, tartrate diacetates, 15 oxidized starches, oxidized heteropolymeric polysaccharides, polyhydroxysulphonates, polycarboxylates such as polyacrylates, polymaleates, polyacetates, polyhydroxyacrylates, polyacrylate/polymaleate and polyacrylate/polymethacrylate copolymers, 20 acrylate/maleate/vinyl alcohol terpolymers, aminopolycarboxylates and polyacetal carboxylates, and polyaspartates and mixtures thereof. Such carboxylates are described in U.S. Patent Nos. 4,144,226, 4,146,495 and 4,686,062. Alkali metal citrates, nitrilotriacetates, 25 oxydisuccinates, acrylate/maleate copolymers and acrylate/maleate/vinyl alcohol terpolymers are especially preferred nonphosphate builders.

Sulphamic acid and/or water soluble salts thereof

30

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Compositions of the present invention may comprise sulphamic acid and/or water soluble salts thereof as whole or part of a soluble builder system. The water soluble salt be a metal salt of sulphamate, such as an alkali or alkaline earth

5 metal salt or sulphamate, or in some cases a transition metal counterion, such as lead or zinc sulphamate.

Alternatively a non-metal counterion may be used, for example ammonium. When a water soluble salt of sulphamic acid is used, it is preferably an alkali or alkaline earth

10 metal sulphamate, in particularly sodium sulphamate. The sulphamic acid typically has the formula $\text{H}_2\text{NSO}_3\text{H}$. When present in a laundry detergent formulation, the sulphamic acid may be wholly or part in a zwitterionic form, of formula $\text{H}_3\text{N}^+\text{SO}_3^-$.

Phosphates

The compositions of the present invention which utilise a water-soluble phosphate builder typically contain this

20 builder at a level of from 1 to 90% by weight of the composition. Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the

25 degree of polymerisation ranges from about 6 to 21, and salts of phytic acid. Sodium or potassium tripolyphosphate is most preferred.

Phosphates are, however, often difficult to formulate, especially into liquid products, and have been identified as

30 potential agents that may contribute to the eutrophication

- 35 -

of lakes and other waterways. As such, the preferred compositions of this invention comprise phosphates at a level of less than about 10% by weight, more preferably less than about 5% by weight. The most preferred compositions of this invention are formulated to be substantially free of phosphate builders.

Zeolites

10 Zeolites may also be used as builders in the present invention. A number of zeolites suitable for incorporation into the products of this disclosure are available to the formulator, including the common zeolite 4A. In addition, zeolites of the MAP variety, such as those taught in
15 European Patent Application EP-B-384,070, which are sold commercially by, for example, Ineos Silicas (UK), as Doucil A24, are also acceptable for incorporation. MAP is defined as an alkali metal aluminosilicate of zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably
20 within the range of from 0.90 to 1.33, more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about
25 1.00. The particle size of the zeolite is not critical. Zeolite A or zeolite MAP of any suitable particle size may be used. In any event, as zeolites are insoluble matter, it is advantageous to minimise their level in the compositions of this invention. As such, the preferred formulations
30 contain less than about 10% of zeolite builder, while especially preferred compositions compress less than about

- 36 -

5% zeolite. Especially preferred is for zeolite to be absent.

Enzyme Stabilisers

5

When enzymes, and especially proteases are used in liquid detergent formulations, it is often necessary to include a suitable quantity of enzyme stabiliser to temporarily deactivate it until it is used in the wash. Examples of
10 suitable enzyme stabilisers are well-known to those skilled in the art, and include, for example, borates and polyols such as propylene glycol. Borates are especially suitable for use as enzyme stabilisers because in addition to this benefit, they can further buffer the pH of the detergent
15 product over a wide range, thus providing excellent flexibility.

If a borate-based enzyme stabilisation system is chosen, along with one or more cationic polymers that are at least
20 partially comprised of carbohydrate moieties, stability problems can result if suitable co-stabilisers are not used. It is believed that this is the result of borates' natural affinity for hydroxyl groups, which can create an insoluble borate-polymer complex that precipitates from solution
25 either over time or at cold temperatures. Incorporating into the formulation a co-stabiliser, which is normally a diol or polyol, sugar or other molecule with a large number of hydroxyl groups, can ordinarily prevent this. Especially preferred for use as a co-stabiliser is sorbitol, used at a
30 level that is at least about 0.8 times the level of borate in the system, more preferably 1.0 times the level of borate

- 37 -

in the system and most preferably more than 1.43 times the level of borate in the system, is sorbitol, which is effective, inexpensive, biodegradable and readily available on the market. Similar materials including sugars such as
5 glucose and sucrose, and other polyols such as propylene glycol, glycerol, mannitol, maltitol and xylitol, should also be considered within the scope of this invention.

The invention will now be illustrated by the following non-
10 limiting examples.

Examples**Example 1**

5 The following proof of concept composition was prepared according to table 1. The example was formulated to provide an effective detergent dose of 2.25g/L. Using the colour change indicator system, one skilled in the art can easily vary the detergent dosing level depending on what is
10 required locally.

SDS, EDTA and Calmagite were sourced from Sigma Aldrich, and TRIS was sourced from BDH.

Ingredient	Wt. %
SDS Sodium dodecyl sulphate (70%)	5.6
EDTA Ethylenediaminetetraaceticacid (disodium salt)	9.4
TRIS Tris (Hydroxymethyl)methylamine	84.8
Calmagite	0.2

15

Table 1 An example of colour change indicator system for the provision of a dosing of 2.25 g/L of composition to an aqueous medium.

20

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To show that this composition can effectively provide a visual cue to a consumer once an effective product dosing is attained; solutions of the formulation were prepared at concentration of 0.5, 1, 1.5, 2, 2.25, 2.5, 3, 3.5 & 4 g/L in demin. water that had been adjusted to 10⁰FH (French Hardness) (0.147 g calcium chloride dehydrate ex. BDH in 100 ml of demin. water).

The absorbance of the each solution was measured in a 1 cm cell over the range 400 to 700 nm (roughly the wavelength perceivable to the human eye).

The wavelength at which the maximum absorbance took place as well as the colour of the solution is shown in table 2.

Product Dose g/L	Absorbance Max (nm)	Colour
0.5	537	Pink
1	535	Pink
1.5	535	Pink
2	535	Pink
2.25	545	Blue
2.5	548	Blue
3	554	Blue
3.5	563	Blue
4	571	Blue

Table 2 Showing the absorbance maxima and resulting colour of the solutions

From the above data, it is clear that such a system can express the desired colour change visual cue so that the consumer knows when an effective product dosing of detergent is present.

- 40 -

Example 2

The following formulation was prepared:-

Ingredient	% by weight
LAS	19.98
STP	79.92
Calmagite	0.1

5

Table 3 Formulation details of example 2

LAS stands for linear alkylbenzene sulphonate, STP stands for sodium tripolyphosphate. Calmagite was the same as for
10 example 1.

Solutions of this formulation were made at various different concentration levels in the same way as example 1. These were 1, 1.2, 1.4, 1.6, and 1.8 g/L. The absorbance of the
15 each solution was measured in a 1 cm cell over the range 400 to 700 nm (roughly the wavelength perceivable to the human eye). This was carried out in a similar fashion to example 1.

20 The wavelength at which the maximum absorbance took place as well as the colour of the solution is shown in table 4.

- 41 -

Product Dose g/L	Absorbance Max (nm)	Colour
1	536	Pink
1.2	536	Pink
1.4	556	Blue
1.6	559	Blue
1.8	561	Blue

Table 4 Showing the absorbance maxima and resulting colour of the solutions

- 5 This example depicts a different system to example 1. In this system, the complexing agent is also acting as the pH buffer. It shows that the system is adaptable to be able to deliver an easily perceivable colour change, and that varying concentrations of detergent can be delivered.

CLAIMS

1. A laundry detergent composition comprising:-

5 a) deterative surfactant;

b) a colour change indicator system comprising:-

i) an indicator dye capable of binding to divalent metal cations;

10 ii) one or more other complexing agents for divalent metal cations, said complexing agent having a greater binding capacity than the indicator dye for said divalent metal cations at the pH of use; and,

c) optionally carriers and adjuncts to 100 wt.%.

15

2. A laundry detergent composition according to claim 1, wherein the colour change indicator system comprises a pH buffer such that the resulting wash liquor is maintained at a stable pH.

20

3. A laundry detergent composition according to claim 2, wherein the pH buffer is non-precipitating.

25 4. A laundry detergent composition according to any one of claims 1 to 3, wherein the divalent metal cations comprise Ca^{++} and/or Mg^{++} .

30 5. A laundry detergent composition according to ant preceeding claim wherein the deterative surfactant is present at a level of at least 19.5wt%.

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6. A laundry detergent composition according to any one of claims 1 to 5, additionally comprising builder.

5 7. A laundry detergent composition according to any one of claims 1 to 6 in a particulate form.

8. A laundry detergent composition according to any one of claims 1 to 7, wherein the composition is a handwash composition.

10

9. Use of a composition according to any one of the preceding claims as a sufficiency of dosage indicator for laundry main wash.

15 10. Use according to claim 9 as a sufficiency of dosage indicator for laundry handwash.

11. A handwash process for laundry cleaning comprising the steps of:

20

a) admixing a laundry handwash detergent composition according to any one of claims 1 to 8 with an aqueous medium comprising water and Mg^{++} and/or Ca^{++} hardness ions,

25

b) optionally adding subsequent portions of said laundry handwash detergent composition wherein addition of the laundry handwash detergent composition is continued until a visual cue is provided by a colour change of the wash liquor, then

30

c) washing laundry in the wash liquor and then

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d) rinsing the laundry by adding further aqueous medium comprising water and Mg^{++} and/or Ca^{++} hardness ions, thereby reversing the colour change.

- 5 12. A process according to claim 11 wherein the wash liquor is buffered to a constant alkaline pH during steps a), b) and c).

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/063343

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/16 C11D3/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/041739 A (PROCTER & GAMBLE [US]; SGARGETTA GIORGIA [IT]; HECHT STACIE ELLEN [US]) 20 April 2006 (2006-04-20) claims tables 4-6 page 17, paragraph 4 - page 18, paragraph 3 page 16, paragraph 4 - page 17, paragraph 2 page 3, paragraph 3 - page 7, paragraph 3	1-8
A	CH 313 346 A (BAERLE & CIE AG [CH]) 15 April 1956 (1956-04-15) the whole document ----- -/--	1-12

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* & * document member of the same patent family

Date of the actual completion of the international search

7 March 2008

Date of mailing of the international search report

14/03/2008

Name and mailing address of the ISA/

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Neys, Patricia

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/063343

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2005/005329 A (RECKITT BENCKISER NV [NL]; CORRADINI FABIO [IT]; KOSUB MIKE [DE]; RECK) 20 January 2005 (2005-01-20) cited in the application claims page 2, line 17 - line 23 page 6, line 1 - line 2 page 12, line 27 - page 13, line 7 -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/063343

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 2006041739	A	20-04-2006	CN	101035887 A	12-09-2007
			EP	1828364 A1	05-09-2007

CH 313346	A	15-04-1956	NONE		

WO 2005005329	A	20-01-2005	AU	2004255919 A1	20-01-2005
			CA	2531405 A1	20-01-2005
			EP	1641714 A2	05-04-2006
			GB	2403719 A	12-01-2005
			US	2007072784 A1	29-03-2007
