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(54) DETERGENT COMPOSITIONS

WASCHMITTELZUSAMMENSETZUNGEN

COMPOSITIONS DETERGENTES

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- **DATABASE WPI Week 199440 Derwent Publications Ltd., London, GB; AN 1994-322449 XP002152298 & JP 06 248300 A (LION CORP), 6 September 1994 (1994-09-06)**
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Description

TECHNICAL FIELD

[0001] The present invention relates to particulate detergent compositions containing the sequestrant, iminodisuccinate or hydroxyiminodisuccinate. The invention is especially of interest for detergent powders of high bulk density (so-called "compact" powders) and to tablets of compacted detergent powder. The invention is especially applicable to laundry detergent powders but is also relevant to powders or tablets for mechanical dishwashing.

BACKGROUND AND PRIOR ART

[0002] Iminodisuccinate (IDS) and hydroxyiminodisuccinate (HIDS) are known as detergency builders and, in bleaching detergent compositions, as stabilisers for peroxy bleach precursors.

[0003] US 3 697 453 (Pfizer) discloses detergent compositions having a pH of from 9 to 12, containing iminodisuccinate as a detergency builder, used together with detergent surfactant in a weight ratio of 0.25:1 to 10:1. IDS as a detergency builder is also disclosed in EP 757 094A (Bayer). HIDS is disclosed in US 5 318 726 (Henkel).

[0004] EP 509 382A (W R Grace & Co/Hampshire Chemical Corporation) discloses a bleaching detergent composition comprising a bleaching agent and a bleach stabiliser of defined formula which includes IDS. The use of IDS as a bleach stabiliser is also disclosed in WO 97 20907A (Procter & Gamble).

[0005] WO 00/34427A (Unilever) discloses and claims non-bleaching laundry detergent compositions containing from 0.05 to 2.5 wt% of IDS or HIDS. The compositions provides improved maintenance and/or restoration of colour fidelity during the wash, especially at low wash pH. The IDS or HIDS is also an effective chlorine scavenger, reducing the in-wash fading of chlorine-sensitive dyes. In addition, the incorporation of the IDS or HIDS improves the stain removal performance of the composition.

[0006] EP 678 572A (Procter & Gamble) discloses a detergent powder composition comprising from 10 to 90 wt% of a complex comprising a sequestrant and a metal ion. The preferred sequestrant is ethylenediamine disuccinate (EDDS) and the preferred metal ion is magnesium.

[0007] IDS is commercially available in sodium salt form, eg as IDS Na-salt from Bayer. The sodium salt is highly water-soluble and the material is supplied as an aqueous solution (approximate IDS Na-salt content 34%) and as a solid white powder prepared from the solution by spray-drying.
If IDS is to be incorporated into an aqueous liquid detergent or into a spray-dried detergent powder via the slurry, the solution form is most conveniently used. However, it is not suitable for the preparation of a powder of high bulk density by a non-tower (non-spray-drying) route because the water content is too high. For such products it is necessary to use IDS in powder form.

[0008] However, the powder is extremely hygroscopic and, according to the manufacturer Bayer's recommendation, must be stored in tightly closed containers. If stored in contact with the atmosphere it rapidly takes up water and deliquesces, ie becomes a liquid. The problem is exacerbated in humid atmospheres so that any storage or handling of the material causes major problems with stickiness. When this sticky raw material is incorporated into a detergent powder, poor powder properties result.

[0009] It has now been found that this problem can be substantially alleviated by converting the IDS partially into calcium form, ie forming complexes with calcium ions. The resulting Ca/Na complexes are stable solids which are significantly less hygroscopic than the sodium salt. They can readily be incorporated into particulate detergent compositions and, surprisingly, the resulting compositions show no loss of sequestrant activity as compared with similar compositions containing the sodium salt.

[0010] GB 2 048 930A (Unilever) discloses bleaching detergent compositions containing an organic phosphonate sequestrant - ethylenediamine tetramethylene phosphonate (EDTMP) or diethylenetriamine pentamethylene phosphonate (DETPMP) - present as a complex of a magnesium, calcium, zinc or aluminium ion, the molar ratio of the metal ion to the phosphonate compound being at least 1:1. The benefit is improved stability of the phosphonate compound in the detergent composition on storage.

[0011] JP 09 110 813A and JP 09 104 897A (Nippon shokubai) disclose a builder powder of reduced hygroscopicity based on IDS, in which sodium IDS is compounded with an inorganic metal salt, preferably zeolite, sodium carbonate or sodium silicate.

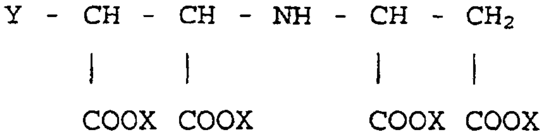
[0012] JP 09 100 497A (Lion) discloses high bulk density detergent powders containing IDS, prepared by granulating together detergent ingredients including an inorganic builder salt, eg zeolite, and sodium IDS or HIDS (3-20 wt% of the final composition). The hygroscopicity of the IDS is exploited to bind fine zeolite particles and thereby improve flow and reduce stickiness.

[0013] B Karoleski and R Hampe of Bayer Corporation, in a paper entitled "Alternatives to Traditional Chelants and Dispersants", HAPPI (Household and Personal Products Industry), Volume 36, No. 11 (November 1999), pages 114 -

118, discuss the sequestrant properties of IDS. The stability constants of complexes with various divalent and polyvalent metal ions, including calcium and magnesium, are disclosed.

DEFINITION OF THE INVENTION

[0014] The present invention provides a particulate detergent composition containing a sequestrant which is a compound of the formula I



$$Y-\underset{\mathrm{COOX}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{COOX}}{\underset{|}{\mathrm{CH}}}-\mathrm{NH}-\underset{\mathrm{COOX}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{COOX}}{\underset{|}{\mathrm{CH_2}}}\qquad\text{(I)}$$

wherein Y is H or OH, and X is a countercation, characterised in that the compound of the formula I is in the form of a calcium ion complex, the molar ratio of calcium ion to the compound of the formula I being from 2:1 to 3:1.

[0015] The invention further provides a process for the preparation of a particulate detergent composition, which includes the step of mixing and/or granulating a compound of the formula I in powder form with other detergent ingredients, wherein the compound of the formula I is in the form of a calcium ion complex, the molar ratio of calcium ion to the compound of the formula I being from 2:1 to 3.1.

DETAILED DESCRIPTION OF THE INVENTION

The IDS or HIDS salt or complex

[0016] The detergent composition of the invention contains a compound of the formula I above as an essential ingredient. When Y is H, the compound is IDS; when Y is OH, the compound is HIDS. For convenience only IDS will be discussed in the description below, but this should be understood to refer equally to HIDS.

[0017] IDS is a pentadentate ligand ie it can form complexes with metal ions in which bonds are formed with the nitrogen atom and all four carboxyl groups. Indeed its efficacy as a detergency builder is based on its capacity to form such complexes with calcium and magnesium ions, and its efficacy as a bleach stabiliser and for colour care is based on its capacity for forming such complexes with heavy metal ions such as iron and copper.

[0018] The reaction between an iminodisuccinate acid anion IDS^{m-} and a metal cation Me^{n+} is a reversible one, represented in the usual case of a 1:1 complex by the equation

$$IDS^{m-} + Me^{n+} \Leftrightarrow IDS\ Me^{(m-n)-}$$

[0019] Similar relationships hold for 2:1, 3:1 and higher complexes (the ratio being of the metal ion to the IDS anion).

[0020] The present inventors have surprisingly found that IDS in the form of a complex with calcium is substantially less hygroscopic than the sodium salt. The complexes have a Ca:IDS molar ratio of 2:1 to 3:1. The 3:1 complex is especially preferred.

[0021] The calcium complexes may be prepared by reacting the sodium salt, in aqueous solution, with the appropriate amount of a soluble calcium salt, preferably calcium chloride. The reaction also produces a soluble inorganic sodium salt (eg sodium chloride).

[0022] According to a preferred embodiment of the invention, the soluble inorganic sodium salt produced as a by-product of the preparation process is removed by using a filtration step. Where this is possible, a further significant reduction of hygroscopicity has been observed. However, it is only possible if there is sufficient difference in solubility between the complex and the inorganic salt by-product, which is highly soluble. The higher the mole ratio of the complex, the lower its solubility, and the 1:1 complex is too soluble to allow separation of the sodium chloride by-product. With the 2:1 complex partial separation is possible and this gives some improvement.

[0023] However, the CaIDS and CaHIDS 3:1 complexes are especially preferred in this respect because their solubility is sufficiently reduced, compared with that of the sodium salt, to allow sodium chloride to be separated by filtration during their preparation, yet is sufficiently high for these materials to be delivered effectively into the wash liquor.

[0024] Thus, an especially preferred embodiment of the invention involves the use of a CaIDS or CaHIDS 3:1 complex which has been prepared by a method which includes removal of any inorganic salt by-product.

Detergent compositions

[0025] The detergent compositions of the invention contain IDS (or HIDS) as an essential ingredient. This may be present at levels sufficient for detergency building, either alone or in conjunction with another detergency builder, or at the much lower levels appropriate for bleach stabilisation, or for colour care benefits and stain removal in non-bleaching formulations as disclosed in WO 00/34427A (Unilever).

[0026] The amount of IDS or HIDS present in the composition may therefore range very widely, for example, from 0.05 to 80 wt%. Suitable ranges are, for example, 5 to 80 wt% if IDS is the sole or principal builder; 1 to 20 wt% if it is present as cobuilder to, for example, zeolite, phosphate or carbonate; 0.5 to 10 wt% for bleach stabilisation; 0.05 to 2.5 wt% for colour care benefits in non-bleaching formulations.

[0027] The compositions of the invention may contain other conventional detergent ingredients as detailed below. Typically a composition in which IDS is present as a cobuilder or a bleach stabiliser may comprise the following:

(a) from 5 to 60 wt% of one or more detergent surfactants,

(b) from 10 to 80 wt% of one or more detergency builders (other than IDS),

(c) from 0.5 to 20 wt% of a compound of the formula I,

(d) optionally other detergent ingredients to 100 wt%.

[0028] A non-bleaching formulation in which a low level of IDS has been included for colour care benefits may suitably comprise:

(a) from 5 to 60 wt% of one or more detergent surfactants,

(b) from 10 to 80 wt% of one or more detergency builders (other than IDS),

(c) from 0.05 to 2.5 wt% of a compound of the formula I,

(d) optionally other non-bleaching detergent ingredients to 100 wt%.

[0029] The detergent composition of the invention is in particulate form. The invention is especially applicable to powders of high bulk density, and to tablets prepared by compacting powder. In these products the use of a hygroscopic material would be especially problematic.

[0030] If in powder form, the composition of the invention preferably has a bulk density of at least 500 g/l, and preferably from 600 to 1000 g/l, more preferably from 800 to 1000 g/l.

[0031] However, the invention is also applicable to powders of lower bulk density. In such a product, for example, the IDS complex may be in admixture mixed with a spray-dried detergent base powder and optionally other conventional detergent ingredients.

[0032] The compositions of the invention may also be in tablet form.

[0033] While the invention is primarily applicable to laundry detergent compositions, it is also relevant to mechanical dishwashing detergents, both powders and tablets, containing IDS.

Preparation of the detergent composition

[0034] As indicated previously, the invention is especially applicable to particulate detergent compositions of high bulk density. Such compositions may be prepared by non-tower (non-spray-drying) processes in which particulate raw materials are mixed and/or granulated. According to the invention, to prepare compositions of this type the IDS complex is mixed and/or granulated with other detergent ingredients. The mixing and/or granulation may suitably be carried out in a high-speed mixer/granulator, for example a Fukae (Trade Mark) FSG mixer or a Loedige Recycler (Trade Mark). The invention is also applicable to detergent powders of lower bulk density. For example, a detergent base powder may be prepared by conventional slurry-making and spray-drying processes, and other ingredients in powder form, including the IDS complex in accordance with the present invention, may be admixed (postdosed) to the base powder.

[0035] The availability of IDS in a non-hygroscopic powder form adds further flexibility in the manufacture of detergent powders, and is especially valuable where different products of different bulk densities are manufactured on the same site.

[0036] Tablets may be prepared by compacting powders containing the IDS complex.

Detergent components

[0037] The compositions of the invention also contain other conventional detergent ingredients. Essential ingredients are surfactants (detergent-active compounds), and (unless IDS is the sole builder) detergency builders.

[0038] The detergent compositions will contain, as essential ingredients, one or more detergent active compounds (surfactants) which may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent active compounds, and mixtures thereof. Many suitable detergent active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

[0039] The preferred detergent active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

[0040] Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkylsulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

[0041] Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

[0042] Cationic surfactants that may be used include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$ wherein the R groups are long or short hydrocarbyl chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising cation (for example, compounds in which R_1 is a C_8-C_{22} alkyl group, preferably a C_8-C_{10} or C_{12}-C_{14} alkyl group, R_2 is a methyl group, and R_3 and R_4, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters).

[0043] In an especially preferred cationic surfactant of the general formula $R_1R_2R_3R_4N^+ X^-$, R_1 represents a C_8-C_{10} or C_{12}-C_{14} alkyl group, R_2 and R_3 represent methyl groups, and R_4 presents a hydroxyethyl group.

[0044] Amphoteric surfactants, amine oxides, and zwitterionic surfactants, for example, betaines, may also be present.

[0045] Preferably, the quantity of anionic surfactant is in the range of from 5 to 50% by weight of the total composition. More preferably, the quantity of anionic surfactant is in the range of from 8 to 35% by weight.

[0046] Nonionic surfactant, if present, is preferably used in an amount within the range of from 1 to 20% by weight.

[0047] The total amount of surfactant present is preferably within the range of from 5 to 60 wt%.

[0048] The compositions may suitably contain from 10 to 80%, preferably from 15 to 70% by weight, of detergency builder. Preferably, the quantity of builder is in the range of from 15 to 50% by weight.

[0049] The detergent compositions may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate (zeolite).

[0050] The zeolite used as a builder may be the commercially available zeolite A (zeolite 4A) now widely used in laundry detergent powders. Alternatively, the zeolite may be maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070B (Unilever), and commercially available as Doucil (Trade Mark) A24 from Crosfield Chemicals Ltd, UK. Zeolite MAP is defined as an alkali metal aluminosilicate of zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, preferably within the range of from 0.90 to 1.20.

[0051] Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The particle size of the zeolite is not critical. Zeolite A or zeolite MAP of any suitable particle size may be used.

[0052] Also preferred according to the present invention are phosphate builders, especially sodium tripolyphosphate. This may be used in combination with sodium orthophosphate, and/or sodium pyrophosphate.

[0053] Other inorganic builders that may be present additionally or alternatively include sodium carbonate, layered silicate, amorphous aluminosilicates.

[0054] Organic builders that may be present, as well as IDS itself, include polycarboxylate polymers such as polyacrylates and acrylic/maleic copolymers; polyaspartates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-di- and trisuccinates, carboxymethyloxysuccinates, carboxy-methyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts.

[0055] IDS and other organic builders may be used in minor amounts as supplements to inorganic builders such as phosphates and zeolites. Especially preferred supplementary organic builders are citrates, suitably used in amounts of from 5 to 30 wt %, preferably from 10 to 25 wt %; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt %, preferably from 1 to 10 wt%.

[0056] Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

[0057] Detergent compositions according to the invention may also suitably contain a bleach system. This is preferably based on peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution. Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate. Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

[0058] The peroxy bleach compound is suitably present in an amount of from 5 to 35 wt%, preferably from 10 to 25 wt%.

[0059] The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt%, preferably from 2 to 5 wt%.

[0060] Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors; and peroxycarbonic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N,N,N',N'-tetracetyl ethylenediamine (TAED). The novel quaternary ammonium and phosphonium bleach precursors disclosed in US 4 751 015 and US 4 818 426 (Lever Brothers Company) and EP 402 971A (Unilever) are also of great interest. Especially preferred are peroxycarbonic acid precursors, in particular cholyl-4-sulphophenyl carbonate. Also of interest are peroxybenzoic acid precursors, in particular, N,N,N-trimethylammonium toluoyloxy benzene sulphonate; and the cationic bleach precursors disclosed in EP 284 292A and EP 303 520A (Kao).

[0061] A bleach stabiliser (heavy metal sequestrant) may also be present. Other than IDS, suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA) and the polyphosphonates such as Dequest (Trade Mark), EDTMP.

[0062] The detergent compositions may also contain one or more enzymes. Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions.

[0063] Preferred proteolytic enzymes (proteases) are catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available. Proteases of both high and low isoelectric point are suitable.

[0064] Other enzymes that may suitably be present include lipases, amylases, and cellulases including high-activity cellulases such as "Carezyme").

[0065] In particulate detergent compositions, detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used in any effective amount.

[0066] Antiredeposition agents, for example cellulose esters and ethers, for example sodium carboxymethyl cellulose, may also be present.

[0067] The compositions may also contain soil release polymers, for example sulphonated and unsulphonated PET/POET polymers, both end-capped and non-end-capped, and polyethylene glycol/polyvinyl alcohol graft copolymers such as Sokolan (Trade Mark) HP22.

[0068] Especially preferred soil release polymers are the sulphonated non-end-capped polyesters described and claimed in WO 95 32997A (Rhodia Chimie).

[0069] Other ingredients that may be present include solvents, hydrotropes, fluorescers, photobleaches, foam boosters or foam controllers (antifoams) as appropriate, sodium carbonate, sodium bicarbonate, sodium silicate, sodium sulphate, calcium chloride, other inorganic salts, fabric conditioning compounds, and perfumes.

EXAMPLES

[0070] The invention will be further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated.

EXAMPLE 1 AND COMPARATIVE EXAMPLE A

Preparation of CaIDS and MgIDS

[0071] An 0.04M aqueous solution of NaIDS (ex Bayer) was prepared and the pH adjusted to 12 with 1M NaOH solution. $CaCl_2$ or $MgCl_2$ solution was added slowly while stirring to give a final mole ratio of Ca or Mg to IDS of 1:1, 2:1 or 3:1.

A white precipitate formed with slow addition of the Ca or Mg salt solution. In the case of low mole ratios of Ca or Mg: IDS the precipitate formed but then re-dissolved. The Mg:IDS also formed a thicker, more gelatinous precipitate than Ca:IDS. After the required amount of Ca or Mg chloride salt solution had been added, the pH was re-adjusted back to 12. The dry salt was obtained by collecting the total liquor and precipitate and freeze drying.

Water uptake measurements

[0072] The dry salt was ground up using a mortar and pestle.

The dry salt was sieved to obtain a fraction with constant size and therefore constant surface area. The size fraction 355-500 micrometres was selected as being a representative portion of normal detergent powders. Approximately 1 g portions of these sieved Ca:IDS and Mg:IDS powders were weighed out into plastic dishes. These open dishes were stored in a humidity cabinet at 20°C/75% RH, the relative humidity being generated by an atmosphere of saturated NaCl (~ 6M).

[0073] The dishes were re-weighed periodically over a period of 7 days' storage under these conditions, and the % water uptake was calculated.

Example 1

Water uptake of CaIDS complexes

[0074]

Storage Time	% Water uptake (at 20°C/75% RH)			
	NaIDS	CaIDS (1:1)	CaIDS (2:1)	CaIDS (3:1)
1 hour	2.02	1.61	1.24	2.01
8 hours	9.87	7.76	5.19	6.94
1 day	23.93	20.06	11.87	12.51
2 days	40.57**	33.23	18.33	17.86
3 days	53.50**	44.28**	24.92	23.86
7 days	83.32**	80.78**	53.56*	50.06

*some stickiness and lump formation observed

**samples had liquefied

[0075] The CaIDS 3:1 complex was still in free-flowing powder form after 7 days.

Comparative Example A

Water uptake results on MgIDS complexes

[0076]

Storage Time	% Water uptake (at 20°C/75% RH)			
	NaIDS	MgIDS (1:1)	MgIDS (2:1)	MgIDS (3:1)
1 hour	2.02	2.03	2.25	2.10
8 hours	9.87	8.51	8.22	8.12
1 day	23.93	22.77	22.34	20.60
2 days	40.57**	32.61*	31.27	28.46
3 days	53.50**	42.26*	40.15*	37.03*
7 days	83.32**	83.64**	78.20**	71.97**

* samples showed signs of some liquid formation

**samples had liquefied completely

EXAMPLE 2

Preparation of CaIDS 3:1 complex

[0077] This Example shows the benefit of separating the sodium chloride formed as a by-product. The procedure was generally similar to that of Example 1, but with an added filtration step.

[0078] A 0.04M solution of NaIDS was prepared and the pH adjusted to 12 with 1M NaOH solution. 0.12M $CaCl_2$ solution was added slowly while stirring, to give a final mole ratio of 3:1 Ca:IDS). A white precipitate formed with slow addition of the Ca salt solution. After the required amount of Ca salt solution had been added, the pH was re-adjusted back to 12.

[0079] The slurry obtained was filtered under vacuum through a 542 filter paper fitted to a Buchner funnel. This removed the majority of the NaCl generated during the reaction of NaIDS with $CaCl_2$. The filter cake was dried in an oven overnight at 120°C.

[0080] Water take-up of this material, and of a control sample prepared without a filtration step, was measured as in Example 1 and the results were as shown below.

Storage Time	% Water uptake (at 20°C/75% RH)	
	Ca IDS (3:1) with NaCl	Ca IDS(3:1) minus NaCl
1 day	19.30	7.03
2 days	25.72	7.29
7 days	34.96	9.44
14 days	47.26	12.02
21 days	55.73	16.06

[0081] Both samples remained as powders throughout the storage period. The sample prepared without filtration showed some slight stickiness after 21 days, although not earlier, while the sample prepared with a filtration step was completely free-flowing even after 21 days' storage.

[0082] The very low water uptake figures for the 3:1 CaIDS without NaCl will be noted.

EXAMPLE 3

Preparation and water uptake of CaHIDS

[0083] 3:1 CaHIDS complexes were prepared by the procedures described in Example 1 (without filtration) and Example 2 (with filtration). The starting NaHIDS was ex Nippon Shokubai.

[0084] The water uptake results were as follows:

Storage Time	% Water uptake (at 20°C/75% RH)		
	NaHIDS	CaHIDS (3:1) + NaCl	CaHIDS (3:1) minus NaCl
5 hours	6.69	7.87	7.00
1 day	26.99	11.26	10.79
2 days	42.96	13.15	11.98
4 days	66.03**	19.59	15.20
7 days	70.70**	21.96	16.58

**samples had liquefied

[0085] Both CaHIDS 3:1 samples were free-flowing powders after 7 days' storage.

EXAMPLE 4

Detergent composition

[0086] A particulate detergent composition was prepared by a conventional slurry-making and spray-drying process to the following formulation:

	wt%
Sodium linear alkylbenzene sulphonate (NaLAS)	22.92
Sodium silicate (anhydrous)	5.37
Sodium tripolyphosphate	18.67
Sodium carboxymethyl cellulose	0.25
Polyacrylate polymer	0.70
Calcite	10.00
Sodium sulphate, fluorescer, water, impurities	to 100

Sample preparation and storage

[0087] 50 g samples of the detergent base powder were weighed into glass jars, and 1.25% by weight IDS or HIDS salt (180-250 micrometre sieve fraction) were added. The jars were sealed, and the detergent powder thoroughly mixed with the IDS or RIDS on a roller mixer for 1 hour.
The contents of each jar were then transferred to open cardboard trays, and stored for a period of 7 days in a controlled temperature/humidity store, (37°C/70% RH).
The powders were re-weighed periodically and % water uptake calculated.

Example 4a

Water uptake measurements (detergent powder + IDS) :

[0088]

Storage Time	% Water uptake (at 37°C/70% RH)		
	No sequestrant	NaIDS 1.25%	CaIDS (3:1, minus NaCl) 1.25%
2 hours	2.69	3.12	3.20
7 days	4.10	6.07	4.98

Example 4b

Water uptake measurements (detergent powder + HIDS) :

[0089]

Storage Time	% Water uptake (at 37°C/70% RH)		
	No sequestrant	NaHIDS 1.25%	CaHIDS (3:1, minus NaCl) 1.25%
2 hours	2.69	3.09	2.90
7 days	4.10	5.48	4.96

[0090] Incorporation of NaIDS or NaHIDS into detergent powder compositions resulted in increased water uptake of the detergent powders on storage as these materials are hygroscopic. This gave rise to increased stickiness of powders especially on storage. Use of the Ca form of IDS or HIDS lowered the level of water uptake minimising any negatives on powder physical properties.

Measurement of caking

[0091] For measurement of caking, homogeneous samples of the stored detergent powders were first obtained by roller mixing in sealed glass jars for 1 hour.

[0092] Compression and caking were measured using an apparatus comprising a graduated open-ended perspex cylinder of height 80 mm and internal diameter 24 mm standing on an aluminium base plate and fitted at its upper end with a plunger having a large flat circular top on which cylindrical weights could be placed.

[0093] The cylinder was filled with powder to a height of 30 mm, the plunger inserted until just touching the top of the powder, and a 1 kg weight placed on the top of the plunger. The weight was removed after 2 minutes, and the the compression of the powder sample (the fall in its level, in mm) was measured using the graduations on the cylinder and recorded.

[0094] The resulting "cake" of powder was expelled from the lower end of the cylinder, by means of the plunger, onto the base plate. 20g weights were added to the top of the powder cake until the cake disintegrated, and the total weight required to break up the cake (the unconfined compression test score or UCT, in g) was recorded.

[0095] Higher UCT values were obtained when a higher level of compression was achieved, ie the "powder cakes" were stronger. Increased compression and higher UCT values were also generally linked to increased water uptake.

Example 4c

Measurement of caking (detergent powder + IDS):

[0096]

	Stored detergent powders (7 days at 37°C/70% RH - open trays)		
	No sequestrant	NaIDS 1.25%	CaIDS 3:1 (minus NaCl) 1.25%
Compression (mm)	7	9	5
UCT (g)	280	340	220

Example 4d

Measurement of caking (detergent powder + HIDS) :

[0097]

	Stored detergent powders (7 days at 37°C/70% RH - open trays)		
	No sequestrant	NaHIDS 1.25%	CaHIDS 3:1 (minus NaCl) 1.25%
Compression (mm)	7	8	6
UCT (g)	280	320	240

EXAMPLE 5

Colour care performance of CaIDS and CaHIDS in detergent powders: restoration/recovery of coloured fabrics that have been colour-damaged by exposure to copper ions

[0098] These experiments demonstrate that the benefits of IDS and HIDS in restoring colour-damaged coloured fabrics are retained if the IDS or HIDS is used in the form of a Ca complex.

[0099] The fabrics used were cotton dyed with Direct Red 80. They were pre-treated with demineralised water containing 0.5 ppm Cu^{2+} ions and having the pH adjusted to 6.5 by means of sodium hydroxide. The pretreatment was carried out using tergotometers at 30°C, 90 rpm and a liquor to cloth ratio of 200:1, then the fabrics were line dried.

[0100] The fabrics were then washed in a wash liquor containing 2.5 g/l of the detergent composition (as used above), and 0.5 ppm Cu^{2+}, in 20/6° Ca/Mg French hard water: the pH was adjusted from 9.9 to 9.5 using dilute sulphuric acid. The washes were carried out in tergotometers at 30°C, 90 rpm and a liquor to cloth ratio of 200:1. The washes were followed by two rinses in 20/6° Ca/Mg French hard water containing 0.05 ppm Cu^{2+} at a liquor to cloth ratio of 200:1, and the fabrics were then line dried.

[0101] The sequestrants, where present, were dosed directly into the wash liquor in amounts to give the equivalent of 1.25% (by weight on the detergent composition) of NaIDS or NaHIDS.

[0102] Colour changes were monitored by reflectance changes at 620 nm, the standard being the fabrics prior to pretreatment. All values were negative, the ideal being the smallest possible negative value. Colour changes were also recorded as degree or % recovery of copper damaged coloured fabrics, ie as a % of the maximum possible recovery.

[0103] The results are shown in the Tables below.

[0104] No significant differences in performance were observed between the NaIDS and the CaIDS. These results show that there is no loss of colour care performance in the wash if IDS is incorporated as a Ca complex.

Example 5a: CaIDS

[0105]

	ΔR at 620 nm			
	No sequestrant	NaIDS	CaIDS (3:1, + NaCl)	CaIDS (3:1, minus NaCl)
After pre-treatment	-15.80	-15.63	-16.35	-14.65
After wash	-10.30	-3.41	-3.56	-3.56
	% Recovery			
After wash	34.8	78.2	78.2	74.4

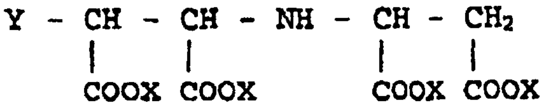
Example 5b: CaHIDS

[0106]

	ΔR at 620 nm			
	No sequestrant	NaHIDS	CaHIDS (3:1, + NaCl)	CaHIDS (3:1, minus NaCl)
After pre-treatment	-24.90	-25.54	-26.67	-28.78
After wash	-15.17	-7.10	-8.08	-10.42
	% Recovery			
After wash	39.1	72.2	69.7	63.8

Claims

1. A particulate detergent composition containing a sequestrant which is a compound of the formula I



$$Y - \underset{\text{COOX}}{\underset{|}{\text{CH}}} - \underset{\text{COOX}}{\underset{|}{\text{CH}}} - \text{NH} - \underset{\text{COOX}}{\underset{|}{\text{CH}}} - \underset{\text{COOX}}{\underset{|}{\text{CH}_2}} \qquad (I)$$

wherein Y is H or OH, and X is a countercation,
characterised in that the compound of the formula I is in the form of a calcium ion complex, the molar ratio of calcium ion to the compound of the formula I being from 2:1 to 3:1.

2. A detergent composition as claimed in claim 1,
characterised in that the molar ratio of calcium ion to the compound of the formula I is 3:1.

3. A detergent composition as claimed in claim 1,
characterised in that the calcium ion complex of the compound of the formula I may be obtained by a process which includes removal of any inorganic salt by-product.

4. A detergent composition as claimed in claim 1,
characterised in that it is a laundry detergent composition comprising

(a) from 5 to 60 wt% of one or more detergent surfactants,

(b) from 10 to 80 wt% of one or more detergency builders,

(c) from 0.5 to 10 wt% of the compound of the formula I in the form of a calcium ion complex,

(d) optionally other detergent ingredients to 100 wt%.

5. A detergent composition as claimed in claim 1,
characterised in that it is a non-bleaching laundry detergent composition comprising:

(a) from 5 to 60 wt% of one or more detergent surfactants,

(b) from 10 to 80 wt% of one or more detergency builders,

(c) from 0.05 to 2.5 wt% of the compound of the formula I in the form of a calcium ion complex,

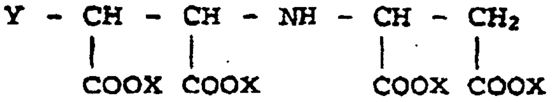
(d) optionally other non-bleaching detergent ingredients to 100 wt%.

6. A detergent composition as claimed in claim 1,
characterised in that it is in powder form and has a bulk density of at least 500 g/l.

7. A detergent composition as claimed in claim 6, which has a bulk density of from 600 to 1000 g/l.

8. A detergent composition as claimed in claim 1,
characterised in that it is in tablet form.

9. A process for the preparation of a particulate detergent composition as claimed in claim 1, which includes the step of mixing and/or granulating a compound of the formula I

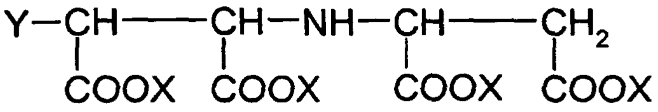


$$Y-\underset{\mathrm{COOX}}{\underset{|}{CH}}-\underset{\mathrm{COOX}}{\underset{|}{CH}}-NH-\underset{\mathrm{COOX}}{\underset{|}{CH}}-\underset{\mathrm{COOX}}{\underset{|}{CH_2}} \qquad (I)$$

wherein Y is H or OH, and X is a countercation, in powder form with other detergent ingredients,
characterised in that the compound of the formula I is in the form of a calcium ion complex, the molar ratio of calcium ion to the compound of the formula I being from 2:1 to 3:1.

Patentansprüche

1. Teilchenförmige Waschmittelzusammensetzung, enthaltend ein Maskierungsmittel, das eine Verbindung der Formel I



$$Y-\underset{\mathrm{COOX}}{\underset{|}{CH}}-\underset{\mathrm{COOX}}{\underset{|}{CH}}-NH-\underset{\mathrm{COOX}}{\underset{|}{CH}}-\underset{\mathrm{COOX}}{\underset{|}{CH_2}} \qquad (I)$$

darstellt,
worin Y H oder OH darstellt und X ein Gegenkation darstellt, **dadurch gekennzeichnet, dass** die Verbindung der Formel I in Form eines Calciumionenkomplexes vorliegt, wobei das Molverhältnis von Calciumion zu der Verbindung der Formel I 2:1 bis 3:1 ist.

2. Waschmittelzusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** das Molverhältnis von Calciumion zu der Verbindung der Formel I 3:1 ist.

3. Waschmittelzusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** der Calciumionenkomplex der Verbindung der Formel I durch ein Verfahren erhalten werden kann, das Entfernen von beliebigem anorganischem Salznebenprodukt einschließt.

4. Waschmittelzusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** sie eine Wäschewaschmittelzusammensetzung ist, umfassend

   (a) 5 bis 60 Gewichtsprozent von einem oder mehreren Waschmitteltensiden,
   (b) 10 bis 80 Gewichtsprozent von einem oder mehreren Waschmittelbuildern,
   (c) 0,5 bis 10 Gewichtsprozent der Verbindung der Formel I in Form eines Calciumionenkomplexes,
   (d) gegebenenfalls weitere Waschmittelbestandteile auf 100 Gewichtsprozent.

5. Waschmittelzusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** sie eine nicht-bleichende Wäschewaschmittelzusammensetzung ist, umfassend:

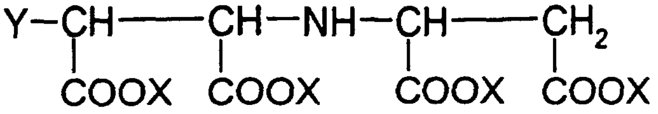
   (a) 5 bis 60 Gewichtsprozent von einem oder mehreren Waschmitteltensiden,
   (b) 10 bis 80 Gewichtsprozent von einem oder mehreren Waschmittelbuildern,
   (c) 0,05 bis 2,5 Gewichtsprozent der Verbindung der Formel I in Form eines Calciumionenkomplexes,
   (d) gegebenenfalls weitere nicht-bleichende Waschmittelbestandteile auf 100 Gewichtsprozent.

6. Waschmittelzusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** sie in Pulverform vorliegt und eine Schüttdichte von mindestens 500 g/l aufweist.

7. Waschmittelzusammensetzung nach Anspruch 6, die eine Schüttdichte von 600 bis 1000 g/l aufweist.

8. Waschmittelzusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** sie in Tablettenform vorliegt.

9. Verfahren zur Herstellung einer teilchenförmigen Waschmittelzusammensetzung nach Anspruch 1, das den Schritt des Vermischens und/oder Granulierens einer Verbindung der Formel I

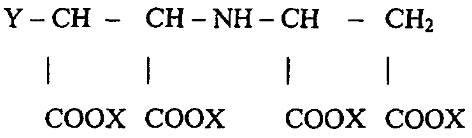


$$Y-\underset{\displaystyle COOX}{\underset{|}{CH}}-\underset{\displaystyle COOX}{\underset{|}{CH}}-NH-\underset{\displaystyle COOX}{\underset{|}{CH}}-\underset{\displaystyle COOX}{\underset{|}{CH_2}} \qquad (I)$$

worin Y H oder OH darstellt und X ein Gegenkation darstellt, in Pulverform mit weiteren Waschmittelbestandteilen einschließt, **dadurch gekennzeichnet, dass** die Verbindung der Formel I in Form eines Calciumionenkomplexes vorliegt, wobei das Molverhältnis von Calciumion zu der Verbindung der Formel I 2:1 bis 3:1 ist.

Revendications

1. Composition détergente particulaire contenant un séquestrant qui est un composé de Formule I :



$$Y-\underset{\displaystyle COOX}{\underset{|}{CH}}-\underset{\displaystyle COOX}{\underset{|}{CH}}-NH-\underset{\displaystyle COOX}{\underset{|}{CH}}-\underset{\displaystyle COOX}{\underset{|}{CH_2}} \qquad (I)$$

dans laquelle Y est H ou OH et X est un cation antagoniste, **caractérisée en ce que** le composé de la formule I se présente sous la forme d'un complexe d'ion calcium, le rapport molaire entre l'ion calcium et le composé de formule I allant de 2 pour 1 à 3 pour 1.

2. Composition détergente selon la revendication 1, **caractérisée en ce que** le rapport molaire entre l'ion calcium et le composé de formule I est de 3 pour 1.

3. Composition détergente selon la revendication 1, **caractérisée en ce que** le complexe d'ion calcium du composé de formule I peut être obtenu par un procédé qui inclut l'élimination de tout sous-produit de sel inorganique.

4. Composition détergente selon la revendication 1, **caractérisée en ce qu'**il s'agit d'une composition détergente pour le linge comprenant :

(a) de 5 à 60 % en poids d'un ou de plusieurs tensioactifs détergents ;
(b) de 10 à 80 % en poids d'un ou de plusieurs adjuvants de détergence ;
(c) de 0,5 à 10 % en poids du composé de formule I sous la forme d'un complexe d'ion calcium ;
(d) optionnellement d'autres ingrédients détergents jusqu'à 100 %.

5. Composition détergente selon la revendication 1, **caractérisée en ce qu'**il s'agit d'une composition détergente non blanchissante pour le linge comprenant :

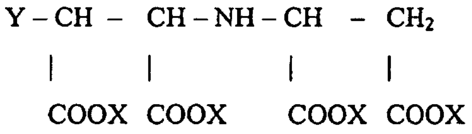
(a) de 5 à 60 % en poids d'un ou de plusieurs tensioactifs détergents ;
(b) de 10 à 80 % en poids d'un ou de plusieurs adjuvants de détergence ;
(c) de 0,05 à 2,5 % en poids d'un composé de formule I sous la forme d'un complexe d'ion calcium;
(d) Optionnellement d'autres ingrédients détergents non blanchissants jusqu'à 100 %.

6. Composition détergente selon la revendication 1, **caractérisée en ce qu'**elle se présente sous la forme d'une poudre et a une densité en masse d'au moins 500 g/l.

7. Composition détergente selon la revendication 6, ayant une densité en masse allant de 600 à 1000 g/l.

8. Composition détergente selon la revendication 1, **caractérisée en ce qu'**elle se présente sous la forme de pastilles.

9. Procédé de préparation d'une composition détergente particulaire selon la revendication 1, qui inclut l'étape consistant à mélanger et/ou granuler un composé de formule 1 :



$$\mathrm{Y}-\underset{\substack{|\\ \mathrm{COOX}}}{\mathrm{CH}}-\underset{\substack{|\\ \mathrm{COOX}}}{\mathrm{CH}}-\mathrm{NH}-\underset{\substack{|\\ \mathrm{COOX}}}{\mathrm{CH}}-\underset{\substack{|\\ \mathrm{COOX}}}{\mathrm{CH_2}}$$

(I)

dans laquelle Y est H ou OH et X est un cation antagoniste, sous la forme d'une poudre avec d'autres ingrédients détergents, **caractérisé en ce que** le composé de formule I est sous la forme d'un complexe d'ion calcium, le rapport molaire entre l'ion calcium et le composé de formule I étant de 2 pour 1 à 3 pour 1.