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(54) Particulate detergent compositions comprising surfactant, carbonate, and hydroxamate

(57) A particulate detergent composition comprising at least 70% by number coated (core and shell) detergent particles comprising 40 to 90 wt% surfactant and 20 to 40 wt% sodium carbonate, the ratio of surfactant to sodium carbonate being at least 1.5:1, characterised in that the coated particles further comprise hydroxamate.

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Description

Technical Field

[0001] This invention relates to particulate detergent compositions comprising surfactant and hydroxamate, particularly to compositions comprising carbonate.

Background

[0002] In WO2010069957 a clay particulate soil cleaning benefit is disclosed for the use of hydroxamates with specified ratios and types of surfactants. The invention may be used in either liquid or solid format cleaning systems. The compositions given are designed to be able to remove everyday dirt and stains that are commonly found in a wash load. Two particular stains that are problematic, especially when children's wear or sport's wear is being washed, are clay soil stains and grass stains. One type of clay that is particularly resistant to removal by surfactants alone is red clay, such as red pottery clay or Red Georgia clay. This is a particulate soil stain.

[0003] Many particulate detergents are formulated to make a highly alkaline wash liquor. The alkalinity assists in the removal of greasy soils. In WO2010069957 an example is given of a relatively low alkalinity composition comprising more sodium carbonate than surfactant.

[0004] There is a need to produce more environmentally compatible detergent compositions by eliminating all components that provide limited, or no, cleaning action. Furthermore, the products should be as compact as possible in order to reduce packaging even further.

[0005] In pending applications, PCT/EP2010/055256 and PCT/EP2010/055257 we propose a particulate detergent based on coating an over sized core of sticky surfactant blend with a thick coat of sodium carbonate. The core may be formed by extrusion and cutting of a very dry surfactant blend. To decrease the surface area to volume ratio the extrudates are made with an abnormally large diameter in excess of 3 mm (typically about 5 mm) and the thickness of the cut portions is relatively thin, at less than 2 mm, to assist with dissolution of the core. The sodium carbonate coating is sprayed on at a level of about 30 wt%. This process arrives at a unique combination of surfactants and sodium carbonate. Hitherto the amount of sodium carbonate has either been much higher than the amount of surfactant or else additional, usually inorganic, builder material such as zeolite or silicate has been included into the composition.

[0006] The choice of surfactant blend allows the particles to give good detergency even without any conventional detergent builder, thus eliminating the need for such builders in the core. Additional materials may be added to the core and / or the coating, as convenient for the processing or composition performance.

[0007] Surprisingly it has been found that the incorporation of hydroxamate into the extruded and coated particles described in PCT/EP2010/055256 and PCT/EP2010/055257 provides advantages, especially at conditions of high water hardness.

Summary of the Invention

[0008] According to the present invention there is provided a particulate detergent composition comprising at least 70% by number coated (core and shell) detergent particles comprising 40 to 90 wt% surfactant and 20 to 40 wt% sodium carbonate, the ratio of surfactant to sodium carbonate being at least 1.5:1, characterised in that the coated particles further comprise hydroxamate. The amount of hydroxamate preferably lies in the range 0.005 to 12 wt% of the particle.

[0009] Preferably, the particles comprise a core comprising surfactant material and a coating comprising sodium carbonate, most preferably the hydroxamate is located in the core. Having the hydroxamate in the core of the particle improves the appearance of the particle. Furthermore, since the hydroxamate is intended to work with the surfactant blend, as explained in WO2010069957, it is desirable that it is released to the wash liquor at the same time as the slower dissolving surfactant in the core.

[0010] The particles preferably comprise levels of sodium carbonate that are less than half the total active detergent. The majority of the sodium carbonate should be provided by the coating. The use of hydroxamate with surfactant and these lower than normal levels of sodium carbonate give a surprising effect on clay soils especially under hard water conditions. The move to relatively unbuilt compositions is desirable from an environmental and sustainability viewpoint as it reduces the chemical loading per wash. However, even the most calcium tolerant surfactant blends tend to suffer reduced wash performance on some stain and soil types when high water hardness levels are encountered. It is undesirable to simply increase the dose of the surfactant to restore the wash performance because this then increases the chemical loading disproportionately to the increased detergency. We have found that the introduction of small amounts of hydroxamate to the wash liquor can provide a synergistic cleaning boost to the detergent particles with low levels of carbonate, especially under these hard water conditions. Because the compositions of the invention are concentrated particulate compositions the amount of hydroxamate in the particle is large as a percentage of the composition.

[0011] Advantageously the core is made by extrusion of a dry surfactant blend. By dry is meant less than 1 wt% water. Preferred cores comprise blends of anionic and nonionic surfactant, the anionic surfactant being present in an excess over the nonionic surfactant. Most preferred cores comprise calcium tolerant blends of surfactants as defined hereafter.

[0012] It is preferred that the coated detergent particle has a core to shell ratio of from 3 to 1:1 by weight, preferably 2.5 to 1.5 to 1 and optimally about 2:1 when the shell comprise an inorganic salt (sodium carbonate).

[0013] The preferred ratio of anionic to nonionic surfactant for particulate red clay soil removal is at least 1:1, more preferably at least 3:2. Preferably, it is at most 9:1. A most preferred range is 1:1 to 9:1, or 3:2 to 9:1.

[0014] The preferred coated detergent particle has perpendicular dimensions x, y and z, wherein x is from 1 to 2 mm, y is from 3 to 8 mm, and z is from 3 to 8 mm, wherein the particle comprises:

(i) from 40 to 90 wt % surfactant selected from: anionic surfactant; and, non-ionic surfactant; preferably 50 to 80;
(ii) from 10 to 40 wt % sodium carbonate, preferably 18 to 35 wt%;
(iii) from 0.5 to 12 wt % hydroxamate, preferably 2 to 8 wt%
(iv) from 0.0001 to 5 wt % perfume;
(v) from 0 to 10 wt % organic polymers; and,
(vi) from 0 to 20 wt %, preferably 0 to 10 wt %, of other ingredients.

[0015] Preferably the sodium carbonate is present as a coating (shell) and the surfactant is present as a core. More preferably the hydroxamate is present in the core.

[0016] The coating may comprise from 0 to 2 wt% of an organic polymer, more preferably from 0 to 0.4 wt% of the particle. Preferred polymers include sodium carboxymethyl cellulose.

[0017] The preferred ratio of hydroxamate to detersive surfactant system (surfactant) for optimum particulate red clay soil removal lies in the range 1:4 to 1: 8000. More preferred is 1:7 to 1:40. An even more preferred range of ratios being 1:10 to 1:25 parts by weight.

[0018] The hydroxamate may be incorporated into the surfactant core at various stages of the manufacturing process and may possibly be incorporated into the coating. Ingredients may alternatively be added as a further coating layer before or after the sodium carbonate coating is applied.

[0019] Unless otherwise stated all wt % refer to the total percentage in the particle as dry weights.

Detailed Description of the Invention

[0020] The particles are preferably substantially the same shape and size as one another. For example the variation in x, y or z should each be less than 20, preferably less than 10%.

[0021] The amount of coating on each coated particle is advantageously from 10 to 40, more preferably 18 to 35 % by weight of the particle.

[0022] The number percentage of the packaged composition of particles comprising the core and shell is preferably at least 85%.

[0023] The coated particles preferably comprise from 0.001 to 3 wt % perfume.

[0024] The core of the coated particles preferably comprises less than 5 wt%, even more preferably less than 2.5 wt% inorganic materials.

[0025] The coating is preferably sodium carbonate in admixture with a minor amount of SCMC and further optionally in admixture with one or more of sodium silicate, water soluble fluorescer, water soluble or dispersible shading dye and pigment or coloured dye. The coating could alternatively be Burkeite, a double salt of sodium carbonate and sodium sulphate. It could even be citric acid, or even a polymer such as CP5. The important thing is that the amount of sodium carbonate in the wash solution must be less than the amount of the surfactant system.

[0026] The particles are desirably oblate spheroids with diameter of 3 to 6 mm and thickness of 1 to 2 mm.

[0027] The particles may be distributed and used in a package of any of the conventionally employed types. The package is preferably resealable. The package may be of any convenient size.

[0028] The cores advantageously have a diameter of greater than 2 mm, preferably greater than 3 mm, most preferably greater than 4 mm and preferably have a diameter of less than 7 mm, most preferably less than 5 mm. they advantageously have a maximum thickness of greater than 0.2 mm and less than 3 mm, preferably less than 2 mm, most preferably less than about 1.5 mm and more than about 0.5 mm, even 0.7 mm. Whilst the preferred core is of circular cross section, they may alternatively have other cross sections such as triangular, rectangular and even complex cross sections, such as one mimicking a flower with rotationally symmetrical "petals". The key being that the average thickness of the core should be kept below the level where dissolution will be slow. This is a thickness of about 2 mm. When the cores have been extruded they are cut so that their major dimension is across the extruder and the minor dimension is along the axis of the extruder. This increases the surface area that is a "cut" surface. It also allows the extruded core to expand considerably along its axis after cutting, whilst maintaining a relatively high surface to volume ratio, which is believed to increase its solubility and also results in an attractive biconvex, or lentil, appearance. Elsewhere we refer to this shape as an oblate spheroid. This is essentially a rotation of an ellipse about its minor axis.

[0029] It is surprising that at very low water contents the LAS containing surfactant blends can be extruded to make solid detergent particles that are hard enough to be used without any need to be structured by inorganic materials or other structurants as commonly found in prior art extruded detergent particles. Thus, the amount of surfactant in the detergent particle can be much higher and the amount of builder in the detergent particle can be much lower than is conventional.

[0030] Preferably, the co-surfactant is chosen from the group consisting of: SLES, and nonionic, together with optional soap and mixtures thereof. The only proviso is that when nonionic is used the upper limit for the amount of nonionic surfactant has been found to be 20 wt% of the total surfactant to avoid the dried material being too soft and cohesive to extrude because it has a hardness value less than 0.5 MPa.

[0031] The cores may be coated by transferring them to a fluid bed and spraying onto them up to 40 wt% (based on coated detergent particle) of inorganic material in aqueous solution and drying off the water.

[0032] In addition to the coated core and shell particles the composition may also comprise, for example, an antifoam granule.

[0033] It is preferred that the coating is coloured. Particles of different colours may be used in admixture. The coating quality and appearance is very good due to the excellent surface of the cut extrudates onto which the coating is applied in association with the large particle size and S/V ratios of the preferred particles.

[0034] It is particularly preferred that the detergent particles comprise perfume. The perfume may be added into the extruder or premixed with the surfactant blend in the mill, or in a mixer placed after the mill, either as a liquid or as encapsulated perfume particles. In an alternative process, the perfume may be mixed with a nonionic material and blended. Such a blend may alternatively be applied by coating the extruded particles, for example by spraying it mixed with molten nonionic surfactant. Perfume may also be introduced into the composition by means of a separate particles comprising perfume and then the detergent particle does not need to comprise any perfume.

The Surfactant Blend

[0035] Surfactant blends that do not require builders to be present for effective detergency in hard water are preferred. Such blends are called calcium tolerant surfactant blends if they pass the test set out hereinafter. Thus, it is advantageous if the extruded core is made using a calcium tolerant surfactant blend according to the test herein described. However, the invention may also be of use for washing with soft water, either naturally occurring or made using a water softener. In this case, calcium tolerance is not so important and surfactant blends other than calcium tolerant ones may be used.

[0036] LAS can be at least partially replaced by MES (methyl ester sulphonate), or, less preferably, partially replaced by up to 20 wt % PAS.

Blending

[0037] The surfactants are mixed together before being input to the drier. Conventional mixing equipment is used. Hydroxamate is also mixed in at this point to ensure that it is well distributed. The hydroxamate is supplied in soapy form and addition to the core later in the process, for example in the extruder, can lead to poor distribution with lumps of hydroxamate material being embedded into the cores.

Drying

[0038] To achieve the very low moisture content of the surfactant blend, scraped film devices may be used. A preferred form of scraped film device is a wiped film evaporator. One such suitable wiped film evaporator is the "Dryex system" based on a wiped film evaporator available from Ballestra S.p.A.. Alternative drying equipment includes tube-type driers, such as a Chemithon Turbo Tube® drier, and soap driers.

Chilling and milling

[0039] The hot material exiting the scraped film drier is subsequently cooled and broken up into suitable sized pieces to feed to the extruder. Simultaneous cooling and breaking into flakes may conveniently be carried out using a chill roll. If the flakes from the chill roll are not suitable for direct feed to the extruder then they can be milled in a milling apparatus and /or they can be blended with other liquid or solid ingredients in a blending and milling apparatus, such as a ribbon mill. Such milled or blended material is desirably of particle size 1 mm or less for feeding to the extruder.

[0040] It is particularly advantageous to add a milling aid at this point in the process. Particulate material with a mean particle size of 10 nm to 10 μm is preferred for use as a milling aid. Among such materials, there may be mentioned, by way of example: aerosil®, alusil®, and microsil®.

Extruding and cutting

[0041] The extruder provides further opportunities to blend in ingredients other than surfactants, or even to add further surfactants. However, it is generally preferred that all of the anionic surfactant, or other surfactant supplied in admixture with water; i.e. as paste or as solution, is added into the drier to ensure that the water content can then be reduced and the material fed to and through the extruder is sufficiently dry. Additional materials that can be blended into the extruder are thus mainly those that are used at low levels in a detergent composition: such as fluorescer, shading dye, enzymes, perfume, silicone antifoams, polymeric additives and preservatives. The limit on such additional materials blended in the extruder has been found to be about 10 wt%, but it is preferred for product quality to be ideal to keep it to a maximum of 5 wt%. Solid additives are generally preferred. Liquids, such as perfume may be added at levels up to 2.5 wt%, preferably up to 1.5 wt%. Solid particulate structuring (liquid absorbing) materials or builders, such as zeolite, carbonate, silicate are preferably not added to the blend being extruded. These materials are not needed due to the self structuring properties of the very dry LAS-based feed material. If any is used the total amount should be less than 5 wt%, preferably less than 4 wt%, most preferably less than 3 wt%. At such levels no significant structuring occurs and the inorganic particulate material is added for a different purpose, for instance as a flow aid to improve the feed of particles to the extruder.

[0042] The output from the extruder is shaped by the die plate used. The extruded material has a tendency to swell up in the centre relative to the periphery. We have found that if a cylindrical extrudate is regularly sliced as it exits the extruder the resulting shapes are short cylinders with two convex ends. These particles are herein described as oblate spheroids, or lentils. This shape is pleasing visually.

Coating

[0043] Coating allows the particles to be coloured easily. It also further reduces the stickiness of the hygroscopic surfactant core to a point where the particles are free flowing. Coating makes them more suitable for use in detergent compositions that may be exposed to high humidity for long periods.

[0044] The extruded particles can be considered as oblate spheroids with a major radius "a" and minor radius "b". Hence, the surface area(S) to volume (V) ratio can be calculated as:

$$\frac{S}{V} = \frac{3}{2b} + \frac{3b}{4\in a^2}\ln\left(\frac{1+\in}{1-\in}\right)\text{mm-1}$$

[0045] When $\in$ is the eccentricity of the particle.

[0046] For use with hydroxamate the coating preferably comprises sodium carbonate, possibly in admixture with sodium sulphate, and even sodium chloride or sodium silicate. Food dyes, shading dyes, fluorescer and other optical modifiers can be added to the coating by dissolving them in the spray-on solution or dispersion. Use of a builder salt such as sodium carbonate is particularly advantageous because it allows the detergent particle to have an even better performance by buffering the system in use at an ideal pH for maximum detergency of the anionic surfactant system. It also increases ionic strength, which improves cleaning in hard water, and it is compatible with other detergent ingredients that may be admixed with the coated extruded detergent particles. If a fluid bed is used to apply the coating solution, the skilled worker will know how to adjust the spray conditions in terms of Stokes number and possibly Akkermans number (FNm) so that the particles are coated and not significantly agglomerated. Suitable teaching to assist in this may be found in EP1187903, EP993505 and Powder technology 65 (1991) 257-272 (Ennis).

[0047] It will be appreciated by those skilled in the art that multiple layered coatings, of the same or different coating materials, could be applied, but a single coating layer is preferred, for simplicity of operation, and to maximise the thickness of the coating. The amount of coating should lie in the range 3 to 50 wt% of the particle, preferably 20 to 40 wt% for the best results in terms of anti-caking properties of the detergent particles.

The particulate detergent composition

[0048] The coated particles dissolve easily in water and leave very low or no residues on dissolution, due to the absence of insoluble structurant materials such as zeolite. The hydroxamate does not generate any residues. The coated particles have an exceptional visual appearance, due to the smoothness of the coating coupled with the smoothness of the underlying cores, which is also believed to be a result of the lack of particulate structuring material in the extruded core particles.

Shape and Size

[0049] The coated detergent particle is preferably curved. The coated detergent particle is preferably lenticular (shaped like a whole dried lentil), an oblate ellipsoid, where z and y are the equatorial diameters and x is the polar diameter; preferably y = z. The size is such that y and z are at least 3 mm, preferably 4 mm, most preferably 5 mm and x lies in the range 1 to 2 mm.

[0050] The coated laundry detergent particle may be shaped as a disc.

Core Composition

[0051] The core is primarily surfactant. It may also include detergency additives, such as perfume, shading dye, enzymes, cleaning polymers and soil release polymers.

Surfactant

[0052] The coated laundry detergent particle comprises between 40 to 90 wt% of a surfactant, most preferably 55 to 75 wt %. In general, the nonionic 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, 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. Preferably the surfactants used are saturated.

1) Anionic Surfactants

[0053] Suitable anionic detergent compounds that may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C8 to C18 alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C9 to C20 benzene sulphonates, particularly sodium linear secondary alkyl C10 to C15 benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. Most preferred anionic surfactants are sodium lauryl ether sulphate (SLES), particularly preferred with 1 to 3 ethoxy groups, sodium C10 to C15 alkyl benzene sulphonates and sodium C12 to C18 alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides. The chains of the surfactants may be branched or linear.

[0054] Soaps may also be present. The fatty acid soap used preferably contains from about 16 to about 22 carbon atoms, preferably in a straight chain configuration. The anionic contribution from soap may be from 0 to 30 wt% of the total anionic. Use of more than 10 wt% soap is not preferred.

[0055] Preferably, at least 50 wt % of the anionic surfactant is selected from: sodium C11 to C15 alkyl benzene sulphonates; and, sodium C12 to C18 alkyl sulphates. Ethoxylated alkyl sulphates (SLES) may also be used as may methyl ester sulphonates (MES). All of these secondary surfactants should be used in minor amounts compared to LAS.

[0056] Preferably, the anionic surfactant is present in the coated laundry detergent particle at levels between 25 to 85 wt%, more preferably 40 to 70wt%.

2) Non-Ionic Surfactants

[0057] Suitable non-ionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Preferred nonionic detergent compounds are C6 to C22 alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C8 to C18 primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 50 EO. Preferably, the non-ionic is 10 to 50 EO, more preferably 20 to 35 EO. Alkyl ethoxylates are particularly preferred.

[0058] Preferably the non-ionic surfactant is present in the coated laundry detergent particle at levels between 5 to 25 wt%, more preferably 7 to 19 wt%.

[0059] Cationic surfactant may be present as minor ingredients at levels preferably between 0 to 5 wt%.

[0060] Preferably all the surfactants are mixed together before being dried. Conventional mixing equipment may be used. The surfactant core of the laundry detergent particle may be formed by roller compaction and subsequently coated e.g. with an inorganic salt.

Calcium Tolerant Surfactant System

[0061] In another aspect the core is calcium tolerant and this is a preferred aspect because this reduces the need for a builder.

[0062] Surfactant blends that do not require builders to be present for effective detergency in hard water are preferred. Such blends are called calcium tolerant surfactant blends if they pass the test set out hereinafter. However, the invention may also be of use for washing with soft water, either naturally occurring or made using a water softener. In this case, calcium tolerance is no longer important and blends other than calcium tolerant ones may be used.

[0063] Calcium-tolerance of the surfactant blend is tested as follows:

> The surfactant blend in question is prepared at a concentration of 0.7 g surfactant solids per litre of water containing sufficient calcium ions to give a French hardness of 40 (4 x 10-3 Molar Ca2+). Other hardness ion free electrolytes such as sodium chloride, sodium sulphate, and sodium hydroxide are added to the solution to adjust the ionic strength to 0.05M and the pH to 10. The adsorption of light of wavelength 540 nm through 4 mm of sample is measured 15 minutes after sample preparation. Ten measurements are made and an average value is calculated. Samples that give an absorption value of less than 0.08 are deemed to be calcium tolerant.

[0064] Examples of surfactant blends that satisfy the above test for calcium tolerance include those having a major part of LAS surfactant (which is not of itself calcium tolerant) blended with one or more other surfactants (co-surfactants) that are calcium tolerant to give a blend that is sufficiently calcium tolerant to be usable with little or no builder and to pass the given test. Suitable calcium tolerant co-surfactants include SLES 1-7EO, and alkyl ethoxylate non-ionic surfactants, particularly those with melting points less than 40°C.

[0065] A LAS/SLES surfactant blend has a superior foam profile to a LAS Nonionic surfactant blend and is therefore preferred for hand washing formulations requiring high levels of foam. SLES may be used at levels of up to 30%. A LAS/NI surfactant blend provides a harder particle and its lower foam profile makes it more suited for automatic washing machine use.

The Coating

[0066] The main component of the coating is preferably a sodium carbonate salt. Other water compatible ingredients may be included in the coating. For example fluorescer, SCMC, shading dye, silicate, pigments and dyes.

Sodium Carbonate

[0067] The coating is preferably 40 to 100 wt % sodium carbonate. So, for example if it is 90% Burkeite then that is considered for the purposes of this patent application to be 45% sodium carbonate. The coating is preferably present at a level that reduces the stickiness of the detergent particle to a point where the particles are free flowing.

[0068] It will be appreciated by those skilled in the art that multiple layered coatings, of the same or different coating materials, could be applied, but a single coating layer is preferred, for simplicity of operation, and to maximise the thickness of the coating. The amount of coating should lay in the range 5 to 40 wt % of the particle, preferably 20 to 40 wt %, even more preferably 25 to 35 wt % for the best results in terms of anti-caking properties of the detergent particles.

[0069] The coating is applied to the surface of the surfactant core, by crystallisation from an aqueous solution or slurry e.g. of sodium carbonate. The spray preferably contains greater than 50g/L, more preferably 200 g/L of the salt. An aqueous spray-on of the coating solution in a fluidised bed has been found to give good results and may also generate a slight rounding of the detergent particles during the fluidisation process. Drying and/or cooling may be needed to finish the process.

[0070] By coating the large detergent particles of the current invention the thickness of coating obtainable by use of a given coating level is much greater than would be achieved on typically sized detergent granules (0.5 to 2 mm diameter spheres).

[0071] For optimum dissolution properties, this surface area to volume ratio must be greater than 3 mm^{-1}. However, the coating thickness is inversely proportional to this coefficient and hence for the coating the ratio "Surface area of coated particle" divided by "Volume of coated particle" should be less than 15 mm^{-1}.

[0072] A preferred calcium tolerant coated laundry detergent particle has a surfactant system which comprises 50 to

95 wt% anionic surfactant, preferably sodium linear alkylbenzene sulphonate.

Dye

[0073] Dye may advantageously be added to the coating, it may also be added to the surfactant mix in the core. In that case preferably the dye is dissolved in the surfactant before the core is formed.

[0074] Dyes are described in Industrial Dyes edited by K.Hunger 2003 Wiley-VCH ISBN 3-527-30426-6.

[0075] In a preferred process, the dye is added to the coating slurry and agitated before applying to the core of the particle. Application may be by any suitable method, preferably spraying on to the core particle as detailed above.

[0076] The dye may be any colour, preferable the dye is blue, violet, green or red. Most preferably the dye is blue or violet.

[0077] The dye is preferably a shading dye for imparting a perception of whiteness to a laundry textile.

[0078] The dye may be covalently bound to polymeric species.

[0079] A combination of dyes may be used.

The coated detergent particle

[0080] The coated detergent particle comprises from 70 to 100 wt %, preferably 85 to 90 wt %, of a detergent composition.

[0081] Preferably, the coated detergent particles are substantially the same shape and size by this is meant that at least 90 to 100 % of the coated laundry detergent particles in the in the x, y and z dimensions are within a 20 %, preferably 10%, variable from the largest to the smallest coated laundry detergent particle in the corresponding dimension.

Water content

[0082] The particle preferably comprises from 0 to 15 wt % water, more preferably 0 to 10 wt %, most preferably from 1 to 5 wt % water, at 293K and 50% relative humidity. This facilitates the storage stability of the particle and its mechanical properties.

Other ingredients

[0083] The ingredients described below may be present in the coating or the core.

Fluorescent Agent

[0084] The coated laundry detergent particle preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 1.0 wt %.

[0085] Suitable Fluorescers for use in the invention are described in chapter 7 of Industrial Dyes edited by K.Hunger 2003 Wiley-VCH ISBN 3-527-30426-6.

[0086] Preferred fluorescers are selected from the classes distyrylbiphenyls, triazinylaminostilbenes, bis(1,2,3-triazol-2-yl)stilbenes, bis(benzo[b]furan-2-yl)biphenyls, 1,3-diphenyl-2-pyrazolines and courmarins. The fluorescer is preferably sulphonated.

[0087] Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN. Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]aminol stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfostyryl)biphenyl.

[0088] Tinopal® DMS is the disodium salt of disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino) stilbene-2-2' disulfonate. Tinopal® CBS is the disodium salt of disodium 4,4'-bis(2-sulfostyryl)biphenyl.

Perfume

[0089] Preferably, the composition comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt %, most preferably 0.1 to 1 wt %. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

[0090] It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components.

[0091] In perfume mixtures preferably 15 to 25 wt% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Preferred top-notes are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

[0092] It is preferred that the coated laundry detergent particles do not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

Polymers

[0093] The composition may comprise one or more polymers. Examples are carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polyethylene imines, ethoxylated polyethylene imines, water soluble polyester polymers polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

[0094] Especially preferred compositions comprise at least 0.5 wt% of soil release polymer. This improves the multiwash performance of the detergent system for the removal of the clay. Inclusion of at least 0.5 wt% anti redeposition polymer is also beneficial due to the very high efficiency of primary detergency soil removal meaning that there is an increased level of soil in the wash liquor, which must then be prevented from redeposition onto the same or a different piece of fabric.

Enzymes

[0095] One or more enzymes are preferably present in the composition.

[0096] Preferably the level of each enzyme is from 0.0001 wt% to 0.5 wt% protein.

[0097] Especially contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.

[0098] Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

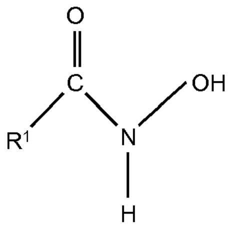
Sequestrants

[0099] Sequestrants may be present in the detergent particles. However, because the hydroxamate technology is affected by competing sequestrants, for maximum performance of the hydroxamate any phosphonate or similar sequestrants that may complex with iron are preferably absent or used at a low level of up to 1 wt%, preferably less that 0.5 wt%.

Hydroxamate

[0100] Whenever either the term 'hydroxamic acid' or 'hydroxamate' is used, this encompasses both hydroxamic acid and the corresponding hydroxamate (salt of hydroxamic acid), unless indicated otherwise.

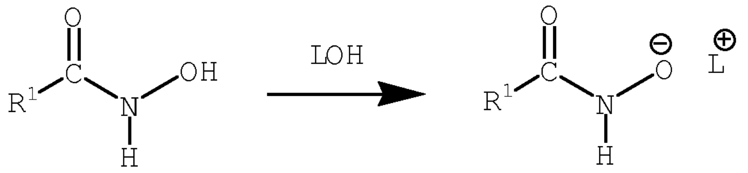
[0101] Hydroxamic acids are a class of chemical compounds in which a hydroxylamine is inserted into a carboxylic acid. The general structure of a hydroxamic acid is the following:



(Formula 1)

in which R1 is an organic residue, for example alkyl or alkylene groups. The hydroxamic acid may be present as its corresponding alkali metal salt, or hydroxamate.

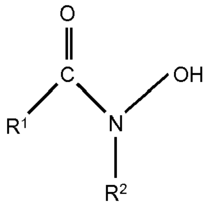
[0102] The hydroxamates may conveniently be formed from the corresponding hydroxamic acid by substitution of the acid hydrogen atom by a cation:



(Formula 2)

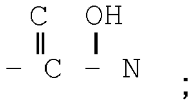
L+ is a monovalent cation such as for example the alkali metals (e.g. potassium, sodium), or ammonium or a substituted ammonium.

[0103] In the present invention the hydroxamic acid or its corresponding hydroxamate has the structure:



(Formula 3)

wherein R1 is
a straight or branched C4-C20 alkyl, or
a straight or branched substituted C4-C20 alkyl, or
a straight or branched C4-C20 alkenyl, or
a straight or branched substituted C4-C20 alkenyl, or
an alkyl ether group CH3 (CH2)n (EO)m wherein n is from 2 to 20 and m is from 1 to 12, or
a substituted alkyl ether group CH3 (CH2)n (EO)m wherein n is from 2 to 20 and m is from 1 to 12, and
the types of substitution include one or more of -NH2, -OH, -S-, -O-, -COOH, and



$$-\overset{\overset{\displaystyle C}{\|}}{C}-\overset{\overset{\displaystyle OH}{|}}{N}\;;$$

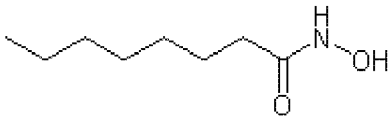
and R2 is selected from hydrogen and a moiety that forms part of a cyclic structure with a branched R1 group

[0104] References to a number of carbon atoms include mixed chain length materials provided that some of the hydroxamate material falls within the ranges specified and the ratios and amounts are determined by excluding any material falling outside of the specified range.

[0105] The preferred hydroxamates are those where R2 is Hydrogen and R1 is C8 to C18 alkyl, preferably normal alkyl, preferably >80% saturated, more preferably > 90% saturated.

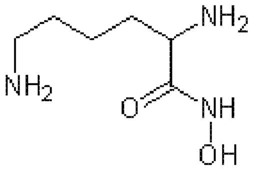
[0106] The hydroxamate containing particulate compositions according to the invention are particularly suitable for use on particulate stains such as soils and clays, especially red clay, and also surprisingly grass.

[0107] The general structure of a hydroxamic acid in the context of the present invention has been indicated in formula 3, and R1, is as defined above. When R1, is an alkyl ether group CH3 (CH2)n (EO)m wherein n is from 2 to 20 and m is from 1 to 12 then the alkyl moiety terminates this side group. Preferably, R1 is chosen from the group consisting of C4, C5, C6, C7, C8, C9, C10, C11, or C12 or C14 normal alkyl group, most preferably R1 is at least a C8-14 normal alkyl group. When the C8 material is used this is called octyl hydroxamic acid. The potassium salt is particularly useful.



octanohydroxamic acid K salt

[0108] However, other hydroxamic acids, whilst less preferred, are suitable for use in the present invention. Such suitable compounds include, but are not limited to, the following compounds:



Lysine Hydroxamate*HCl

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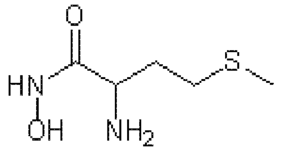
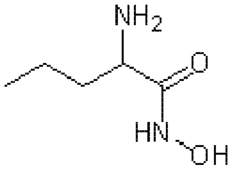


Methionine Hydroxamate



Norvaline Hydroxamate

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[0109] Such hydroxamic acids are commercially available.

[0110] The hydroxamate is thought to act by binding to metal ions that are present in the soil on the fabric. This binding action, which is, in effect, the known sequestrant property of the hydroxamate is not, in itself, of any use to remove the soil from the fabric. The key is the "tail" of the hydroxamate i.e. the group R1 minus any branching that folds back onto the amate Nitrogen via group R2. The tail is selected to have an affinity for the surfactant system. This means that the soil removal ability of an already optimised surfactant system is further enhanced by the use of the hydroxamate as it, in effect, labels the difficult to remove particulate material (clay) as "soil" for removal by the surfactant system acting on the hydroxamate molecules now fixed to the particulates via their binding to the metal ions embedded in the clay type particulates. The detersive surfactants will adhere to the hydroxamate, leading overall to more surfactants interacting with the fabric, leading to better soil release. Therewith the hydroxamic acids act as a linker molecule facilitating the removal and suspension of the particulate soil from the fabric into a wash liquor and thus boosting the primary detergency. The hydroxamates have a higher affinity for transition metals, like iron, than for alkaline earth metals like calcium and magnesium, therefore the hydroxamic acid primarily acts to improve the removal of soil on fabric, especially particulate soils, and not additionally as a builder for calcium and magnesium.

[0111] A preferred hydroxamate is the coco hydroxamic acid available under the trade name RK853 from Axis House. Another preferred material is RK842 (an Alkyl hydroxamic acid made from Palm Kernel Oil) from Axis House.

[0112] The invention will now be further described with reference to the following nonlimiting examples.

Examples

[0113] In example 1 coated large detergent particles are manufactured, following the process in PCT/EP2010/055256.

EXAMPLE 1 and COMPARATIVE EXAMPLE A - Preparation of the coated particles

[0114] Raw Materials used were:

Anionic (LAS): Unger Ufasan 65

Nonionic (NI): BASF Lutensol A030 and alcohol ethoxylate with average 30 moles ethoxylation
Coco hydroxamic Acid: Axis House RK 853 (coco hydroxamic acid) For example 1 raw materials were mixed together to give a 69 wt% active paste comprising 80.10 parts LAS (linear alkyl benzene sulphonate), 14.14 parts Nonionic Surfactant and 5.76 parts coco hydroxamic acid.

[0115] For comparative example A raw materials were mixed together to give a 67 wt% active paste comprising 85 parts LAS (linear alkyl benzene sulphonate) and 15 parts Nonionic Surfactant.

[0116] Each paste was pre-heated to the feed temperature and fed to the top of a wiped film evaporator to reduce the moisture content and produce a solid intimate blend, which passed the calcium tolerance test. The conditions used to produce these LAS/NI based blends are given in Table 1.

Table 1

	Jacket Vessel Temp.	81 °C
Feed	Nominal Throughput	55 kg/hr
	Temperature	59°C
	Density	1.08 kg/l
Product	Moisture(KF*)	0.85 %
	Free NaOH	0.06 %
*analysed by Karl Fischer method		

[0117] On exit from the base of the wiped film evaporator, the dried blends dropped onto a chill roll, where they were cooled to less than 30°C.

[0118] After leaving the chill roll, the cooled dried blend particles were milled using a hammer mill, 2% Alusil® was also added to the hammer mill as a mill aid. The resulting milled materials are hygroscopic and were stored in sealed containers.

[0119] The cooled dried milled compositions were fed to a twin-screw co-rotating extruder fitted with a shaped orifice plate and cutter blade. A number of other components were also dosed into the extruder as shown in Table 2.

Table 2

	Example 1	Example A
Extruder	Parts solids (final particle = 100)	Parts solids (final particle = 100)
LAS/NI/(HA) mixture	70.68	69.43
SCMC	0.91	0.95
Perfume	0.73	0.76

[0120] The average particle diameter and thickness of samples of the extruded core particles were found to be 4.46 mm and 1.13 mm respectively. The standard deviation was acceptably low (less than 10%).

[0121] These core particles were then coated using a Strea 1 fluid bed. The coating was added as an aqueous solution and coating completed under conditions given in Table 3. Coating wt% is based on weight of the coated particle.

Table 3

Example	1	A
Mass Solid [kg]	1.25	1.25
Coating Solution (includes dye and fluorescer)	Sodium Carbonate (30%)	Sodium Carbonate (30%)
Mass Coating Solution [kg]	1.8	1.8
Air Inlet Temperature [°C]	80	80
Air Outlet Temperature [°C]	38	38
Coating Feed Rate [g/min]	16	16

(continued)

Example	1	A
Coating Feed temperature [°C]	55	55

[0122] Coated particles compositions are given in Table 4.

Table 4

	Example 1	Example A
Extruder (core)	Parts (final particle = 100)	Parts (final particle = 100)
LAS/NI mixture	66.60	69.43
Including hydroxamate	4.08	-
SCMC	0.91	0.95
Perfume	0.73	0.76
Fluid bed (coating)		
Carbonate	28.53	26.50
Dye	0.04	0.04
Fluorescer	0.28	0.29

Example 2 and Comparative Example B

[0123] Wash testing of Compositions comprising particles of Examples 1 and A

(Examples B and 2)

[0124] Active = LAS/Nonionic 85/15. Comparative example B is made up of 92.9 wt% of particles of Comparative Example A and 7.1 wt% of antifoam.

Table 5 - Composition B -Comparative (dry weights)

		% in Primary lenticular particle	% in Composition
LAS	Core	59.02	54.83
Nonionic	Core	10.41	9.68
SCMC	Core	0.95	0.88
Perfume oil	Core	0.76	0.71
Alusil® (flow aid)	Core	-	-
Sodium carbonate	Coating	28.53	26.5
Fluorescer	Coating	0.29	0.27
Dye	Coating		0.04
		100	92.90
Antifoam	secondary particle		7.1
			100

[0125] Example 2 is made up of 93.17 wt % of particles of Example 1 and 6.13 wt% antifoam.

Table 6 - Example 2

		% in Primary lenticular particle	% in Composition
LAS	core	56.61	52.74
Nonionic	core	9.99	9.31
SCMC	core	0.91	0.85
coco hydroxamic acid	core	4.08	3.80
Alusil® (flow aid)	core	-	-
Perfume oil	core	0.73	0.68
Sodium carbonate	coating	27.36	25.49
Fluorescer	coating	0.28	0.26
Dye	coating	0.04	0.04
		100	93.17
Antifoam	secondary particle		6.83
			100

[0126] Both Examples 2 and B formulations were used at 1.3g/L in a tergo wash at 48°FH to wash Indian Red Mud Stains from cotton and polyester, the resultant SRI_{aw} are given in Table 7.

Measurement of Soil Release Index (SRI)

[0127] SRI is a measure of how much of a stain on textile is removed during a washing process. The intensity of any stain can be measured by means of a reflectometer in terms of the difference between the stain and a clean cloth giving ΔE^* for each stain. It is defined as ΔE^* and is calculated as:

$$\Delta E^* = \sqrt{(L^*_{stain-before} - L^*_{clean-cloth})^2 + (a^*_{stain-before} - a^*_{clean-cloth})^2 + (b^*_{stain-before} - b^*_{clean-cloth})^2}$$

L*, a*, and b* are the coordinates of the CIE 1976 (L*, a*, b*) colour space, determined using a standard reflectometer. ΔE^* can be measured before and after the stain is washed, to give ΔE^*_{bw} (before wash) and ΔE^*_{aw} (after wash). SRI_{aw} is then defined as:

$$SRI_{aw} = 100 - \Delta E^*_{aw}$$

[0128] A SRI_{aw} of 100 means complete removal of a stain.

[0129] ΔE^*_{aw} is the difference in L a b colour space between the clean (unwashed) fabric and the stain after wash. So a ΔE^*_{aw} of zero means a stain that is completely removed. Therefore, a SRI_{aw} of 100 is a completely removed stain. The clean (or virgin) fabric is an "absolute standard" which is not washed. For each experiment, it refers to an identical piece of fabric to that which the stain is applied. Therefore, its point in L a b colour space stays constant.

Table 7

Example	SRI_{aw} Indian Red Mud from Knitted Polyester	SRI_{aw} Indian Red Mud from Knitted Cotton
B (comparative)	77.9	59.1
2 (with coco hydroxamic acid)	81.8	60.1

[0130] Similar results are obtained by use of octyl hydroxamate in place of coco hydroxamic acid.

Comparative Examples C and D using higher amounts of carbonate

[0131]

Table 8

	Comparative Example C	Comparative Example D
NaLAS (Anionic)	33%	31%
Neodol 25-7 (Nonionic)	17%	16%
Na_2CO_3 (Sodium Carbonate)	50%	48%
Octyl hydroxamate, potassium salt		5%
Active: carbonate	1:1	approx 1:1 (very small excess of carbonate)

[0132] Comparative compositions C and D were used in the following cleaning experiment.
Tergo Wash study at 26°FH
Comparative compositions B and C dosed at 1.5g/L
Run time 12 mins @ 100rpm

Table 9

Composition	SRI_{aw} Indian Red Mud from Knitted Polyester
C (comparative)	76.6
D (comparative with octyl hydroxamate)	71.7

[0133] This shows that at these low ratios of active detergent to carbonate there is no benefit from inclusion of the hydroxamate. Indeed the reverse appears to be the case. The use of 7EO nonionic in place of the 30EO nonionic used in example2 should lead, if anything, to improved SRI_{aw}

[0134] On the other hand from Example 1, it can be seen that by moving to the higher ratios of active detergent to carbonate the hydroxamate has a significant effect, even if the surfactant level is reduced by the inclusion of the hydroxamate.

Claims

1. A particulate detergent composition comprising at least 70% by number coated (core and shell) detergent particles comprising 40 to 90 wt% surfactant and 20 to 40 wt% sodium carbonate, the ratio of surfactant to sodium carbonate being at least 1.5:1, **characterised in that** the coated particles further comprise hydroxamate.

2. A composition according to claim 1 in which the amount of hydroxamate lies in the range 0.005 to 12 wt% of the particle.

3. A composition according to any preceding claim in which the amount of sodium carbonate is less than half the total active detergent.

4. A composition according to any preceding claim in which the coated particles comprise a core comprising surfactant material and a coating comprising sodium carbonate.

5. A composition according to any preceding claim in which the hydroxamate is located in the core.

6. A composition according to any preceding claim in which the majority of the sodium carbonate is provided by the coating.

7. A composition according to any preceding claim in which the core is made by extrusion of a dry less than 1 wt% water surfactant blend.

8. A composition according to any preceding claim in which the core comprises a blend of anionic and nonionic

surfactant, the anionic surfactant being present in an excess over the nonionic surfactant.

9. A composition according to any preceding claim in which the core comprises calcium tolerant blends of surfactants as defined herein.

10. A composition according to any preceding claim in which the coated detergent particle has a core to shell ratio of from 3 to 1:1 by weight, preferably 2.5 to 1.5 to 1 and optimally about 2:1.

11. A composition according to any preceding claim in which the ratio of anionic to nonionic surfactant is at least 1:1, more preferably at least 3:2, preferably, it is at most 9:1 most preferred is the range is 1:1 to 9:1, even 3:2 to 9:1.

12. A composition according to any preceding claim in which the coated detergent particle has perpendicular dimensions x, y and z, wherein x is from 1 to 2 mm, y is from 3 to 8 mm, and z is from 3 to 8 mm, wherein the particle comprises:

(i) from 40 to 90 wt % surfactant selected from: anionic surfactant; and, non-ionic surfactant, preferably 50 to 80 wt%.
(ii) from 10 to 40 wt % sodium carbonate, preferably 18 to 35 wt%;
(iii) from 0.5 to 12 wt % hydroxamate, preferably 2 to 8 wt%
(iv) from 0.0001 to 5 wt % perfume;
(v) from 0 to 10 wt % organic polymers; and,
(vi) from 0 to 20 wt %, preferably 0 to 10 wt %, of other ingredients.

Preferably the sodium carbonate is present as a coating and the surfactant is present as a core. More preferably the hydroxamate is present in the core.

13. A composition according to any preceding claim in which the coating comprises from 0 to 2 wt% of an organic polymer, more preferably from 0 to 0.4 wt% of the particle.

14. A composition according to claim 13 in which the polymer is sodium carboxymethyl cellulose.

15. A composition according to any preceding claim in which the ratio of hydroxamate to detersive surfactant system (surfactant) is in the range 1:4 to 1: 8000, preferably 1:7 to 1:40 most preferably 1:10 to 1:25 parts by weight.

16. Use of a particulate composition comprising at least 15% sodium carbonate and surfactant at least 1.5 times the level of the sodium carbonate and hydroxamate in a fabric washing process carried out in 35 deg F or higher water to remove clay soils from fabric.

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EUROPEAN SEARCH REPORT

Application Number
EP 10 18 7505

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	WO 2010/069957 A1 (UNILEVER) 24 June 2010 (2010-06-24) * page 15, line 16 - line 21; claims * -----	1-16	INV. C11D1/52 C11D3/10 C11D17/06 C11D3/32
A	DE 43 13 137 A1 (BASF AG) 27 October 1994 (1994-10-27) * page 6, line 24; claims * -----	1-16	
A	EP 0 388 389 A2 (MONSANTO EUROPE SA) 19 September 1990 (1990-09-19) * claims * -----	1-16	
			TECHNICAL FIELDS SEARCHED (IPC)
			C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	2 March 2011	Hillebrecht, Dieter

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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& : member of the same patent family, corresponding document

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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 10 18 7505

02-03-2011

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