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(54) Title: BLEACHING CATALYST ADMIXED WITH AN INSOLUBLE SUPPORT MATRIX

(57) Abstract: A composition comprises a bleaching catalyst admixed with an insoluble support matrix.



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BLEACHING CATALYST ADMIXED WITH AN INSOLUBLE SUPPORT MATRIX

The present invention relates to a composition comprising a bleaching catalyst admixed with a support matrix.

Inorganic peroxygen compounds, especially hydrogen peroxide and solid peroxygen compounds which dissolve in water to release hydrogen peroxide, such as sodium perborate and sodium carbonate perhydrate, have long been used as oxidizing agents for purposes of disinfection and bleaching. The oxidizing action of these substances in dilute solutions is heavily dependent on the temperature; for instance, with H_2O_2 or perborate in alkaline bleaching liquors, sufficiently rapid bleaching of soiled textiles is obtained only at temperatures above about 80°C. At lower temperatures the oxidizing action of the inorganic peroxygen compounds can be enhanced by adding what are called bleach activators, for which numerous proposals have been disclosed in the literature, principally from the classes of the N-acyl or O-acyl compounds, examples being polyacylated alkylenediamines, especially tetraacetythylenediamine, acylated glycolurils, especially tetraacetyl glycoluril, N-acylated hydantoins, hydrazides, triazoles, hydrotriazines, urazoles, diketopiperazines, sulfurylamides and cyanurates, and also carboxylic anhydrides, especially phthalic anhydride, carboxylic esters, especially sodium nonanoyloxybenzenesulfonate, sodium isononanoyloxybenzenesulfonate and acylated sugar derivatives, such as pentaacetylglucose. By addition of these substances the bleaching action of aqueous peroxide liquors can be increased to such an extent that even at temperatures around 60°C essentially the same activities occur as with the peroxide liquor alone at 95°C.

Given the concern for energy-saving laundering and bleaching methods, in recent years application temperatures well below 60°C have gained in importance, in particular below 45°C down to the cold water temperature, below 20°C.

Previously the use of transition metal salts and transition metal complexes has been described, for example in European patent applications EP 392 592, EP 443 651, EP 458 397, EP 544 490, EP 549 271 and WO 01/48138, referred to as bleaching catalysts.

It has now been observed that textiles, particularly coloured textiles, fade after a number of washes in the presence of a bleach catalyst. It is theorised that some catalysts previously used not only catalyze the activity of the peroxygen compound but also remain at least partly on their surfaces being bleached, and even when the cleaning operation has ended. These transition metal salts can then be oxidized and so cause colour damage, and, in extreme cases, the risk of oxidative damage to the textiles since they directly contact the textile. As an example a deposit of Mn (II), is readily oxidized to Mn (IV) dioxide, which is a very strong oxidizing agent, particularly toward easily oxidizable substances, such as organic dye compounds.

All of the bleaching catalysts known have the disadvantage that they are brought into intimate contact with the surfaces of the articles being treated and as such typically a portion of the catalyst adheres to those surfaces or even penetrate those surfaces. This gives rise to a risk of unwanted colour changes and in rare cases, there may even be holes / tears, as a result of fibre damage.

According to a first aspect of the invention there is provided a composition comprising a bleaching catalyst admixed with an insoluble support matrix.

Preferably the matrix is insoluble in aqueous media.

It has been found that the supported bleach catalyst of the present invention has a number of advantageous properties. The principle advantageous property is that the bleach catalyst, particularly the transition metal thereof when present (when used in a washing / bleaching operation) is not substantive upon an item being washed or bleached. Thus detrimental damage to the item is drastically reduced.

Another advantage of the present invention (when used in a washing / bleaching operation) is the catalysis of the oxidizing action and bleaching action of inorganic peroxygen compound at low temperatures. Effective catalysis is observed below 80°C and in particular from about 12°C to 40°C.

Another advantage of the present invention (when used in a washing / bleaching operation) is to allow for reduction of peroxygen amount and / or bleach activator (e.g. TAED) in a cleaning formulation while maintaining bleaching performance, thus allowing for cost reduction.

Being reusable and recoverable, a further advantage of the present invention is the repeated application of the novel solid oxidation bleaching catalyst. Such repeated applications can be useful in waste water treatment/water purification, for example in the textile industry and in pulp / cellulose bleaching operations.

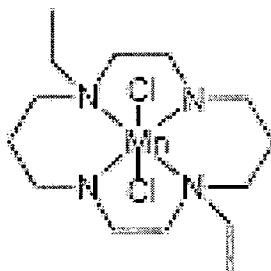
Preferably the bleach catalyst comprises a transition metal compound based upon one or more of manganese, cop-

per, iron, silver, platinum, cobalt, nickel, titanium, zirconium, tungsten, molybdenum, ruthenium, cerium, lanthanum or vanadium. Most preferably the bleach catalyst comprises a transition metal compound based upon manganese.

The manganese bleach catalyst may be selected from wide range of manganese compounds. Suitable inorganic compounds (often salts) of manganese (e.g. Mn (II)) include hydrated / anhydrous halide (e.g. chloride / bromide), sulphate, sulphide, carbonate, nitrate, oxide. Further examples of suitable compounds (often salts) of manganese (e.g. Mn (II)) include hydrated / anhydrous acetate, lactate, acetyl acetate, cyclohexanebutyrate, phthalocyanine, bis (ethylcyclopentadienyl), bis (pentamethylcyclopentadienyl).

Most preferably the bleach catalyst comprises manganese (II) acetate tetrahydrate and/or manganese (II) sulphate monohydrate.

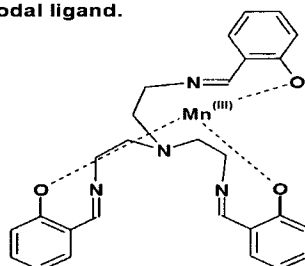
Alternatively the bleach catalyst may comprise:-



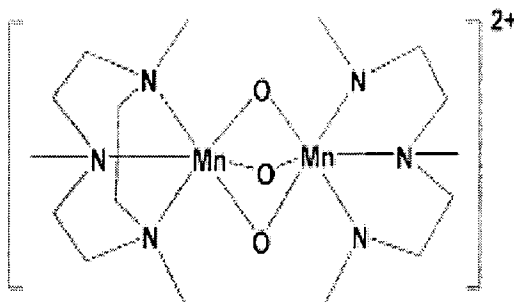
(1, 8 - diethyl-1, 4, 8, 11-TetraAzaCycloTetraDecane) manganese (II) chloride [Mn-TACTD].

Alternatively the bleach catalyst may comprise:-

Manganese (III) Catalyst with an organic tripodal ligand.



Alternatively the bleach catalyst may comprise:-



Generally the bleach catalyst comprises from 0.001% to 10.00%, preferably from 0.01% to 5.00% more preferably from 0.15% to 2.5% of the composition, with the remainder of the composition comprising the support matrix.

Generally the composition is for use in a washing operation, e.g. a textile washing operation in an automatic washing machine. The composition may be used for multiple washing operations; in this case the composition may comprise a shaped article.

Preferably the shaped article is an article which is commonly used in a washing operation but which has been modified to comprise the composition of invention. One particularly preferred such article is a "dosing ball", which are commonly used, particularly in laundry washing

operations, for the dosing of the correct amount of detergent into the washing cycle. Such dosing balls are by their nature reusable and thus the dosing ball is able to provide a bleach catalyst function over a plurality of wash cycles. The whole / a portion of the dosing may comprise the composition.

Another preferred article is a bucket / container which is used in combination with a bleach based formulation in a cleaning operation, e.g. for hard surface cleaning (floor cleaning or glass/window cleaning) or for a manual laundry operation. The bucket / container are preferably made by injection moulding of plastic (PP, PE, ABS, PMMA, polyamide, PVC, PU or any other plastic material).

A yet further article is a plastic table surface such as the kind used for manual laundry cleaning (in some developing countries).

Another article is a brush used in combination with a bleach based formulation in a cleaning operation, e.g. for rubbing clothes/laundry, dish / house ware or for toilet / ceramic cleaning.

Further articles include roll balls for pre-treating laundry, cleaning cloths, internal plastic components of automatic laundry washing machines and dishwashing machine/, reusable plastic food containers / cutlery.

Alternatively the shaped article may comprise a powder, a particle, a flake, a sheet or a fibre (e.g. a micro-fibre / nano-fibre) or a sponge.

The shaped article may be in the form of a foam.

These micro-structures may be agglomerated together into a macro-structure, e.g. the particles may be partially coalesced to make a honeycomb type structure or the fi-

bres may be coalesced to make a woven / non-woven mat macro-structure.

Where the support is a particle, the preferred particle size is in the range of from 10nm to 10mm, more preferably from 0.1mm to 10mm, most preferably from 0.3mm to 0.5mm. The particles are preferably spherical.

Where the support is fibre, the preferred diameter in the range of from 30 nm to 2000 μ m, more preferably from 60nm to 1000 μ m.

The support matrix generally comprises a polymeric material. Suitable polymeric materials may be selected from the group of polyurethanes; polyolefins / hydrocarbons, e.g. polypropylene, polyethylene, polystyrene, polybutadiene; polyamides; polyvinyl chloride; polyesters, e.g. poly methyl methacrylate, poly vinyl acetate; phenolic resins; copolymers, e.g. polymethylmethacrylate with n-butylacrylate and styrene; natural / modified natural polymers, e.g. cellulose, rubber, latex, styrene-butadiene rubber, butyl rubber, chlorinated / hydrochlorinated rubber, nitrile rubber, vulcanized rubber, siliconised rubber; polycarbonates; silicone resins (e.g. polydimethylsilicone); fluorinated resins, e.g. PTFE.

The support matrix may comprise an inorganic material. Suitable inorganic materials include zeolite, silica, alumina, zirconia, phosphates (e.g. AlPO_4), ceramic, glass, bauxite, anatase (TiO_2) and carbon.

According to a second aspect of the invention there is provided a method of producing a composition comprising a bleaching catalyst admixed with an insoluble support matrix.

Preferably the method comprises one or more techniques selected from the group of spinning, electro-spinning, solvent casting, thermal treatment, extrusion, co-extrusion, moulding, screw injection moulding, injection moulding, blow moulding, machine moulding, thermal press moulding, free moulding, compression moulding, transfer moulding, roto-moulding, jet moulding, steam chest moulding, sheet moulding, sheet moulding compound SMC, laminated moulding, cast moulding, moulding powder, moulding pressure, forming, vacuum forming, plug-assist vacuum forming, hot forming, free-blow forming, high-rate forming, magnetic forming, rubber forming, drape forming, plug-and-ring forming, hot powder forming, snapback forming, matched-die forming, cavity forming, cavity assist-forming, shock-forming, electrochemical forming, electro forming, pressing, cold forging and/or polymerisation.

Preferably thermal treatment (or thermoforming) involves heating the support material (e.g. a polymer such as PMMA) above its melting temperature and/or above its T_g (glass transition temperature), admixing the bleach catalyst therewith and allowing the admixture to cool.

Preferably casting involves dissolution of both the support and the oxidation catalyst in a solvent followed by deposition of the solution onto a surface (e.g. stainless steel or semiconductor material) and evaporation of the solvent with production of a free-standing solid support. Suitable solvents include: chlorinated organic solvents (e.g. chloroform), ketones (e.g. acetone or methyl ethyl ketone), dimethylsulfoxide (DMSO), alcohols, aliphatic or aromatic hydrocarbons, glycol ethers or organic acids, (e.g. acetic acid or formic acid).

Preferably extrusion and co-extrusion involves passing a composition comprising the support and the catalyst

through an extrusion machine or a press machine. The extrusion is preferably performed at an elevated temperature which may be affected by heating or by the pressure applied by the extruder.

The extrusion conditions depend to a degree upon the exact nature of the composition being extruded and by the type of machine used. A suitable extrusion operating temperature is, for example, 90-260°C. A suitable extrusion operating screw velocity is, for example, 25-250 rpm (rotation per minute), preferably 50-125 rpm. A suitable extrusion operating pressure is, for example, 30-250 bar. The extrudate is preferably in the form of pellets or strands or noodles.

Preferably electro spinning involves dissolution of both the support and the oxidation catalyst in a solvent followed by discharge of the solvent admixture through an orifice into a chamber where evaporation of the solvent occurs. Electric charging of the admixture occurs on or before discharge from the orifice. The charging of the admixture causes the admixture to distribute itself widely and sparsely leading to the production of fine fibres.

Preferably polymerisation involves formation of a polymeric support, by polymerisation of the polymer constituents in the presence of the oxidation catalyst to form a polymer matrix having the oxidation catalyst distributed there-through. The polymer matrix may be porous and / or be in the form a sponge. Preferred polymers suitable for use in this method include polymers formed in a condensation reaction such as polyesters and polyurethanes. Indeed polyurethanes are particularly suitable since foams and sponges may be readily made from such polymers.

Preferably the supported bleach catalyst is for incorporation in a detergent composition, e.g. a dishwashing, laundry, hard surface cleaning and / or disinfecting composition. Generally the composition is for use in the appropriate washing operation in a washing machine or other washing vessel such as a sink, bucket, etc. Alternatively the composition may be used in an additive (e.g. additives which are complementary to a detergent product used in a washing operation) or in addition to a product which contains a bleach.

The detergent composition may comprise a homogenous product, e.g. a uniform powder / liquid or alternatively the detergent composition may have a plurality of individual phases, e.g. such as a multi-phase tablet or a number of liquids contained in a multi-chamber container / bottle. Where a plurality of individual phases is present the supported bleach catalyst may be present in only a limited number of the phases, e.g. for a two phase tablet one phase may contain the supported bleach catalyst and one phase could be bleach catalyst free (and may contain a bleach, such as a source of peroxide / active oxygen).

The detergent composition typically comprises at least one of surfactant (anionic, non-ionic, cationic or amphoteric), builder, bleach, bleach activator, bleach stabilizer, bleaching catalyst, enzyme, polymer, co-builder, alkalizing agent, acidifying agent, anti-redeposition agent, silver protectant, colourant, optical brightener, UV stabilizer, fabric softener, fragrance, soil repellent, antcrease substance, antibacterial substance, colour protectant, discolouration inhibitor, vitamin, phyllosilicate, odor-complexing substance, rinse aid, foam inhibitor, foaming agent, preservative, or auxiliary.

The invention is now illustrated by reference to the following non-limiting examples.

Examples

Example 1: Catalyst Preparation

20g of Polydimethylsilicone (PDMS) (Sylgard 184 by Dow Corning) was weighed in a beaker. 10mg of catalyst Mn-TACN or Mn Acetate and 1g of curing agent was added and mixed. The admixture was left for 24 hours to cure. The cured resin formulation was in the form of a disc having a diameter of 5cm and a height of 1.3cm.

Example 2: Oxidation Catalysis Study

The following reagents were prepared, in deionised water.

<u>Reagent</u>	<u>g/L</u>	<u>ppm</u>
Sodium Percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$)	1.38	395 H_2O_2
TAED	0.30	300
Mn-TACN (homogeneous)	0.005	5
Cat (Example 1) (MnTACN)	0.025	25
Mn-Acetate (homogeneous)	0.005	5
Cat (Example 1) (Mn-Acetate)	0.025	25
Saffron	0.35	35

A solution containing sodium percarbonate and bleach TAED was compared vs. a solution containing PCB, TAED and the catalyst Mn (homogeneous) or vs. a solution containing PCB + TAED + the catalyst Mn (heterogeneous).

Protocol Used: Beaker Test

Saffron solution (fresh, protected from light)

Deionised water

Temperature: 20°C

Reaction studied over 30 minutes.

UV/VIS Abs at 430nm to monitor the oxidation rate on substrate (saffron).

Note: the lower the absorbance residue, the better the catalytic effect/performance.

Results

Time (min)	PCB + TAED	HOMOGENEOUS CATALYSES PCB + TAED + CAT		HETEROGENEOUS CATALYSES PCB + TAED + CAT	
		Mn TACN	Mn Acetate	Mn TACN	Mn Acetate
0	100	100	100	100	100
2	100	99	98	100	99
4	100	98	93	95	98
6	98	97	86	93	97
8	96	95	82	88	95
10	94	91	80	85	91
12	92	87	79	80	87
14	90	82	75	73	85
16	87	73	74	68	83
18	85	64	69	62	82
20	83	55	68	58	79
22	82	41	66	53	78
24	79	30	65	47	76
26	76	23	65	45	75
28	75	18	63	43	73

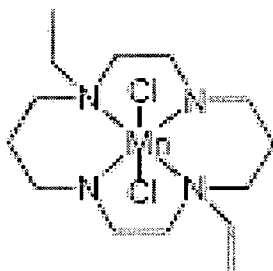
(Each value is the average of three measurements.)

The results show that the use of Mn-TACN is effective as oxidation catalyst (vs. no catalyst) and that heterogeneous catalysis is good on the bleaching of saffron.

CLAIMS

1. A composition comprising a catalyst admixed with an insoluble support matrix.
2. A composition comprising a bleaching catalyst admixed with an insoluble support matrix.
3. A composition according to claim 2, wherein the bleach catalyst comprises a transition metal compound based upon one or more of manganese, copper, iron, silver, platinum, cobalt, nickel, titanium, vanadium, cerium, lanthanum, zirconium, tungsten, molybdenum, ruthenium.
4. A composition according to claim 3, wherein the bleach catalyst comprises a transition metal compound based upon manganese.
5. A composition according to claim 4, wherein the bleach catalyst comprises a hydrated / anhydrous compound of manganese selected from the group comprising the halide (chloride/bromide), sulphate, sulphide, carbonate, nitrate, oxide, acetate, lactate, acetyl acetate, cyclohexanebutyrate, phthalocyanine, gluconate, bis (ethylcyclopentadienyl), bis (pentamethylcyclopentadienyl), polyol, sorbitol, iditol, mannitol, xylitol, arabitol, lactose, dulcitol, adonitol, erythritol, inositol, catechol.

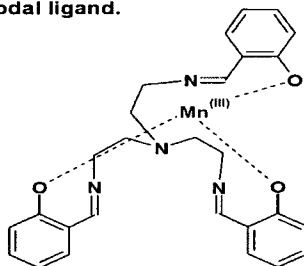
6. A composition according to claim 4, wherein the bleach catalyst comprises:-



(1, 8 - diethyl-1 , 4, 8, 11 - TetraAzaCycloTetraDecane)
Manganese (II) chloride.

7. A composition according to claim 4, wherein the bleach catalyst comprises:-

Manganese (III) Catalyst with an organic tripodal ligand.



8. A composition according to claim 3, wherein the bleach catalyst comprises: manganese (II) acetate tetrahydrate and/or manganese (II) sulphate monohydrate.

9. A composition according to any one of the preceding claims, wherein the bleach catalyst comprises from 0.0001% to 20%, preferably from 0.001% to 10.00%, preferably from 0.01% to 5.00% more preferably from 0.15% to 2.5% of the composition.

10. A composition according to any one of the preceding claims where the matrix exhibits porosity.

11. A composition according to any one of the preceding claims, wherein the support matrix is a shaped article or gadget.

12. A composition according to claim 11, wherein the shaped article is a detergent dosing ball or a part of an automatic washing machine.

13. A composition according to claim 11, wherein the support is at least one of a powder, a particle, a flake, an agglomerate, a sponge, a sheet or a fibre (e.g. a micro-fibre or a nano-fibre).

14. A composition according to claim 13, wherein the support is a particle having a particle diameter in the range of from 10nm to 10mm.

15. A composition according to claim 13, wherein the support is a fibre having a diameter in the range of from 30 nm to 2000 μ m, more preferably from 60nm to 1000 μ m.

16. A composition in accordance with any one of preceding claims in which the support matrix comprises a polymeric material selected from the group of poly methyl methacrylate, polyurethanes; polyolefins / hydrocarbons, e.g. polypropylene, polyethylene, polystyrene, polybutadiene; polyamides; polyvinyl chloride; polyesters, poly vinyl acetate; phenolic resins; copolymers, e.g. polymethylmethacrylate with n-butylacrylate and styrene; natural / modified natural polymers, e.g. cellulose, rubber, latex, styrene-butadiene rubber, butyl rubber, chlorinated / hydrochlorinated rubber, nitrile rubber, vulcanized rubber, siliconised rubber; polycarbonates; silicone resins (e.g. polydimethylsilicone); fluorinated resins, e.g. PTFE.

17. A composition in accordance with any one of claims 1 to 15 in which the support matrix comprises one or more of zeolite silica, alumina, zirconia, phosphates (e.g. AlPO_4), ceramic, glass, bauxite, anatase (TiO_2), carbon.

18. A method of producing the bleach catalyst composition in accordance with any one of preceding claims in which the technique of thermal treatment, casting, extrusion and / or electro-spinning is used.

19. A method of producing the bleach catalyst composition in accordance with any one of preceding claims in which the technique of driving a thermoplastic polymer above its glass transition temperature is used.

20. A method of producing the bleach catalyst composition in accordance with claim 18, in which the technique of casting / solvent casting is used.

21. A method of producing the bleach catalyst composition in accordance with claim 19, in which the technique of extrusion is used.

22. A method of producing the bleach catalyst composition in accordance with claim 18, in which the technique of electro-spinning is used.

23. A detergent composition comprising a bleach catalyst composition in accordance with any one of claims 1 to 17.

24. A detergent comprising the composition any one of claims 1 to 17 and at least one of surfactant (non-ionic, anionic, cationic or amphoteric), builder, bleach, bleach activator, bleach stabilizer, bleaching catalyst, enzyme, polymer, cobuilder, alkalizing agent, acidifying agent, antiredeposition agent, silver protectant, colourant, optical brightener, UV stabilizer, fabric softener, fragrance, soil repellent, antcrease substance, antibacterial substance, colour protectant, discolouration inhibitor, vitamin, phyllosilicate, odor-complexing substance, rinse aid, foam inhibitor, foaming agent, preservative, or auxiliary.

25. Use of a detergent composition according to claim 24 in a dishwashing, laundry and / or hard surface cleaning operation and/ or a sanitizer/disinfectant operation.

26. Use of a heterogeneous catalyst according to claim 1 for application in waste water treatment, in the textile industry, in hair care / hair bleaching formulations, in pulp and cellulose bleaching operations.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/001001

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D3/39 C11D17/04
ADD.

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

B. FIELDS SEARCHED

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

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

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

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/132456 A1 (RECKITT BENCKISER NV [NL]; RECKITT BENCKISER UK LTD [GB]; BALDAN SILVI) 6 November 2008 (2008-11-06) claims 1-26	1-26
X	EP 1 621 605 A1 (CIBA SC HOLDING AG [CH] CIBA HOLDING INC [CH]) 1 February 2006 (2006-02-01) paragraph [0023] - paragraph [0027]; claims 1-18 ----- -/--	1-4,7, 9-11,13, 14,16, 23-25

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

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

23 July 2010

Date of mailing of the international search report

30/07/2010

Name and mailing address of the ISA/

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Richards, Michael

INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 889 900 A1 (BOLTON MANITOBA SPA [IT]) 20 February 2008 (2008-02-20) paragraph [0045] - paragraph [0048]; claims 1-30 -----	1-4, 7, 10-13, 15, 16, 18, 19, 22-26
X	EP 1 170 356 A1 (PROCTER & GAMBLE [US]) 9 January 2002 (2002-01-09) paragraph [0132] - paragraph [0136]; claims 1-16 -----	1-4, 9-13, 15, 16, 23-25
X, P	WO 2010/010334 A1 (RECKITT BENCKISER NV [NL]; ZAMUNER DORA [IT]; RECKITT BENCKISER UK LTD) 28 January 2010 (2010-01-28) page 6, line 4 - line 21; claims 1-15 -----	1-12, 16, 18-20, 23-26
A	WO 03/054128 A1 (HENKEL KGAA [DE]; GENTSCHEV PAVEL [DE]; DOERING STEVE [DE]; BREYER JAC) 3 July 2003 (2003-07-03) claims 1-23 -----	1-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

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