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(54) **Title**: LAUNDRY TREATMENT COMPOSITIONS

(57) **Abstract**: According to the invention there is provided a granular laundry treatment composition including a spherical SiO_2 particle for use in the wash cycle. A method for applying these compositions during the wash cycle of a laundry process as well as the use of these particles to reduce clothes damage is also included.

LAUNDRY TREATMENT COMPOSITIONS

FIELD OF INVENTION

The present invention relates to wash added, laundry detergent compositions and methods for using the same during the wash cycle of a consumer laundry process.

BACKGROUND

Coloured clothes are extremely popular with consumers. To remove dirt on washing, the clothes are vigorously agitated in water with a washing formulation. This process leads to damage on the surface of the clothes, which reduces their aesthetic appeal. This damage is particularly a problem when granular laundry compositions are used.

WO 2007/111887 (Proctor & Gamble) discloses liquid compositions comprising hueing dye and a pearlescent agent. The pearlescent agent is added to counteract the darkening effect of the hueing dye on the appearance of the liquid composition. The pearlescent agent may be organic or inorganic in nature, with glass or metal oxide coated glass being disclosed.

US 4,051,046 (Procter & Gamble) discloses detergent compositions comprising surfactant and low concentrations of substantially water-insoluble particulate material with a range of 1 to 50 micrometers for providing fabric benefits. The document also discloses that the use of particulate water-insoluble materials having an average diameter of more

than about 50 micrometers will not procure the mentioned fabric benefits.

SUMMARY OF INVENTION

We have found that SiO_2 particles provide improved colour care by reducing damage caused by fabric laundering.

In one aspect the present invention provides a granular laundry treatment composition containing less than 1 wt.% of phosphate comprising:

(i) from 0.1 wt.% to 40 wt.%, preferably 0.5 to 5 wt.%, of a spherical SiO_2 particle, the SiO_2 particle having a size in the range from 0.1 to 5000 microns;
(ii) from 2 to 70 wt.% of a surfactant; and,
(iii) from 1 to 50 wt.% of a builder.

Preferably the spherical SiO_2 particle is chosen from sand, therein having a size in the range of 1 to 2000 microns, and/or glass, therein having a size in the range of from 100 to 2000 microns.

A second aspect of the invention provides a domestic method of treating a textile, the method comprising the steps of:

(i) treating a textile with an aqueous solution of from 1 to 20 g/l of the composition of the first aspect; and,
(ii) rinsing and drying the textile.

A third aspect of the invention provides the use of spherical SiO_2 particles to reduce damage to clothes being laundered during a domestic main wash process.

Preferably in the aforementioned use, the spherical SiO_2 particle is chosen from sand, therein having a size in the range of 1 to 2000 microns, and/or glass, therein having a size in the range of from 100 to 2000 microns.

DETAILED DESCRIPTION OF THE INVENTION

The amount of components in the granular laundry treatment composition quoted herein are wt.% of total composition unless otherwise stated.

The spherical SiO_2 particles should have a roundness (ratio of axes) of >80%, preferably >94%. The roundness (ratio of axes) is a measurement of the length/width relationship with values in the range 0 - 1. The length is the shortest axis and the width is the longest axis. A perfect circle has a roundness value of 1.0 and a thin rectangle values approaching 0. To calculate the roundness, images of the particles should be taken, preferably with a suitable microscope, for example a PharmaVision 830 available from Malvern™.

The spherical SiO_2 particle is preferably chosen from sand, therein having a size in the range of 1 to 2000 microns, and/or glass, therein having a size in the range of from 100 to 2000 microns.

Preferably the size of the spherical SiO_2 particle is 100 to 2000 microns, more preferably 100 to 1000 microns, even more preferably 100 to 500 microns, for example 100 to 200 microns.

The size of the spherical SiO_2 particle is measured using graded sieves and it is that which is retained or passes through such sieves.

The spherical SiO_2 particle comprises SiO_2 at a level of from 50 to 100 wt.%, preferably from 55 to 100 wt.%, more preferably from 65 to 100 wt.%. Alternatively, the SiO_2 particles may contain other components, examples of such being Na_2O, CaO and MgO. If present at all, the other components are preferably present at 45 wt.% or less, more preferably 35 wt.% or less based on wt.% of the SiO_2 particle.

SURFACTANT

The composition comprises between 2 to 70 wt.% of a surfactant, most preferably 10 to 30 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.

Suitable nonionic 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. Specific nonionic detergent compounds are C_6 to C_{22} 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 C_8 to C_{18} primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

Suitable anionic detergent compounds which 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 C_8 to C_{18} alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C_9 to C_{20} benzene sulphonates, particularly sodium linear secondary alkyl C_{10} to C_{15} 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. The preferred anionic detergent compounds are sodium C_{11} to C_{15} alkyl benzene sulphonates and sodium C_{12} to C_{18} 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.

Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C_{16} to C_{18} primary alcohol sulphate together with a C_{12} to C_{15} primary alcohol 3 to 7 EO ethoxylate.

The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25 to 90 wt.% of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 5 wt.% to about 40 wt.% of the surfactant system.

BUILDERS OR COMPLEXING AGENTS

The composition comprises from 1 to 50 wt.% of a builder.

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

It is preferred that when an insoluble inorganic builder, e.g., zeolite, is used the size is in the range 0.1 to 10 microns (as measured by The Mastersizer 2000 particle size analyzer using laser diffraction ex Malvern™).

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

The composition may also contain 0-50 wt.% of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below. Many builders are also bleach-stabilising agents by virtue of their ability to complex metal ions.

Zeolite and carbonate (carbonate (including bicarbonate and sesquicarbonate) are preferred builders.

The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 15 wt.%. Aluminosilicates are materials having the general formula:

0.8-1.5 M_2O. Al_2O_3. 0.8-6 SiO_2

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. The ratio of surfactants to aluminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term 'phosphate' embraces diphosphate, triphosphate, and phosphonate species. However, the composition comprises less than 1 wt.% of such phosphate builders. Preferably the laundry detergent formulation is a non-phosphate built laundry detergent formulation.

Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).

We have also found that the presence of an inorganic builder, in particular a zeolite or other insoluble inorganic particulates, contributes to the abrasion of fabrics under wash conditions. The use of spherical SiO_2 particles ameliorates this problem.

SHADING AGENT

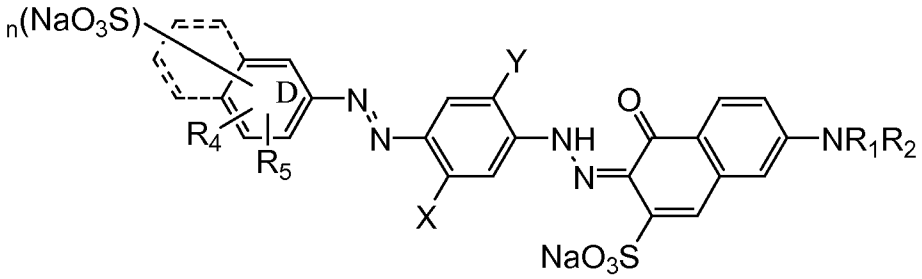
The granular laundry treatment composition preferably comprises a blue or violet shading agent in the range from 0.0001 to 0.01 wt.%. The shading agents reduce the perception of damage to many coloured garments and increase whiteness of white garments.

The shading agents are preferably selected from blue and violet dyes of the solvent disperse basic, direct and acid type listed in the colour index (Society of Dyers and Colourists and American Association of Textile Chemists and Colorists 2002).

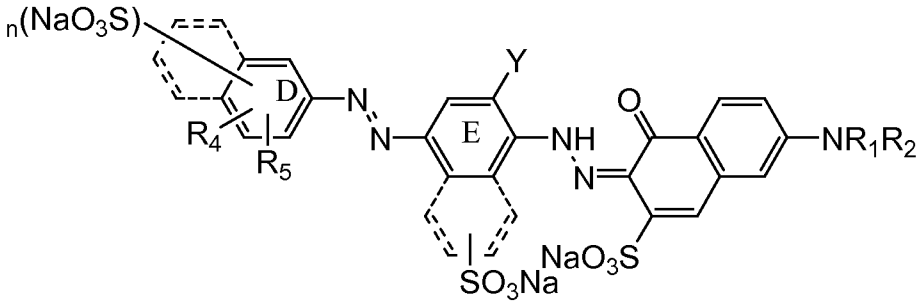
Preferably a direct violet or direct blue dyes is present. Preferably the dyes are *bis*-azo, *tris*-azo dyes or triphendioxazine dye. The carcinogenic benzidene based dyes are not preferred.

Bis-azo copper containing dyes such as direct violet 66 may be used.

The most preferred bis-azo dyes have the following structure:



or



wherein:

ring D and E may be independently naphthyl or phenyl as shown;

R_1 is selected from: hydrogen and C1-C4-alkyl, preferably hydrogen;

R_2 is selected from: hydrogen, C1-C4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;

R_3 and R_4 are independently selected from: hydrogen and C1-C4-alkyl, preferably hydrogen or methyl;

X and Y are independently selected from: hydrogen, C1-C4-alkyl and C1-C4-alkoxy; preferably the dye has X= methyl; and, Y = methoxy and n is 0, 1 or 2, preferably 1 or 2.

Preferred bis-azo dyes are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, and direct violet 99.

Preferred solvent and disperse dyes, are selected from, mono-azo or anthraquinone dyes, most preferably, solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63 and disperse violet 77.

A preferred pigment is pigment violet 23.

ENZYMES

The granular laundry treatment composition preferably comprises one or more enzymes which provide cleaning performance and/or fabric care benefits. Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, mannanases, pectate lyases, keratinases, reductases, oxidases, phenoloxidases,- lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, arabinosidases, hyaluronidase, chondroitinase, laccase, and amylases, or mixtures thereof. A typical combination is an enzyme cocktail that may comprise, for example, a protease and lipase in conjunction with amylase. When present in a cleaning composition, the aforementioned additional enzymes may be present at levels from about 0.00001 wt.% to about 2 wt.%, from about 0.0001 wt.% to about 1 wt.% or even from

about 0.001 wt.% to about 0.5 wt.% enzyme protein by weight of the composition.

Preferred enzymes are cellulases.

FLUORESCENT AGENT

The composition 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 0.1 wt.%. 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]trazole, 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)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfoslyryl)biphenyl.

PERFUME

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.

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.

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.

Perfume and top note may be used to cue the fabric care benefit of the invention.

It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

POLYMERS

The composition may comprise one or more polymers. Examples are carboxymethylcellulose, poly(ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates,

maleic/acrylic acid copolymers and lauryl methacrylate/ acrylic acid copolymers.

Polymers present to prevent dye deposition, for example poly(vinylpyrrolidone), poly(vinylpyridine-N-oxide), and poly(vinylimidazole), are preferably absent from the formulation.

Experimental

Example 1

Three knitted cotton fabric swatches (20 by 20 cm) dyed with Vat Blue 4 were washed in a compartment of a Quickwash Plus ™ fabric testing system (SDL international). In a separate compartment equivalent knitted cotton swatches were placed, but these were dyes with Reactive Orange 16. The machine was filled with 3.5 litres of 26° French Hard water and 24.5 g of Persil Colour Powder (ex UK) a Las/Non-ionic surfactant powder built with zeolite and carbonate. To this was added 0.5 g of antifoam. The wash took 15 minutes, and following this the machine was drained, spun, and then three 90 second rinses performed, draining and spinning after each. Following the wash the fabric was tumble dried. The procedure was repeated 5 times. The whole experiment was then repeated but with the addition of 1g/L of various additives.

Following the washes the reflectances of the VAT Blue cloths at 430nm and the Reactive Orange cloths at 650nm were measured on a Murakami Goniospectrophotometer with an

incident angle of 65° and a measurement angle of 55°. The reflectance of the new cloths was 27.20 for the Vat Blue and 65.13 for the reactive Orange. The reflectance was compare to the reflectance of new unwashed fabric, and expressed as $\Delta R = |R(new) - R(washed)|$. The ΔR(powder control) for Vat Blue was 6.06 and for Reactive Orange was 5.36. In the results shown in table 1 the average ΔR for the blue and orange cloths is given to 1 decimal place.

Table 1

Product	**$\Delta R_{average}$**
Powder Control	5.7
Glass bead diameter 100-200μm	4.5
Glass bead diameter 400-800μm	4.6
Sand, average diameter 180μm	4.5
Grey Silica-alumino ceramic microsphere diameter 1-40μm	5.2
White Silica-alumino ceramic microsphere Mean diameter 1-40μm	5.1

Glass beads were obtained from Sigmund Lindner and had a SiO_2 content of 72.5%

Sand was obtained from Schlingmeier Quartz sand and had a SiO_2 content of 98.9%

Silica-alumino ceramic microsphere particles were obtained from 3M.

The Silica-alumino ceramic microsphere examples are comparative, and show the advantage of the SiO_2 particles in comparison to other spherical inorganic particles.

The SiO_2 particles maintain the cloth closer to the new, as indicated by smaller ΔR_{430} values.

Example 2

Exemplary Granular Laundry Formulations A,B,C,D

Formulation	**A**	**B**	**C**	**D**
NaLAS	15	20	10	14
NI(7EO)	-	-	-	10
Na tripolyphosphate	-	15	-	-
Soap	-	-	-	2
Zeolite A24	7	-	-	17
Sodium silicate	5	4	5	1
Sodium carbonate	25	20	30	20
Sodium sulphate	40	33	40	22
Carboxy methylcellulose	0.2	0.3	-	0.5
Sodium chloride	-	-	-	5
Lipase	0.005	0.01	-	0.005
Protease	0.005	0.01	-	0.005
Amylase	0.001	0.003	-	-
Cellulase	0.003	0.003	-	-
Fluorescer	0.1	0.15	0.05	0.3
Direct Violet 9	0.005	0.00015	-	0.0002
Solvent Violet 13	-	0.002	-	0.001
Glass bead diameter 40-70μm	1.5	0.5	1	1
Sulfonated Zn Pthalocyanine photobleach	0.002	0.004	-	-
Water, impurities & minors	To 100 wt.%	To 100 wt.%	To 100 wt.%	To 100 wt.%

Enzyme levels are given as percent pure enzyme. Levels of direct violet 9, solvent violet 13 and Sulfonated Zn Pthalocyanine photobleach are given as pure dye. NI(7EO) refers to R-$(OCH_2CH_2)_nOH$, where R is an alkyl chain of C12 to C15, and n is 7.

The formulations are prepared by adding direct violet 9, and the Sulfonated Zn Pthalocyanine photobleach into the slurry which is then spray dried. Alternatively, the dyes and photobleach may be added via post-dosed $MgSO_4$ granules.

The solvent violet 13 was dissolved in non-ionic surfactant (7E0) to give a 0.5 wt% solution and granulated onto bentonite clay, to give a granule containing 0.2wt% dye. This was post-dosed to the formulation.

The glass bead (Sigmund Lindner) was added in two ways, by addition to the slurry and by post-dosing. It was noted the bead aided flow of the powder.

CLAIMS

1. A granular laundry treatment composition containing less than 1 wt.% of phosphate, comprising:

(i) from 0.1 wt.% to 40 wt.% of a spherical SiO_2 particle, the SiO_2 particle having a size in the range from 0.1 to 5000 microns;

(ii) from 2 to 70 wt.% of a surfactant; and,

(iii) from 1 to 50 wt.% of a builder.

2. A granular laundry treatment composition according to claim 1, wherein the spherical SiO_2 particle is chosen from sand, therein having a size in the range of 1 to 2000 microns, and/or glass, therein having a size in the range of from 100 to 2000 microns.

3. A granular laundry treatment composition according to claim 1 or claim 2, wherein the spherical SiO_2 particles have a roundness of >80%.

4. A granular laundry treatment composition according to claim 3, wherein the spherical SiO_2 particles have a roundness of >94%.

5. A granular laundry treatment composition according to any one of claims 1 to 4, wherein the spherical SiO_2 particle is present at a level of from 0.5 to 5 wt.%.

6. A granular laundry treatment composition according to any one of claims 1 to 5, wherein the spherical SiO_2 particle comprises from 50 to 100 wt.%, preferably 55 to 100 wt.%, more preferably 65 to 100 wt.% of SiO_2.

7. A granular laundry treatment composition according to any one of claims 1 to 6, wherein the builder comprises zeolite, the zeolite having a size in the range from 0.1 to 10 microns.

8. A granular laundry treatment composition according to any one of claims 1 to 7, wherein the laundry treatment composition comprises a blue or violet shading agent in the range from 0.0001 to 0.01 wt.%.

9. A granular laundry treatment composition according to any one of claims 1 to 8, wherein the laundry treatment composition comprises one or more enzymes, at a level of from about 0.00001 wt.% to about 2 wt.%, preferably the enzyme is a cellulase.

10. A domestic method of treating a textile, comprising the steps of:

(i) treating a textile with an aqueous solution of from 1 to 20 g/l of the composition of any one of claims 1 to 9; and,
(ii) rinsing and drying the textile.

11. Use of spherical SiO_2 particles to reduce damage to clothes laundered during a domestic main wash process.

12. Use of spherical SiO_2 particles according to claim 11, wherein the spherical SiO_2 particle is chosen from sand, therein having a size in the range of 1 to 2000 microns, and/or glass, therein having a size in the range of from 100 to 2000 microns.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/050698

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/12

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

B. FIELDS SEARCHED

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 051 046 A (DIEHL FRANCIS LOUVAINE ET AL) 27 September 1977 (1977-09-27) examples I,V,VI,IX,X,XII,XIII column 15, line 58 - column 16, line 9 column 26 column 15, line 21 - column 21, line 48 column 15, line 42 - column 15, line 50 column 20, line 29 - column 20, line 31	1-11

☐ 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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 April 2009	11/05/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Culmann, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/050698

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4051046 A	27-09-1977	NONE	