LAUNDRY DETERGENT COMPOSITION CONTAINING AMPHOTERIC POLYMER

The invention relates to a solid laundry detergent composition containing an amphoteric polymer, said amphoteric polymer being characterized in that at least 30% of its monomeric units are betaine units represented by the following formula (I):

\[
H_3C_6CO(NH)_2+R_1^+(CR_2^-)_{n-p}+R_2^-(CH_2)_{2p-n}X^- \quad (I)
\]

wherein: \( R_1^+ \) represents a hydrogen atom or a linear or branched \( \text{C}_1 \text{ to } \text{C}_6 \) alkyl group; \( R_2^- \) and \( R_3^- \), independently of each other, represent an alkyl, hydroxyalkyl or aminoalkyl group in which the alkyl group is a linear or branched \( \text{C}_1 \) to \( \text{C}_4 \) alkyl; \( n \) is an integer in the range of 1 to 4; \( p \) is an integer in the range of 2 to 8; \( X^- \) represents \( \text{COO}^- \).

The inventors have discovered that laundry detergent compositions containing the aforementioned amphoteric polymer are capable of increasing the oil repellency of fabrics.
LAUNDRY DETERGENT COMPOSITION CONTAINING AMPHOTERIC POLYMER

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a solid laundry detergent composition for improved grease cleaning. The laundry detergent composition is particularly effective in removing greasy stains from fabrics and enhancing oil repellency of fabrics. The solid laundry detergent composition of the present invention contains an amphoteric polymer in the form of a polybetaine-type polymer.

BACKGROUND OF THE INVENTION

Improved removal of greasy stains is a constant aim for laundry detergent manufacturers. Washing with ordinary detergents often does not remove these stains adequately, because the active ingredients are diluted in the wash rather than being concentrated at or near the stained portions. Furthermore, ordinary detergents do not effectively tackle redeposition of grease onto the fabric during washing.

Laundry detergent compositions which are specifically designed for removing greasy stains from fabrics have been described in the art. US 2015/0267147 AA (Henkel), for instance, describes a laundry detergent composition that contain porous polyamide particles having an oil absorption capacity of at least 60 g/100 g for removing greasy stains from textiles.

To remove greasy stains from fabric, it is also known to apply a separate stain treatment. US 2001/0014658 AA (Ecolab) describes a process for removing hydrophobic and particulate soil from laundry items, the process comprising the steps of: (a) contacting a soiled laundry item with an aqueous treatment comprising an effective treating amount of a hydrophobic ethoxylate surfactant composition; and (b) laundering the treated laundry item with a conventional aqueous laundry detergent.

Polybetaines are amphoteric polymers in which pendant groups have betaine-type structure. The cationic-anionic inner-salt pendant of polybetaines comprises a
positively charged ion in the form of a quaternary ammonium ion and a negative species that is separated from the positively charged ammonium group by an alkyl spacer. Examples of such negatively charged species include carboxylates, phosphonates and sulfonates. Therefore, polybetaines can be divided into polycarboxybetaines, polyphosphobetaines and polysulfobetaines, respectively.

US 2006/0217286 AA (Rhoda Chimie) describes a composition for the cleaning or the rinsing of hard surfaces comprising at least one surface-active agent and at least one polybetaine (B).

JP 10-195498 A (Lion Corp, 1998) describes a liquid detergent composition with solid granules dispersed therein, said composition further comprises a dispersion stabilizer in the form of a cationic high molecular compound and an amphoteric polymer compound. N-methacyrlyolethyl-N,N- dimethylammonium-a-N-methylcarboxybetaine-based polymer is mentioned as an example of a suitable amphoteric polymer.

JP 11-335239 A (Lion Corp, 1999) describes a stain remover composition comprising (A) an amphoteric polymer and/or a cationic polymer compound and (B) benzyl alcohol and/or N-methylpyrrolidone, said composition having pH of 3.0 to 9.0. N-methacyrlyolethyl N,N-dimethylammonium-a-N- methylcarboxybetaine-butyl methacrylate copolymer is mentioned as an example of a suitable amphoteric polymer.

SUMMARY OF THE INVENTION

The present inventors have developed a solid laundry detergent composition that is particularly effective in removing greasy stains from fabrics and in enhancing the oil repellency of fabrics. The detergent composition of the present invention contains 0.1 to 20 wt.% of an amphoteric polymer having molecular weight of at least 5,000 Da, said amphoteric polymer further being characterized in that at least 30% of the monomeric units of the amphoteric polymer are betaine units represented by the following formula (I):

\[ \text{H}_2\text{C}=\text{C}(\text{R}^1)\text{-C}(\text{O})0-(\text{CH}_2)^{1\text{m}}\text{-N}^+\text{(R}^2\text{)}(\text{R}^3\text{)}-(\text{CH}_2)^p\text{-X}.................(I)\]

wherein:
• $R^1$ represents a hydrogen atom or a linear or branched C1-C6 alkyl group;
• $R^2$ and $R^3$, independently of each other, represent an alkyl, hydroxyalkyl or aminoalkyl group in which the alkyl group is a linear or branched C1-C6 alkyl;
• $n$ is an integer in the range of 1 to 4;
• $p$ is an integer in the range of 2 to 8;
• $X$ represents COO$^-$.

The inventors have discovered that the aforementioned amphoteric polymer can be used to significantly enhance the oil repellency of fabrics. Thus, the amphoteric polymer can be used in a post wash composition or in the form of a main wash composition to reduce the extent of redeposition of grease and to enhance future removal of greasy stains. Greasy stains generally have a tendency to redeposit on the fabrics during the wash cycle. Although the inventors do not wish to be bound by theory, it is believed that when a stained fabric is brought into contact with an aqueous medium containing the amphoteric polymer, the polymer attaches itself to the fabric, thereby enhancing the oleophobicity (i.e., oil repelling property) of the fabric. The improved oil repellency is hypothesized to be due to the superhydrophilic nature of the amphoteric polymers, which adsorb a thin monolayer of moisture on the surface of the fabric, thereby rendering the fabric oil repellent.

DETAILED DESCRIPTION OF THE INVENTION

Accordingly, a first aspect, the invention relates to a solid laundry detergent composition containing 0.1 to 20 wt.% of an amphoteric polymer having molecular weight of at least 5,000 Da, said amphoteric polymer further being characterized in that least 30%, preferably at least 50%, of the monomeric units of the amphoteric polymer are betaine units represented by the following formula (I):

$$\text{H}_2\text{C} = \text{C}(\text{R}^1)\cdot\text{C}(0)0\cdot(\text{CH}_2)n \cdot \text{N}^+\cdot(\text{R}^2)(\text{R}^3)\cdot(\text{CH}_2)p\cdot\text{X}$$

wherein:

- $R^1$ represents a hydrogen atom or a linear or branched C1 to C6 alkyl group;
- $R^2$ and $R^3$, independently of each other, represent an alkyl, hydroxyalkyl or aminoalkyl group in which the alkyl group is a linear or branched C1 to C6 alkyl;
- $n$ is an integer in the range of 1 to 4;
p is an integer in the range of 2 to 8;

X represents COO⁻.

The term "laundry detergent composition" as used herein refers to a composition that can be used to remove or to aid the removal of stains from fabric. Examples of laundry detergent compositions include detergent compositions that are used in the washing or laundry and ancillary detergent compositions that are used to treat fabrics so as to enhance the stain releasing behaviour of the fabrics during a subsequent wash. It is colloquially referred to as Next-Time-Cleaning-Benefits.

The term "amphoteric polymer" as used herein, unless indicated otherwise, encompasses both amphoteric homopolymers and amphoteric copolymers.

The laundry detergent composition according to the present invention is very effective in removing greasy stains from fabrics and it further improves the tendency of the washed fabrics to easily release such greasy stains by enhancing the oil repellency of the fabric. Here the term "greasy stains" refers to stains comprising hydrophobic material such as fats, oils, waxes and mineral oil.

The solid laundry detergent composition of the present invention preferably is a powder (e.g. a granulate) or a shaped solid article, e.g. a bar or cake which could be a soap-based composition or a composition based on non-soap surfactants like linear alkyl benzene sulphonates.

The amphoteric polymer is preferably introduced in the detergent composition in the form of polymer-containing particles that contain 30 to 95 wt.% of carrier material and at least 0.3 wt.% of the amphoteric polymer. More preferably, these polymer-containing particles contain 10 to 50 wt.% of carrier material and at least 0.5 wt.%, more preferably at least 5 wt.% of the amphoteric polymer. Typically, the detergent composition contains not more than 20 wt.% of the amphoteric polymer.
The aforementioned polymer-containing particles typically have a diameter in the range of 0.1 to 1000 µη. More preferably, the polymer-containing particles have a diameter in the range of 10 to 800 µη, most preferably of 20 to 500 µη.

In a preferred embodiment, the amphoteric polymer is contained in polymer-containing particles that comprise one or more core particles and a coating that contains the amphoteric polymer. The one or more core particles are preferably made of silicate mineral. Examples of suitable silicate materials include feldspar, montmorillonite, bentonite, zeolite and combinations thereof.

In another preferred embodiment, the amphoteric polymer is contained in polymer-containing particles containing at least 30 wt.% of water-soluble carrier material. More preferably, the polymer-containing particles contain at least 30 wt.% of water-soluble carrier polymer. Examples of suitable water-soluble carrier polymer include polyethyleneglycol, ethylene-vinyl alcohol, ethylene-vinyl acetate and combinations thereof.

The solid laundry detergent composition of the present invention preferably contains 0.2 to 10 wt.%, more preferably 0.3 to 8 wt.% and most preferably 0.4 to 3 wt.% of the amphoteric polymer.

The amphoteric polymer employed in the present detergent composition preferably has a molecular weight of at least 8,000 Da, more preferably of 12,000 to 100,000 Da and most preferably of 15,000 to 50,000 Da.

The monomeric units represented by above mentioned formula (I) preferably represent at least 50%, more preferably at least 70%, even more preferably at least 90% and most preferably at least 95% of the monomeric units of the amphoteric polymer.

R¹ in formula (I) preferably represents C₁ to C₃ alkyl, more preferably it represents methyl or ethyl, and most preferably it represents methyl group.
In a preferred embodiment, \( R^2 \) and \( R^3 \) in formula (I) independently of each other represent \( C_i \) to \( C_3 \) alkyl, more preferably methyl or ethyl. Most preferably, \( R^2 \) and \( R^3 \) each represents methyl group.

The integer \( n \) in formula (I) preferably is 1 to 3. Most preferably \( n \) is 2.

The integer \( p \) in formula (I) preferably is 2 to 4. Most preferably \( p \) is 3.

In accordance with a one preferable embodiment, \( X \) in formula (I) represents COO\(^-\). Carboxybetaine methacrylate is an example of betaine monomer in which \( X \) represents COO\(^-\).

In accordance with another preferred embodiment the composition may additionally comprise the amphoteric polymer where \( X \) in formula (I) represents SO\(3^-\). Sulfobetaine methacrylate is an example of betaine monomer in which \( X \) represents SO\(3^-\).

Unlike the compositions described in JP 10-195498 A and JP 11-335239 A, the amphoteric polymer employed in accordance with the present invention is not a copolymer comprising methacryloylalkyl dimethylammonium-methylcarboxybetaine-butyl methacrylate.

According to a preferred embodiment, the amphoteric polymer of the present invention is a homopolymer, i.e. a polymer in which all monomeric units are betaine units according to formula (I).

Alternatively, in case the amphoteric polymer is a copolymer, it is preferred that at least 20% of the monomeric units of the copolymer are diallyldialkylammonium units, preferably diallyldimethylammonium units.

The laundry detergent composition of the present invention typically comprises 0.01 to 10 wt.%, more preferably 0.02 to 5 wt.% and most preferably 0.025 to 1 wt.% of surfactants selected from anionic surfactants, zwitterionic surfactants and nonionic surfactants.
Preferably, the detergent composition contains at least 0.01 wt.%, more preferably at least 0.02 wt.% and most preferably at least 0.025 wt.% of nonionic surfactant.

According to a particularly preferred embodiment, the detergent composition contains at least 0.01 wt.%, more preferably at least 0.02 wt.%, most preferably at least 0.025 wt.% poly(ethylene glycol) alkyl ether represented by the following formula:

\[ \text{CH}_3(\text{CH}_2)_r(\text{OCH}_2\text{CH}_2)_s\text{OH} \]

wherein \( r \) is an integer in the range of 7 to 17; and \( s \) is an integer in the range of 1 to 25.

In another preferred embodiment, the detergent composition contains 30 to 95 wt.% of builder, more preferably 40 to 90 wt.% of builder and most preferably 50 to 75 wt.% of builder.

Inorganic builders that may be used include sodium carbonate; aluminosilicates, such as zeolites; and layered silicates; and inorganic phosphate builders such as sodium orthophosphate, pyrophosphate and tripolyphosphate.

Organic builders that may be used include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di and trisuccinates, carboxymethyloxy succinates, carboxymethyloxyxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulfonated fatty acid salts.

Another aspect of the present invention relates to the use of an amphoteric polymer as defined herein before for removing greasy stains from a fabric or for improving the oil repellency of a fabric, said use comprising contacting the fabric with an aqueous liquid containing 0.01 to 2 wt.% of the amphoteric polymer.

In a preferred embodiment of the aforementioned use, the aqueous liquid further contains 0.01 to 2 wt.% of nonionic surfactant, more preferably 0.02 to 1 wt.% of an nonionic surfactant represented by aforementioned formula.
The invention is further illustrated by the following non-limiting examples.

**EXAMPLES**

5  **Example 1**

**Monomer Synthesis**

2-Carboxy-N,N-dimethyl-N-(2'-(methacryloyloxy)ethyl)ethylimminium inner salt (CBMA) monomer was synthesized according to the method described by Zhang et al. (*Superlow Fouling Sulfobetaine and Carboxybetaine Polymers on Glass Slides*, Langmuir, Vol. 22, no. 24, 2006, 10073). Gamma-propiolactone in dry acetone was added dropwise into a solution of 2-(N,N'-dimethylamino)ethyl methacrylate in anhydrous acetone and the reaction was stirred at 15 °C for 24 hours. The solvent was subsequently evaporated to obtain a viscous liquid of the CBMA monomer.

**Polymer Syntheses**

Free radical polymerization of the CBMA monomer was carried out in an aqueous medium using the method described by Lee et al. (*Synthesis and solubility of the poly(sulfobetaine)s and the corresponding cationic polymers: Synthesis and characterization of sulphobetaines and the corresponding cationic monomers by nuclear magnetic resonance spectra*, Polymer (1994), vol. 35, no. 10, 2210 - 2217). Potassium persulfate was used as an initiator and polymerization was carried out in an inert atmosphere under stirring at 60 to 70 °C for 8 hours. Molecular weight of the CBMA homopolymer was in the range of 10,000 to 100,000 Da.

A copolymer of the CBMA monomer and N,N-diallyl-N,N-dimethyl ammonium chloride (DADMAC) was prepared following a free radical polymerization technique described by Thomas et al. (*Synthesis, Characterization, and Aqueous Solution Behavior of Electrolyte- and pH-Responsive Carboxybetaine-Containing Cyclopolymers*, Macromolecules (2003), 36(26), 9710-9715). Potassium persulphate was used as the initiator and the polymerization was carried out for 8 hours at 70 °C under nitrogen.
blanket. Molecular weight of the CMBA/DADMAC copolymer was in the range of 10,000 to 100,000 Da. The ratio of the two monomers used was 65 mol% CBMA and 35 wt% DADMAC.

Free radical polymerization of SBMA (sulphobetaine methacrylate; Sigma Aldrich) monomer was carried out in an aqueous medium using the method described by Lee et al. (*Synthesis and solubility of the poly(sulfobetaine)s and the corresponding cationic polymers: Synthesis and characterization of sulphobetaines and the corresponding cationic monomers by nuclear magnetic resonance spectra*), Polymer (1994), vol. 35, no. 10, 2210 - 2217). Potassium persulfate was used as an initiator and the polymerization was carried out in an inert atmosphere by stirring at 60 to 70 °C for 8 hours. Molecular weight of the SBMA homopolymer was in the range of 10,000 to 100,000 Da.

**Example 2**

**Pretreatment tests**

Polyester swatches were treated with polymer solutions containing different concentrations of the CBMA homopolymer of Example 1, and a control sample that did not contain any polymer. The swatches were allowed to dry, followed by staining (0.2 mL) with artificial sebum and ageing for 24 hours. This swatches was then washed in a Tergotometer at 110 rpm under ambient conditions in 24 °F (French hardness) water (no additives or surfactants were used), followed by drying.

The SRI (Stain Removal Index) of the dried washed fabric samples was determined. The SRI-values were determined by measuring reflectance of the fabric swatches measured at R460 (values at 460 nanometer, UV excluded and included) using a MICROTEK® Artix Scanner F1 with Software: Silverfast Ai Studio, Lasersoft Imaging.

The results of these measurements are shown in Table 1.
Example 3

Example 1 was repeated except that this time polyester and cotton swatches were first stained with a model sebum, followed by ageing for 24 hours. These stained fabric samples were washed in a Tergotometer at 110 rpm at ambient temperature in water (24 °F) in the presence of 1.5 g/l of Surf Excel®, which is a commercial detergent composition of Unilever.

The results are tabulated in Table 2.

Example 4

Example 1 was repeated, except that this time the aged stained fabric samples were washed in a Tergotometer at 110 rpm at ambient temperature in water (24 °F). The results are tabulated in Table 3.
Example 5

Polyester swatches were treated with polymer solutions of the copolymer polyCBMA-co-DADMAC of Example 1. The solutions contained different concentrations of the copolymer or did not contain any copolymer (control, refer Table 4).

The treated swatches were allowed to dry, followed by staining (0.2 mL) with artificial sebum and ageing for 24 hours. The fabric was then washed in a Tergotometer at 110 rpm at ambient temperature in water (24 °F, no additives/surfactants were used), followed by drying.

The SRI of the dried washed fabric samples was determined in the same way as in Example 1. The results of these measurements are shown in Table 4.

Table 4

<table>
<thead>
<tr>
<th>Concentration of CBMA-co-DADMAC copolymer</th>
<th>SRI</th>
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<tbody>
<tr>
<td>0 wt.% copolymer (Control )</td>
<td>80.8</td>
</tr>
<tr>
<td>0.05 wt.% copolymer</td>
<td>86.5</td>
</tr>
<tr>
<td>0.2 wt.% copolymer</td>
<td>83.7</td>
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</table>

Example 6

Polyester swatches were treated with polymer solutions of the homopolymer polySBMA of Example 1. The solutions contained different concentrations of the homopolymer or did not contain any homopolymer (control, refer Table 5).

Table 3

<table>
<thead>
<tr>
<th>Concentration of CBMA homopolymer</th>
<th>SRI</th>
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<tr>
<td>0 wt.% polymer (Control )</td>
<td>72.7</td>
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<tr>
<td>0.02 wt.% polymer</td>
<td>74.2</td>
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<tr>
<td>0.05 wt.% polymer</td>
<td>74.9</td>
</tr>
<tr>
<td>0.2 wt.% polymer</td>
<td>83.6</td>
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</table>
The swatches were allowed to dry, followed by staining (0.2 mL) with artificial sebum and ageing for 24 hours. The fabric was then washed in a Tergotometer in water (no additives/surfactants were used), followed by drying.

The SRI of the dried washed fabric samples was determined in the same way as in Example 1. The results of these measurements are shown in Table 5.

Table 5

<table>
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<tr>
<th>Concentration of SBMA homopolymer</th>
<th>SRI</th>
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<tr>
<td>0 wt.% polymer (Control)</td>
<td>80.8</td>
</tr>
<tr>
<td>0.2 wt.% polymer</td>
<td>88.7</td>
</tr>
<tr>
<td>1 wt.% polymer</td>
<td>86.2</td>
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CLAIMS

1. A solid laundry detergent composition containing 0.1 to 20 wt.% of an amphoteric polymer having molecular weight of at least 5,000 Da, said amphoteric polymer further being characterized in that least 30%, preferably at least 50% of the monomeric units of the amphoteric polymer, are betaine units represented by the following formula (I):

\[ H_2C=\text{C}(R^1)-\text{C}(0)-(\text{CH}_2)_n-N+\text{N}^+(R^2)-(R^3)-(\text{CH}_2)p-X \]  

wherein:

- \( R^1 \) represents a hydrogen atom or a linear or branched \( \text{C}_0 \text{ to C}_6 \) alkyl group;
- \( R^2 \) and \( R^3 \), independently of each other, represent an alkyl, hydroxyalkyl or aminoalkyl group in which the alkyl group is a linear or branched \( \text{C}_0 \text{ to C}_6 \) alkyl;
- \( n \) is an integer in the range of 1 to 4;
- \( p \) is an integer in the range of 2 to 8;
- \( X \) represents \( \text{COO}^- \).

2. Laundry detergent composition according to claim 1, wherein the amphoteric polymer is contained in polymer-containing particles that contain 30 to 95 wt.% of carrier material and at least 0.3 wt.% of the amphoteric polymer.

3. Laundry detergent composition according to claim 1 or 2, wherein \( R^1 \) represents \( \text{C}_0 \text{ to C}_3 \) alkyl group.

4. Laundry detergent composition according to claim 3, wherein \( R^1 \) represents methyl group.

5. Laundry detergent composition according to any one of the preceding claims 1 to 4, wherein \( R^2 \) and \( R^3 \), independently of each other, represent \( \text{C}_0 \text{ to C}_3 \) alkyl groups.
6. Laundry detergent composition according to claim 5, wherein \( R^2 \) and \( R^3 \) each represents methyl group.

7. Laundry detergent composition according to any of claims 1 to 6, wherein the amphoteric polymer is a homopolymer.

8. Laundry detergent composition according to any of claims 1 to 6, wherein the amphoteric polymer is a copolymer, wherein at least 20% of the monomeric units of the copolymer are diallyldialkylammonium units, preferably diallyldimethylammonium units.

9. Laundry detergent composition according to any of claims 1 to 8 wherein the detergent composition is a powder or a shaped solid article.

10. Laundry detergent composition according to any of claims 1 to 9 wherein the composition contains at least 0.025 wt.% nonionic surfactant.

11. Laundry detergent composition according to claim 10, wherein the nonionic surfactant is represented by the following formula: \( (\text{CH}_3\text{CH}_2)_r(\text{OCH}_2\text{CH}_2)_s\text{OH} \) wherein \( r \) is an integer in the range of 7 to 17 and \( s \) is an integer in the range of 1 to 25.

12. Use of an amphoteric polymer as defined in any one of claims 1 to 11 for removing greasy stains from a fabric or for improving the oil repellency of a fabric, said use comprising contacting the fabric with an aqueous liquid containing 0.01 to 2 wt.% of the amphoteric polymer.

13. Use according to claim 12, wherein the aqueous liquid further comprises 0.025 to 5 wt.% nonionic surfactant.
INTERNATIONAL SEARCH REPORT

PCT/EP2017/072863

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/37 C11D3/00
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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 2016/087258 AI (HENKEL AG &amp; CO KGAA [DE]; FRAUNHOFER GES ZUR FÖRDERUNG DER ANGEWANDTEN) 9 June 2016 (2016-06-09) claims examples page 14, last paragraph</td>
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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 application or patent but published on or after the international filing date
  *L* documents which may throw doubts on priority claim(s) or which are cited to establish the publication date of another citation or other special reason (as specified).
  *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

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

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

*Z* document member of the same patent family

Date of the actual completion of the international search
9 November 2017

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
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Date of mailing of the international search report
16/11/2017

Authorized officer
Neys, Patricia
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