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(54) SHAPED TOILET CLEANER BLOCK

(57) The invention relates to a shaped toilet cleaner block comprising:

- 1-40 wt.% nonionic surfactant, including at least 1 wt.% of fatty alcohol alkoxylate selected from C<sub>8-22</sub> alcohols alkoxylated with ethylene oxide (EO) and/or propylene oxide (PO) with a degree of alkoxylation of 12 to 30;
- 10-50 wt.% C<sub>8-18</sub> alkyl benzene sulfonate;
- $\bullet$  5-40 wt.% C<sub>8-18</sub> alkyl sulfate;
- $\bullet$  less than 15 wt.%  $\rm C_{12\text{--}18}$  fatty acid monoethanolamide; and
- 20-80 wt.% filler.

The shaped toilet cleaner block of the present invention offers the important advantage that it can easily and reproducibly be produced in attractive shapes by means of extrusion at very high speed. The extruded strand of the present toilet cleaner composition can be cut into toilet cleaner blocks at high frequency without difficulty, yielding blocks with very regular, undamaged cut surfaces. The shaped toilet cleaner block of the present invention further offers the advantage that it is washed away by the repeated flushing operations in a very regular and uniform way.

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#### Description

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#### **TECHNICAL FIELD OF THE INVENTION**

<sup>5</sup> **[0001]** The present invention relates to toilet cleaner blocks, more particularly to toilet cleaner blocks containing fatty alcohol alkoxylate, alkylbenzene sulfonate, alkyl sulfate and filler.

**[0002]** The invention also provides a process for the manufacture of the toilet cleaner block and a system comprising such toilet cleaner block and a release device.

#### BACKGROUND OF THE INVENTION

[0003] Toilet cleaner blocks, have long been employed under the toilet rim (so-called rim blocks) as well as in water tanks (in-tank blocks or cistern blocks) for cleaning, disinfecting, and perfuming of toilets.

[0004] Once put into place, either in the cistern or in the toilet bowl, the toilet block slowly releases active ingredients and disintegrates into the water.

**[0005]** Rim blocks typically contain active ingredients such as surfactants, perfume, acids, bases, salts, thickeners, antimicrobials, preservatives, sequestrants, bleaching agents, corrosion inhibitors, flush regulators, enzymes, microorganisms, active substances for biofilm removal, lime-scale inhibitors, soil-adhesion inhibit etc. Rim blocks also often contain a substantial amount of filler, such as sodium sulfate or sodium carbonate.

[0006] Colourants are commonly applied in rim blocks for esthetic reasons, but also to allow the consumer to quickly assess whether the rim block is due to be replaced.

**[0007]** Solid toilet blocks are typically manufactured and shaped by an extrusion process. In case of rim blocks the shaped toilet blocks are inserted into suitable baskets for use in the toilet bowl.

**[0008]** For the industrial production of toilet blocks by means of extrusion it is important that a strand of toilet cleaner composition can be produced at high speed, that the composition and appearance of the strand does not vary and that it can be cut into separate pieces (blocks) at high frequency without damaging these pieces and without product loss.

**[0009]** WO 00/58433 describes lavatory cleansing blocks comprising at least two phases, one phase comprising a perfume and the second phase comprising an alcohol ethoxylate, ethoxylates with 8 or less moles of alkylene oxide. The patent examples describe lavatory blocks comprising 50 wt.% of a Phase A, said phase A containing 15 wt.% sodium dodecylbenzenesulfonate, 6 wt.% sodium lauryl sufate, 4.7 wt.% calcium carbonate, 3.1 wt.% sodium sulfate and 3 wt.% alcohol ethoxylate.

[0010] WO 2010/130645 describes a spherically shaped toilet cleaner block comprising:

- a) perfume;
- b) at least one nonionic surfactant;
- c) at least one alkyl benzene sulfonate; and
- d) at least one olefin sulfonate; and

wherein said spherically shaped toilet cleaner block has a sphericity  $\psi$  between 0.8 and 1.

[0011] There is a need for shaped toilet cleaner blocks that have an appealing appearance, that provide constant performance during the full use cycle in terms of cleaning action, perfume release and foaming, and that can easily be manufactured by high speed extrusion.

## **SUMMARY OF THE INVENTION**

**[0012]** The inventors have developed a shaped toilet cleaner block that meets all of the aforementioned desiderata. The shaped toilet cleaner block of the present invention comprises

- 1-40 wt.% nonionic surfactant, including at least 1 wt.% of fatty alcohol alkoxylate selected from C<sub>8-22</sub> alcohols alkoxylated with ethylene oxide (EO) and/or propylene oxide (PO) with a degree of alkoxylation of 12 to 30;
- 10-50 wt.% C<sub>8-18</sub> alkyl benzene sulfonate;
- 5-40 wt.% C<sub>8-18</sub> alkyl sulfate;
- less than 15 wt.% C<sub>12-18</sub> fatty acid monoethanolamide; and
- 20-80 wt.% filler.

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**[0013]** The shaped toilet cleaner block of the present invention offers the important advantage that it can easily and reproducibly be produced in attractive shapes by means of extrusion at very high speed. The extruded strand of the present toilet cleaner composition can be cut into toilet cleaner blocks at high frequency without difficulty, yielding blocks

with very regular, undamaged cut surfaces.

**[0014]** The shaped toilet cleaner block of the present invention further offers the advantage that it is washed away by the repeated flushing operations at a constant rate and in a very regular and uniform way. The toilet cleaner block provides good cleaning and disinfecting action, perfume release and foaming when the block is contacted with water during flushing of the toilet bowl throughout the its life cycle, which life cycle ends when the toilet block has been completed degraded by dissolution into the flush water.

**[0015]** The invention also relates to a process of manufacturing the aforementioned toilet cleaner block, said process comprising:

- combining the fatty alcohol alkoxylate, the C<sub>8-18</sub> alkyl benzene sulfonate, the C<sub>8-18</sub> alkyl sulfate and the filler to produce an extrusion blend;
  - · extruding said extrusion blend to produce an extruded strand;
  - cutting said extruded strand into blocks.
- [0016] The invention further provides a toilet cleaning system comprising at least one toilet cleaner block according to the present invention and a release device that is configured for reversible positioning under the rim of a toilet bowl in the path of toilet flush water.

#### **DETAILED DESCRIPTION OF THE INVENTION**

**[0017]** A first aspect of the present invention relates to a shaped toilet cleaner block that meets all of the aforementioned desiderata. The shaped toilet cleaner block of the present invention comprises

- 1-40 wt.% nonionic surfactant, including at least 1 wt.% of fatty alcohol alkoxylate selected from C<sub>8-22</sub> alcohols alkoxylated with ethylene oxide (EO) and/or propylene oxide (PO) with a degree of alkoxylation of 12 to 30;
- 10-50 wt.% C<sub>8-18</sub> alkyl benzene sulfonate;
- 5-40 wt.% C<sub>8-18</sub> alkyl sulfate;
- less than 15 wt.% C<sub>12-18</sub> fatty acid monoethanolamide; and
- 20-80 wt.% filler.

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**[0018]** The toilet cleaner block of the present invention preferably is designed for use under the toilet rim of the toilet bowl. The toilet block *per se* typically has a weight in the range of 10-200 grams, more preferably of 20-100 grams and most preferably 40-60 grams.

**[0019]** The water content of the toilet cleaner block typically is less than 10 wt.%, more preferably less than 8 wt.%, most preferably less than 6 wt.%.

**[0020]** The toilet cleaner block preferably has a density of 1.2 to 1.9 g/ml, more preferably of 1.4 to 1.8 g/ml and most preferably of 1.5 to 1.7 g/ml.

**[0021]** The combination of the nonionic surfactant, the  $C_{8-18}$  alkyl benzene sulfonate, the  $C_{8-18}$  alkyl sulfate and the filler typically constitutes at least 60 wt.%, more preferably at least 70 wt.% and most preferably at least 80 wt.% of the block.

### **Surfactants**

**[0022]** The toilet cleaner block of the present invention contains at least one nonionic surfactant in the form of fatty alcohol alkoxylate and at least two different anionic surfactants ( $C_{8-18}$  alkyl benzene sulfonate and  $C_{8-18}$  alkyl sulfate). Besides nonionic and anionic surfactants, the cleaner block may suitably contain further surfactants, such as cationic surfactants and amphoteric surfactants.

[0023] The toilet cleaner block preferably contains nonionic surfactants and anionic surfactants in a weight ratio in the range of 1:15 to 1:2, more preferably in the range of 1:12 to 1:4.

[0024] Nonionic and anionic surfactants preferably represent at least 60 wt.%, more preferably at 80 wt.% and most preferably at least 90 wt.% of the total amount of surfactant that is contained the toilet cleaner block.

**[0025]** The toilet cleaner block of the present invention typically contains at least 20 wt.% surfactant, more preferably at least 25 wt.% surfactant, even more preferably at least 30 wt.% surfactant. The total surfactant content of the block preferably does not exceed 80 wt.%.

### Nonionic surfactant

[0026] Examples of nonionic surfactant that may be employed in the present toilet cleaner block besides the fatty alcohol alkoxylate include ethylene oxide/propylene oxide block polymers, fatty acid alkanolamides, fatty acid polyglycol

ethers, alkyl polyglycosides, fatty acid glucamides and combinations thereof.

[0027] The toilet cleaner block preferably contains 2-35 wt.%, more preferably 2.5-25 wt.%, even more preferably 3-15 wt.% of nonionic surfactant.

**[0028]** According to a particularly preferred embodiment, the toilet cleaning block contains at least 1.5 wt.%, more preferably at least 2 wt.%, even more preferably at least 2.5 wt.% of fatty alcohol alkoxylate.

**[0029]** The block preferably contains less than 15 wt.%, more preferably less than 12 wt.%, even more preferably less than 8 wt.% of nonionic surfactant other than the fatty alcohol alkoxylate.

**[0030]** The fatty alcohol alkoxylate employed in the toilet cleaner block is preferably selected from alkoxylated  $C_{12-20}$  fatty alcohols, more preferably from alkoxylated  $C_{16-18}$  fatty alcohols.

[0031] The fatty alcohol alkoxylate in the toilet cleaner block is preferably selected from ethoxylated fatty alcohols with a degree of ethoxylation of 16 to 28, even more preferably with a degree of ethoxylation of 20 to 27.

**[0032]** According to a particularly preferred embodiment, the fatty aclcohol aloxylate employed in the toilet cleaner block is ethoxylated  $C_{16-18}$  fatty alcohol with a degree of ethxylation of 24 to 26.

## 15 Alkyl benzene sulfonate

[0033] The toilet cleaner block of the present invention preferably contains 15-40 wt.%, more preferably 18-35 wt.% and most preferably 20-30 wt.%  $C_{8-18}$  alkyl benzene sulfonate

**[0034]** The toilet cleaner block preferably contains at least 10 wt.%, more preferably at least 15 wt.%, even more preferably at least 18 wt.% of  $C_{10-14}$  alkyl benzene sulfonate.

**[0035]** The alkyl benzene sulfonate employed in the toilet cleaner block preferably is a salt selected from alkali metal salts, earth alkaline metal salts, ammonium salts and combinations thereof. More preferably, the alkyl benzene sulfonate is an alkali metal salt, most preferably a sodium salt.

## C<sub>8-18</sub> alkyl sulfate

[0036] The toilet cleaner block typically contains 8-30 wt.%, more preferably 10-28 wt.% and most preferably 12-20 wt.% of the alkyl sulfate.

[0037] According to a particularly preferred embodiment, the block contains at least 5 wt.%, preferably at least 7 wt.% and most preferably at least 8 wt.% of  $C_{10-14}$  alkyl sulfate.

**[0038]** The alkyl sulfate employed in the block preferably is a salt selected from alkali metal salts, earth alkaline metal salts, ammonium salts and combinations thereof. More preferably, the alkyl sulfate is an alkali metal salt, most preferably a sodium salt.

### 35 Fillers

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**[0039]** In a preferred embodiment, the filler in the toilet cleaner block is an inorganic salt selected from sulfates, carbonates, halides, phosphates and combinations thereof. Even more preferably, said inorganic salt is selected from sulfates, carbonates and combinations thereof.

[0040] The inorganic salt that may be employed as a filler in the toilet cleaner block is preferably selected from alkali metal salts, earth alkaline metal salts, ammonium salts and combinations thereof, even more preferably it is selected from alkali metal salts, most preferably it is selected from sodium salts.

[0041] The amount of filler in the toilet cleaner block preferably is in the range of 30-65 wt.%, more preferably 35-60.

**[0042]** According to a particularly preferred embodiment, the toilet cleaner block of the present invention contains at least 20 wt.%, preferably at least 30 wt.%, more preferably at least 35 wt.% sodium sulfate.

### Colourant

**[0043]** The toilet cleaner block of the present invention preferably contains a colourant. The inclusion of a colourant in the toilet cleaner block not only serves to increase the appeal of the product, but it is also makes it easier to verify how much product is left after repeated flushes.

[0044] The toilet cleaner blocks of the present invention offer the advantage that colourant is gradually released from the block.

**[0045]** Accordingly, in a highly preferred embodiment, the toilet cleaner block contains at least 10 mg/kg, more preferably at least 30 mg/kg and even more preferably at least 50 mg/kg of colourant.

**[0046]** The toilet block of the present can suitably be provided in a variety of colours, including green, blue, red, violet, pink and yellow.

#### Builder

[0047] The toilet cleaner block may suitably contain builder. Examples of builders that may be included in the block include low molecular weight polycarboxylic acids and salts thereof, the homopolymeric and copolymeric polycarboxylic acids and salts thereof, citric acid and salts thereof, carbonates, phosphates, silicates, zeolites and combinations thereof. [0048] Preferably, the toilet cleaner block contains 0.5-20 wt.%, more preferably 0.8-15 wt.%, even more preferably 1-10 wt.% builder.

**[0049]** According to a preferred embodiment, he toilet cleaner block contains at least 0.8 wt.%, preferably at least 1 wt.% of builder selected from phosphate, citrate and combinations thereof.

### Perfume

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[0050] The toilet cleaner block of the present invention preferably contains perfume.

[0051] The composition preferably comprises one or more fragrances in an amount of 0.01 to 10 wt %, more preferably 0.05 to 8 wt %, even more preferably 0.1 to 5 wt %. In this regard for example, d-limonene, citral, linalool or combinations of these fragrance components may be utilized as the perfume component.

#### Other ingredients

<sup>20</sup> **[0052]** Other ingredients that may applied in the toilet cleaner block of the present invention include bleaching agents, polymers, corrosion inhibitors, flush regulators, adhesion inhibitors, pH regulators, enzymes and preservatives,

**[0053]** Bleaching agents that may suitably be applied in the toilet cleaner blocks of the present invention include peroxides, peracids and/or perborates. A bleach activator can also be used in addition to the bleaching agent.

## 25 Polymers

[0054] Polymers, such as acrylic polymers, can suitably be incorporated in the toilet cleaner block to reduce formation of lime scale and soil redoposition.

**[0055]** Flush regulators can be employed in the toilet cleaner block to regulate degradation of the block. Solid long-chain fatty acids, such as stearic acid, are preferred regulators.

[0056] Enzymes that may be applied in the toilet cleaner block include proteases, lipases, amylases, hydrolases and/or cellulases.

## Toilet cleaning system

**[0057]** Another aspect of the invention relates to a toilet cleaning system comprising at least one toilet cleaner block as defined herein before and a release device that is configured for reversible positioning under the rim of a toilet bowl in the path of toilet flush water.

[0058] According to a particularly preferred embodiment, the release device comprises:

- at least one container configured to hold said toilet cleaner block;
- an inlet opening in the upper portion of said container, said inlet being configured to allow toilet flush water to enter
  the container when said system is positioned under the rim of a toilet bowl in the path of toilet flush water and said
  toilet is flushed:
- an outlet opening moulded into a lower portion of said container, said outlet being configured to drain toilet flush water from the container into said toilet bowl; and
  - a distribution element arranged on said release device, said element configured to distribute and direct said flush water.

## 50 Manufacturing Process

**[0059]** Yet another aspect of the invention relates to a process of manufacturing a toilet cleaner block as defined herein before, said process comprising:

- combining the nonionic surfactant, the C<sub>8-18</sub> alkyl benzene sulfonate, the C<sub>8-18</sub> alkyl sulfate and the filler;
  - extruding said extrusion blend to produce an extruded strand;
  - · cutting said extruded strand into blocks.

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**[0060]** As explained herein before, the toilet cleaner block of the present invention can be produced at very high extrusion speeds. According to a particularly preferred embodiment of the present process, the extrusion blend is extruded at a speed of at least 3.0 m/min, more preferably at least 5.0 m/min and even more preferably 6.0-16.0 m/min

**[0061]** The cutting frequency in the present process preferably exceeds 1 s<sup>-1</sup>, more preferably it exceeds 3 s<sup>-1</sup> and even more preferably it is in the range of 4-15 s<sup>-1</sup>. Here the cutting frequency equals the number of blocks that are produced from the extruded strand per second.

**[0062]** In a preferred embodiment of the present process the extrusion blend is extruded at a temperature in the range of 20-80 °C, more preferably in the range of 30-75 °C, even more preferably in the range of 40-70 °C.

**[0063]** The blocks obtained by cutting of the extruded strand may be subjected to further processing steps, such as shaping. The cut blocks may, for instance, be shaped in rotationally symmetric objects by shaping the cut blocks in a ball rolling machine or in a press. Other suitable shaping processes include casting and calendaring.

[0064] The invention is further illustrated by the following non-limiting examples.

#### **EXAMPLES**

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### Example 1

[0065] Toilet cleaner blocks according to the present invention were manufactured by means of extrusion on the basis of the formulation shown in Table 1.

Table 1

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	Concentration (wt%)	
Sodium sulfate	50.48	
Sodium Dodecylbenzenesulfonate	24.00	
Sodium Lauryl Sulfate	15.00	
Ethoxylated alcohols <sup>1</sup>	5.00	
Perfume (including citral, limonene and linalool)	3.00	
Pentasodium triphosphate	1.65	
Lauryl Alcohol	0.25	
Sodium citrate	0.60	
Polymeric Blue Colourant	0.02	
1 An alkylpolyethylene glycol ether made from a linear, saturated ethoxylaton of 25	I C <sub>16</sub> C <sub>18</sub> fatty alcohol having a nominal degree	

<sup>[0066]</sup> The extrusion conditions employed during manufacture are shown in Table 2

Table 2

Extrusion speed	8.8 m/min
Extrusion temperature	60 °C
Cutting frequency	6-7 s <sup>-1</sup>

**[0067]** The toilet cleaner blocks so obtained has a very regular shape with clean cutting surfaces. The properties of the blocks are listed in Table 3.

Table 3

Shape	hexagonal cylinder
Dimensions (height x diameter)	20 x 22 mm
Weight	11 g
Density	1.6 - 1.65 g/ml

### (continued)

Shape	hexagonal cylinder
Colour	Blue
Moisture	1.7 wt.%

[0068] Five toilet cleaner blocks as described above were introduced in a single release device made of transparent material and comprising five baskets for holding the toilet cleaner blocks, each of said baskets containing a flush water distribution element. The five baskets were arranged in a row and the release device contained a flexible hook for fixating the row of baskets in a horizontal fashion underneath the toilet rim.

[0069] The performance of the above described toilet cleaner system was tested by subjecting the system to a sequence of toilet flushes (15 or 25 flushes/day, average water temperature: 21.5 °C; average room temperature 17.3 °C).

[0070] The results of these experiments are summarized in Tables 4a and 4b.

#### Table 4a

15 flushes/day	
Life span	11.5 days / 172 flushes
Dissolution after	
- 15 flushes	0.91%
- 60 flushes	0.74 %
- 105 flushes	0.50 %
Foam level	The foam level immediately after flush can be considered discreet with a total and good coverage of the toilet bowl. The foam bubbles have a medium/small size that means a good and creamy foam.
Foam stability	After 5 minutes from the flush, the foam is still present: the height is slightly decreased, as usually happens with all toilet blocks, but the coverage of the toilet bowl is anyway total and good.

#### Table 4b

	Table 4b		
25 flushes/day			
Life span	9 days / 225 flushes		
Dissolution after			
- 25 flushes	0.84 %		
- 100 flushes	0.56 %		
- 175 flushes	0.30 %		
Foam level	The foam level immediately after flush can be considered good with a total and good coverage of the toilet bowl. The foam bubbles have a medium/small size that means a good and creamy foam.		
Foam stability	After 5 minutes from the flush, the foam is still present: the height is slightly decrease, as usually happens with all toilet blocks, but the coverage of the toilet bowl is anyway total and good.		

[0071] These results demonstrate that the life span of the toilet cleaner system was good. In addition, the results demonstrate that the toilet cleaner blocks dissolved at an almost linear rate during their lifespan. Also the foam profile (coverage, height and stability) achieved with the system was found to be good.

## **Comparative Example**

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[0072] Example 1 was repeated, except that this time sodium dodecyl benzenesulfonate was fully replaced by sodium

C<sub>14-16</sub> olefin sulfate.

[0073] It was found that the formulation containing  $C_{14-16}$  olefin sulfate could not be extruded as efficiently as the formulation containing dodecyl benzenesulfonate.

#### Claims

- 1. A shaped toilet cleaner block comprising:
- 1-40 wt.% nonionic surfactant, including at least 1 wt.% of fatty alcohol alkoxylate selected from C<sub>8-22</sub> alcohols alkoxylated with ethylene oxide (EO) and/or propylene oxide (PO) with a degree of alkoxylation of 12 to 30;
  - 10-50 wt.% C<sub>8-18</sub> alkyl benzene sulfonate;
  - 5-40 wt.% C<sub>8-18</sub> alkyl sulfate;
  - $\bullet$  less than 15 wt.%  $\rm C_{12\text{--}18}$  fatty acid monoethanolamide; and
- 15 • 20-80 wt.% filler.
  - 2. Toilet cleaner block according to claim 1, wherein the combination of the nonionic surfactant, the C<sub>8-18</sub> alkyl benzene sulfonate, the C<sub>8-18</sub> alkyl sulfate and the filler constitutes at least 60 wt.%, preferably at least 70 wt.% and most preferably at least 80 wt.% of the block.
  - 3. Toilet cleaner block according claim 1 or 2, wherein the block contains at least 1.5 wt.%, preferably at least 2 wt.%, more preferably at least 2.5 wt.% of fatty alcohol alkoxylate.
  - Toilet cleaner block according to any one of the preceding claims, wherein the fatty alcohol alkoxylate is selected from alkoxylated  $C_{12-20}$  fatty alcohols, preferably from alkoxylated  $C_{16-18}$  fatty alcohols.
    - Toilet cleaner block according to any one of the preceding claims, wherein the fatty alcohol alkoxylate is selected from ethoxylated fatty alcohols with a degree of ethoxylation of 16 to 28, more preferably of 20 to 27.
- 30 6. Toilet cleaner block according to any one of the preceding claims, wherein the block contains 2-35 wt.%, preferably 2.5-25 wt.%, more preferably 3-15 wt.% of nonionic surfactant.
  - 7. Toilet cleaner block according to any one of the preceding claims, wherein the block contains 15-40 wt.%, preferably 20-35 wt.% of the  $C_{8-18}$  alkyl benzene sulfonate.
  - 8. Toilet cleaner block according to any one of the preceding claims, wherein the block contains 8-30 wt.%, preferably 10-28 wt.% of the alkyl sulfate.
- 9. Toilet cleaner block according to any one of the preceding claims, wherein the block contains 30-65 wt.%, preferably 40 35-60 wt.% filler.
  - 10. Toilet cleaner block according to any one of the preceding claims, wherein the filler is an inorganic salt selected from sulfates, carbonates, halides, phosphates and combinations thereof.
- 45 11. Toilet cleaner block according to claim 10, wherein the block contains at least 20 wt.%, preferably at least 30 wt.%, more preferably at least 35 wt.% sodium sulfate.
  - 12. Toilet cleaner block according to any one of the preceding claims, wherein the block contains nonionic surfactants and anionic surfactants in a weight ratio in the range of 1:15 to 1:2, preferably of 1:12 to 1:4.
  - 13. A process of manufacturing a toilet cleaner block according to any one of the preceding claims, said process comprising:
    - combining the nonionic surfactant, the C<sub>8-18</sub> alkyl benzene sulfonate, the C<sub>8-18</sub> alkyl sulfate and the filler;
    - extruding said extrusion blend to produce an extruded strand;
    - · cutting said extruded strand into blocks.
  - 14. Process according to claim 13, wherein the extrusion blend is extruded at a speed of at least 3 m/min.

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	15.	A toilet cleaning system comprising at least one toilet cleaner block according to any one of claims 1-12 and a release device that is configured for reversible positioning under the rim of a toilet bowl in the path of toilet flush water.
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## **EUROPEAN SEARCH REPORT**

**Application Number** 

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Х	US 2013/239313 A1 (SCHII [DE] ET AL) 19 September * paragraphs [0013], [0 [0030] - [0036], [0045] [0074]; claims; examples	^ 2013 (2013-09-19) 0020], [0021], ], [0066] -	1-15	ADD. C11D1/14 C11D1/22 C11D1/72 E03D9/02
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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 O: non-written disclosure P: intermediate document		T: theory or principle E: earlier patent door after the filing date D: document cited in L: document cited for &: member of the sau document	ument, but publise the application r other reasons	shed on, or

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

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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