Title: SELF-ADHESIVE HARD SURFACE CLEANING COMPOSITION

Abstract: The present invention provides a hard surface cleaning composition in the form of a toilet block, wherein said composition comprises: (a) 20 to 80% by weight of glycerine monoester forming a cubic or hexagonal phase in the presence of solvent; (b) 1 to 25% by weight of biocide material; and (c) 15 to 45% by weight of said solvent. The invention also provides a method for the manufacture of said toilet block and a method for providing hygiene in a toilet.
Self-adhesive hard surface cleaning composition

Field of the invention
The present invention relates to a hard surface cleaning composition in the form of a toilet block, and its use.

Background of the invention
Hard surface cleaning blocks, such as lavatory blocks are known in the art and are typically configured to provide an automatic and sustained release of active ingredients to a liquid passing the block and/or the release of perfume to the air. For example, they may be suspended in a container under the rim of a lavatory bowl or urinal such that, during a flushing cycle, water from the cistern flows over the block thereby dissolving a portion of the block and releasing active ingredients of the block into the lavatory bowl. They may also be used inside a dish washing machine or even for the purpose of manual dishwashing.

Different means of applying blocks to a toilet have been disclosed in the art. Holders for solid detergent blocks are for instance disclosed in EP-B1-586 137. An alternative to the lavatory block is a liquid dispenser device, such as the device disclosed in GB2389123.

Both the liquid and the solid rim device require a holder connecting the lavatory block to the toilet rim. Present day consumers do not like the idea of having to touch and handle a device that has been in the toilet for weeks, when refilling or replacement is required. Due to environmental reasons, disposal of such devices is also not appreciated by the consumers.
Attempts have been made to solve this problem, by various means. One such alternative is a tablet for use in the water cistern. However, this kind of device cannot be used in built-in water cisterns that are becoming more and more popular. Another alternative is a pump device having a dispenser at the toilet rim and a separate bottle with cleaning liquid outside the toilet. This option has the disadvantage of a tube connecting the rim device to the bottle with cleaning liquid.

Hard surface cleaning blocks in different forms are disclosed in the art. Solid blocks in a holder are for instance disclosed in EP-B1 553 162. An alternative to the solid block is a liquid dispenser device, such as the device disclosed in GB2389123. The hard surface cleaning composition can even be applied directly onto the surface as disclosed in EP-A1-1 086 199, where a self adhesive paste is disclosed. Alternatively, WO-2008/058853 discloses a detergent composition comprising an adhesive phase.

In these and other hard surface cleaning blocks, the delivery of perfume to a room is the main objective.

Hard surface cleaning blocks optionally comprising biocide are disclosed in the art. However, to be able to dose an effective amount of biocide to provide hygiene from a small hard surface cleaning block over a large number of flushes, requires a high level of biocide. A hard surface cleaning block comprising such a biocide compound in such effective amount to provide hygiene to a hard surface, in particular to a toilet bowl, remains to be desired.
US 6,667,287 discloses a light duty liquid cleaning composition comprising a biocide (benzalkonium chloride) for providing hygiene to a toilet.

WO-2008/125451 discloses a hard surface cleaning composition in the form of a toilet block that provides hygiene to a hard surface and that can be easily positioned onto said hard surface. Furthermore, the composition disclosed by this document rinses away in a number of flushes while releasing a hygiene agent at a uniform rate. According to the teaching of this document it is preferred to use an adhesive layer between one of the sides of the toilet block and the hard surface at which it is to be applied, so as to improve the adhesion of said toilet block.

In this connection, it is an object of the present invention to provide a hard surface cleaning composition in the form of a toilet block that provides hygiene to a hard surface, whereby said cleaning composition as such has favourable adhesive properties such that it can be easily positioned onto said hard surface, even a wet surface, without the need for a separate adhesive layer. More in particular, it is an object of the invention that the adhesive properties of the cleaning composition are such that it survives more than 150 flushes after having been positioned in the toilet bowl at a position where the force of water is maximum.

It is a further object of the invention that said hard surface cleaning composition rinses away in a number of flushes, releases a hygiene agent at a rate sufficient to provide adequate hygiene throughout the operating life of the toilet block, and does not leave behind any residue that cannot be easily removed with e.g. a toilet brush.
It is also an object of the invention to provide such a cleaning composition in solid or semi-solid form.

We have surprisingly found that at least one of these objects is achieved when using a hard surface cleaning composition in the form of a toilet block and comprising glycerine monoester, biocide material and water, whereby said glycerine monoester forms a cubic or hexagonal phase in the presence of a solvent.

**Definition of the invention**

Accordingly, the present invention provides a hard surface cleaning composition in the form of a toilet block, wherein said composition comprises:

(a) 20 to 80% by weight of glycerine monoester forming a cubic or hexagonal phase in the presence of a solvent;
(b) 1 to 25%, preferably 5 to 15% by weight of biocide material; and
(c) 15 to 45% by weight of said solvent.

Preferably, the monoglycerine ester is glycerine monooleate.

The invention further provides a method for manufacturing the hard surface cleaning composition of the invention.

The invention also provides a method for providing hygiene in a toilet, said method comprising the steps of (a) applying the hard surface cleaning composition of the invention to the toilet surface and (b) flushing the toilet with water.

These and other aspects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. For the avoidance of doubt, any feature of one aspect of the
present invention may be utilised in any other aspect of the invention. It is noted that the examples given in the description below are intended to clarify the invention and are not intended to limit the invention to those examples per se. Similarly, all percentages are weight/weight percentages unless otherwise indicated. Numerical ranges expressed in the format "from x to y" are understood to include x and y. When for a specific feature multiple preferred ranges are described in the format "from x to y", it is understood that all ranges combining the different endpoints are also contemplated.

**Detailed description of the invention**

The hard surface cleaning composition according to the invention comprises a glycerine monoester and biocide material whereby said glycerine monoester, which is a surfactant, forms a cubic or hexagonal phase in contact with a solvent during preparation of the composition. The invention relates to the cleaning formulation and the process for making said composition which may be used to stick directly on a hard surface. The self-sticking behaviour is due to the formation of a cubic or hexagonal phase.

The solvent present in the composition of the invention and needed for obtaining the cubic or hexagonal phase is preferably selected from the group consisting of glycerine, propylene glycol, ethylene glycol, water and mixtures thereof. More preferably, said solvent contains water. When the solvent contains water, the glycerine monoester present in the composition of the invention will form—at least partly—a cubic phase.

Said cubic phase may have different rheological properties depending on whether it is present as bicontinuous phase or
discontinuous phase. In the present invention the phase transition behaviour of the composition in presence of a solvent provides a way to stick the composition in the toilet (i.e. onto the surface of the toilet bowl), thus providing a self adhesive system. It has been found that the cubic phase has good adhesion properties and has got very high viscosity, thus providing the possibility to attach the cleaning composition to a wet surface.

In use, the composition of the invention gradually erodes or dissolves when contacted or flushed with water, thereby gradually releasing active ingredients to the toilet. The composition of the invention preferably last for at least 100, more preferably at least 150, still more preferably at least 200 flushes.

Toilet compositions generally do not last for more than 500 flushes, more preferably not more than 400 flushes and most preferably not more than 300 flushes.

The hard surface cleaning composition of the invention may be a solid, semi-solid or gel like composition in the meaning of Rompp Lexicon Chemie, 10th edition, Stuttgart/New York, 1997.

**Surfactant system**

The glycerine monoester present in the cleaning composition of the invention is a nonionic type of surfactant which forms a cubic or hexagonal phase in contact with a solvent. This cubic phase may be a bicontinuous cubic phase or a discontinuous cubic phase. Said cubic phase was found to have very good adhesion properties.

Preferably, the glycerine monoester is glycerine monooleate.
Preferred types of glycerine monooleate are Monomuls 90-O 18 (ex Cognis) and Cithrol GMO 90 (ex Croda).

The glycerine monoester alone or possibly in contact with small quantity of anionic surfactants gives suitable foaming and adhesion properties to the toilet block product. Additional nonionic surfactants selected from the group of fatty alcohol ethoxylates polysorbates may also be present. Preferred polysorbates are short chain (C10-C12, saturated or unsaturated) polysorbates, such as Tween 20, or longer chain (up to C18, unsaturated) polysorbates, such as Tween 80. Polysorbate nonionic surfactants were found to have excellent foaming properties.

Anionic and amphoteric surfactants may also be present in the surfactant system. The anionic and amphoteric surfactants form liquid crystalline phases above the Krafft point. These liquid crystalline phases may further improve the adhesion properties of the composition to the hard surface.

Anionic and amphoteric surfactants with a Krafft Point below room temperature are suitable for this application. Anionic surfactants such as alfa olefin sulfonate, sodium lauryl ether sulphate and sodium lauryl sulphate are suitable for this application. CMEA, CDEA and the amphoteric surfactants such as CAP Betaine may also be used to get similar result. These surfactants can be used in the formulation at a level of 0-10%, more preferably 2-5% by weight. Higher levels have been observed to give a softer product.

The glycerine monoester (which forms a cubic or hexagonal phase in the presence of the solvent) is present in the cleaning
composition of the invention in a concentration of preferably at least 30%, more preferably at least 40%, most preferably at least 60%. On the other hand, the said monoester is present in the composition in a concentration of not more than 80%, preferably not more than 70%.

Biocide material
The biocide material is preferably selected from CTAC (cetyl trimethyl ammonium chloride), and BAC (benzalkonium chloride) and didecyldimethylammonium chloride, dodecyldipropylene triamine and poly (hexamethylenebiguanide ) hydrochloride. BAC is the most preferred type of biocide. These quarternary ammonium biocides with different chain lengths have been found to give different hygiene properties. Surprisingly it has been observed that the hygienic properties of a quarternary ammonium biocide having at least one alkyl chain with a length of at least 14 carbon atoms (C14) show a better biocidal effect than the quarternary ammonium biocides having a shorter chain. The preferred chain length is C14-C16, more preferably a mixture of C14-C16, with 80-98%w of C14. The biocide is preferably present in a concentration of from 1 to 15%, more preferably 5 to 15%, by weight.

Optional ingredients
The hard surface cleaning composition according to the invention may further comprise detergent active, builders, dyes, perfume, hygiene agents, antioxidants, radical scavengers, chelating agents, hydro tropes, anticorrosion agents, opacifiers, brighteners, preservatives and/or abrasives such as silica, kaolin, talc etc. However, further ingredients that compromise the preferred transparent or translucent character of the composition are not preferred.
Perfume is preferably present in the cleaning composition of the invention, in a preferred concentration of 3 to 15% by weight.


The composition may optionally comprise humectant. Humectants maintain both structure and clarity. When present, said humectants will enable retention of water within the toilet block formulation of the invention and also increase the stability of said toilet block such that phase transition of the glycerine ester present is prevented. Preferred humectants are polyhydroxylated organic compounds, such as sorbitol and sucrose. In this connection, it is noted that the solvents glycerol and polyethylene glycol (PEG) are also suitable as humectants.

The humectant may be present in a concentration of 0 to 40% by weight of the composition. The humectant is preferably present in a concentration of at least 5%, but preferably not more than 20%, more preferably not more than 10%.

Solvents other than the solvent needed for forming the cubic or hexagonal phase, may also be present in the composition. Preferred -additional- solvents include poly alkylene glycols (e.g. PEG, PPG) and short chain organic solvents (e.g. ethanol.
or isopropanol). The additional solvent may be present in the composition in a concentration of 0 to 10%, preferably 1-10% by weight of the composition.

**Composition size and shape**

The shape of the hard surface cleaning composition may affect its adhesive properties. It is preferred to have hydrodynamic shapes, which help in better control of the erosion properties of the block which in turn helps in better adhesion to the surface. Thus, round, smooth shapes are preferred over square/rectangular blocks with sharp edges, due to superior hydrodynamic behaviour.

The composition life is directly related to its formulation and the size. A normal size toilet block is between about 4 and 50 grams, preferably about 4 to 15 g.

It is preferred to provide a toilet block that is at least partially transparent or translucent. By at least partially transparent or translucent is meant that a 1 cm thick sample of the material transmits at least 5% of visible light, preferably at least 20% of visible light, more preferably at least 50% of visible light. More preferably the block is transparent. By transparent is meant that a 1 cm thick sample of the block transmits at least 70% of visible light, preferably at least 90%. Due to the presence of a dye, and almost inevitable absorption and/or scattering of some of the light, the transmission is generally below 95% of visible light.
Application
The composition of the invention may be applied to the internal surface of a toilet bowl from a tube or in a preformed shape so as to be used for toilet cleaning.

In a preferred embodiment, a method for providing hygiene to a toilet is provided. In that method, a hard surface cleaning composition according to the invention is attached to the toilet bowl surface which is preferably a wet surface. When attaching said composition to the bowl surface, the surfactant phase (cubic or hexagonal) present in the composition ensures good adhesion to the wet toilet bowl surface.

When the toilet is flushed, the toilet block composition of the invention is wetted and a small portion thereof is dissolved in the flush water, preferably about 0.01% to 2.0% by weight, preferably 0.1% to 1%.

Hardness of the composition
The hard surface cleaning composition of the invention may be a solid, semi-solid or gel like composition in the meaning of Rompp Lexicon Chemie, 10th edition, Stuttgart/New York, 1997
The composition hardness may be analysed using a Penetrometer PNR10 (ex SUR Berlin). The method involves using a probe to mechanically penetrate the sample of interest using a known force. The penetrometer needle is positioned manually close to the surface of sample under test and impact measurement carried out. The result is displayed in ‘mm’ penetration depth into the sample and replicate readings carried out on a different part of the composition. Low values correlate to hard samples, while higher values correspond to softer materials.
Suitable compositions of the invention have a hardness of about 1 to 14 mm, more preferably 1 to 9 mm penetration measured using the method above.

**Process for manufacturing**

The invention provides a method for the manufacturing of a toilet block comprising the cleaning composition of the invention, comprising the steps of:

- heating the glycerine monoester to 35 to 60°C, preferably about 40°C,
- adding the biocide in the form of a homogeneous liquid containing the solvent needed for forming the cubic or hexagonal phase, and fully dissolving the biocide,
- optionally adding perfume and colour ingredients at this temperature, and
- pouring the thus-formed gel in a mould of a desired shape.

The product in the mould may be kept at room temperature for solidification or it may be passed through a cooling tunnel for quick solidification. Once the product is solidified in the mould it may be packed in any desired packaging.

Depending upon the formulation, it is also possible to use injection moulding or normal conventional extrusion process to make these blocks.

The invention is now illustrated by the following non-limiting examples.
Example 1

The compositions of this example, each of which are in the form of a toilet block, were attached to the internal surface of a toilet bowl and tested for the number of flushes they lasted while maintaining the right product dosing to the toilet. The compositions 1-5 are according to the present invention, whereas composition A is a comparative composition only containing glycerine monooleate and water. In Table 1, all tested formulations are shown as well as the no. of flushes that they last.

Table 1: Cleaning formulations containing glycerine monooleate and water (in % wt)

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<td>No. of flushes</td>
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As can be seen, the toilet blocks with the indicated compositions 1-5 last for at least 150 flushes. Furthermore, the adhesive properties of all tested toilet blocks 1-5 were such that they survived the indicated numbers of flushes. In addition, the dissolution behaviour of these tested blocks was found to be very good in the sense that the tested blocks were found to dissolve homogeneously.

On the other hand the toilet block with the composition A (which is not according to the present invention) was found to be both insoluble and opaque.
Claims

1. A hard surface cleaning composition in the form of a toilet block, wherein said composition comprises:
   (a) 20 to 80% by weight of glycerine monoester forming a cubic or hexagonal phase in the presence of solvent;
   (b) 1 to 25%, preferably 5 to 15% by weight of biocide material; and
   (c) 15 to 45% by weight of said solvent.

2. A composition according to claim 1, wherein the glycerine monoester is present at a concentration of 40 to 70% by weight.

3. A composition according to claim 1 or claim 2, wherein the glycerine monoester is glycerine monooleate.

4. A composition according to anyone of claims 1-3, wherein the biocide material is selected from the group consisting of benzalkoniumchloride, didecyldimethylammonium chloride, dodecyldipropylene triamine and poly(hexamethylenebiguanide) hydrochloride.

5. A composition according to claim 4, wherein the biocide material is benzalkoniumchloride.

6. A composition according to anyone of claims 1-5, wherein the composition is at least partially transparent or translucent.

7. A composition according to anyone of claims 1-6, wherein said composition has self-adhesive properties when applied to a wet surface.
8. A composition according to anyone of claims 1-7, wherein the composition additionally comprises an anionic or an amphoteric surfactant, having a Krafft point below room temperature.

9. A composition according to anyone of claims 1-8, wherein the composition additionally comprises 3-15% by weight of a perfume.

10. A composition according to anyone of claims 1-9, wherein the block hardness is 1-14 mm (as defined herein).

11. Process for the manufacture of a block according to anyone of claims 1-10, comprising the steps of:
   (a) heating the glycerine monoester to a temperature of 35 -60 C, preferably 40 C,
   (b) adding the biocide in a homogeneous liquid containing the solvent needed for forming the cubic or hexagonal phase; and fully dissolving the biocide;
   (c) pouring the thus-formed gel into a mould to solidify.

12. Method for providing hygiene in a toilet comprising the steps of:
   (a) applying the composition according to anyone of claims 1-10 to the toilet surface; and
   (b) flushing the toilet with water.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER


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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>us 6 569 478 BI (LESER MARTIN CH ET AL) 27 May 2003 (2003-05-27) column 4, lines 41-49; claim 1</td>
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<td>wo 00/33816 AI (THE VICTORIA UNIVERSITY OF MANCHESTER [GB] ) 15 June 2000 (2000-06-15) page 6, lines 11-22 page 7, lines 1-6 ----</td>
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[X] Further documents are listed in the continuation of Box C. [X] 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

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"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 novel or cannot be considered to involve an inventive step when the document is taken into account in combination 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

25 May 2012

Date of mailing of the international search report

06/06/2012

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax. (+31-70) 340-3016

Authorized officer

Pentek, Eric
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