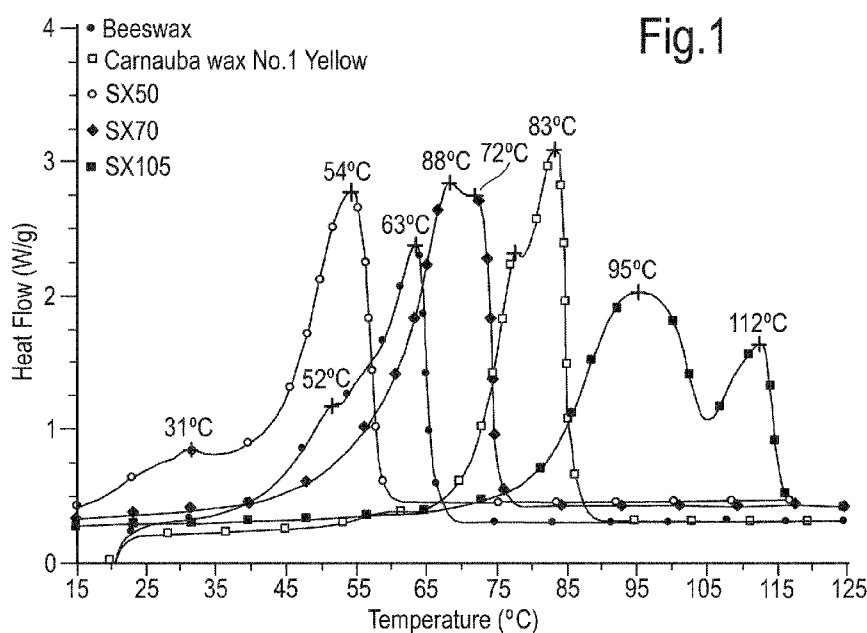




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- (71) Applicant (for all designated States except KH, LT, US):  
**SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, 2596 HR The Hague (NL).
- (71) Applicant (for US only): **SHELL OIL COMPANY** [US/US]; Shell Plaza 1, Houston, Texas 77252-2463 (US).
- (72) Inventors: **VERBIST, Guy, Lode, Magda, Maria**; Grasweg 31, 1031HW Amsterdam (NL). **WEIJERS, Cees**; Den Dolech 2, 5612AZ Eindhoven (NL). **CHRISTOVA-ZDRAVKOVA, Christina**; Den Dolech 2, 5612AZ Eindhoven (NL).
- (74) Agent: **MATTHEZING, Robert, Maarten**; PO Box 384, 2501 CJ The Hague (NL).
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[Continued on next page]

(54) Title: ANTI-GRAFFITI COATINGS



(57) Abstract: The present invention relates to anti-graffiti composition comprising Fischer-Tropsch derived wax, wherein the Fischer-Tropsch derived wax has a congealing point of at least 105°C and at most 130°C.



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**Declarations under Rule 4.17:**

**Published:**

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))* — *with international search report (Art. 21(3))*

- 1 -

## ANTI-GRAFFITI COATINGS

Field of the Invention

5 The present invention relates to an anti-graffiti composition comprising Fischer-Tropsch derived wax and to the use of said composition for coating a surface. The present invention also relates a process to prepare the anti-graffiti composition.

Background of the Invention

10 Concrete structures are present everywhere in modern cities and architecture. Their outer surface is of target of vandalism, in particular graffiti spray painting, which is undesired from an aesthetic point of view. The removal and cleaning cost of such acts of vandalism can  
15 present a significant cost to the infrastructure owner. There are products that can protect concrete surfaces such that spray paint graffiti can be removed by cleaning with (hot) high pressure hosing.

However, the anti-graffiti compositions comprising  
20 natural waxes have a comparatively low melting point impacting the protective layer durability when hot pressure hosing. These natural waxes are for example described in in the "International Journal for Applied Science, 4-2011, Natural waxes-Properties, Compositions  
25 and Applications, E. Endlein, K Peleikis; Natural Waxes-Properties, Compositions and Applications".

It is an object of the invention to provide an anti-graffiti composition which allow protective layers with a higher stability against hot pressure hosing.

30 It is a further object of the invention to provide protective layers with are also color stable and do not show yellowing overtime.

- 2 -

Summary of the invention

From a first aspect, above and other objects may be achieved according to the present invention by providing an anti-graffiti composition comprising Fischer-Tropsch  
5 derived wax, wherein the Fischer-Tropsch derived wax has a congealing point of at least 105°C and at most 130°C.

It has been found according to the present invention that the anti-graffiti composition comprising Fischer-Tropsch derived waxes with a high melting point allow  
10 protective layers with a high stability against hot pressure hosing.

From a second aspect, the invention embraces a use of anti-graffiti composition for coating a surface.

It has been found that the surface coated with the anti-graffiti composition comprising a Fischer-Tropsch  
15 derived wax protect the layers of the surface against hot pressure hosing.

A further advantage is that the Fischer-Tropsch derived may remain at the surface after removing the graffiti (as opposed to low melting waxes), and continue  
20 to protect the surface with the need to re-apply.

From a third aspect, the invention embraces a process to prepare anti-graffiti composition. An advantage of the use of Fischer-Tropsch derived wax is  
25 that the Fischer-Tropsch derived wax has very low levels of aromatics, sulphur, napthenics and impurities. In addition, the Fischer-Tropsch derived waxes have high melting temperatures. Also, a Fischer-Tropsch wax with a congealing point of 105°C has a melting point above the  
30 boiling point of water (100°C at atmospheric conditions) and hence the layer will not melt under a removal process by hot water.

Detailed description of the invention

According to the present invention an anti-graffiti composition comprises Fischer-Tropsch derived wax,  
5 wherein the Fischer-Tropsch derived wax has a congealing point of at least 105°C and at most 130°C.

The Fischer-Tropsch derived wax is derived from a Fischer-Tropsch process. Fischer-Tropsch product stream is known in the art. By the term "Fischer-Tropsch derived  
10 wax" is meant a paraffin wax is, or is derived from a Fischer-Tropsch process. A Fischer-Tropsch derived paraffin wax may also be referred to a GTL (Gas-to-Liquids) product. An example of a Fischer-Tropsch process is given in WO2002/102941, EP 1 498 469 and  
15 WO2004/009739, the teaching of which is incorporated by reference.

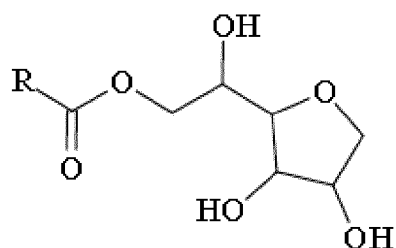
The Fischer-Tropsch derived wax comprises paraffins, primarily n-paraffins. Preferably, the Fischer-Tropsch derived wax comprises more than 85 wt.% of n-paraffins,  
20 preferably more than 90 wt.% of n-paraffins.

Preferably, the Fischer-Tropsch derived wax has a congealing point of at least 50°C. Also, the Fischer-Tropsch derived wax has a congealing point of at least 70°C. In addition, the Fischer-Tropsch derived wax has a  
25 congealing point of at least 105°C and at most 130°C.

Suitably, the anti-graffiti composition also comprises a surfactant and water. Typically, a surfactant that may be used in anti-graffiti compositions is Anionic e.g. sodium dodecyl sulfate, cationic e.g.  
30 Cetylpyridinium chloride, non-ionic e.g. Tween 60, Span 60 and or Zwitterionic e.g. Cocamidopropyl hydroxysultaine.

- 4 -

Preferably, the surfactant has the formula I

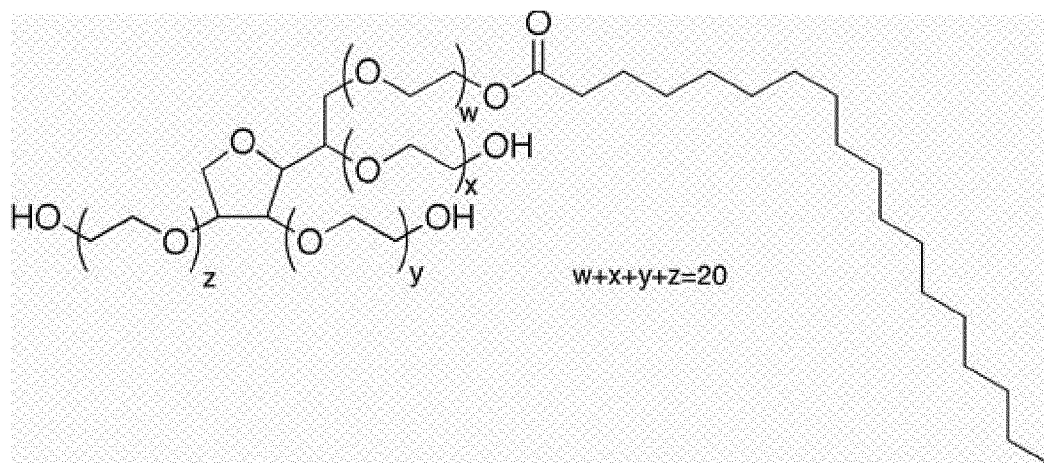


5

wherein R is in a range between 10 and 20 carbon atoms, R is preferably 17 carbon atoms and wherein R is a saturated or a unsaturated carbon chain

10

or the formula II



15

Wherein R is in a range between 10 and 20 carbon atoms, preferably 17 carbon atoms and  $x+y+z+w=20$ , and wherein R

- 5 -

is a saturated or a unsaturated carbon chain or a mixture of the surfactants having formula I and formula II.

5 Preferably, the ratio of surfactant to Fischer-Tropsch derived wax is in a range between 20 to 200 wt.%, preferably in a range between 30 and 80 wt.% based on the total amount of the anti-graffiti composition. Also, the ratio of Fischer-Tropsch derived wax to water is from 25:75 to 5:95, preferably  
10 1 to 25.

In another aspect, the present invention provides a process wherein the Fischer-Tropsch derived wax is emulsified with surfactant and water.

15 Preferably, the process for preparing a Fischer-tropsch derived wax suspension comprises the following steps:

- (a) Heating of a wax, surfactant(s) and water mixture to a temperature above the of the congealing point of a Fischer-Tropsch derived wax;
- (b) Applying high shear mixing for 5 minutes using a  
20 Silverson L4RT high shear mixer fitted with an Emulsor screen at 5000 rpm;
- (c) Cool down to solidify the wax in suspension.

In a further aspect, the present invention provides the use of anti-graffiti composition for coating a surface.  
25 Also, the anti-graffiti composition is preferably used for coating the surface, which surface is of masonry, concrete, natural stone, mortar, brick work, cement composites or artificial stone. These surfaces may for example cover constructions, bridges or overlays.

30 Preferably, the process for preparing a Fischer-tropsch derived wax coated surface comprises the following steps:

- 6 -

- (a) Heating of a surface of a wall above the temperature of the congealing point of a Fischer-Tropsch derived wax;
- (b) Melting the Fischer-Tropsch derived wax on the heated surface of the wall of step (a);
- 5 (c) Impregnating the surface coated with molten Fischer-Tropsch wax by rubbing with a tissue paper for 1 minute to obtain a Fischer-Tropsch derived coated surface.

Suitably, the process for graffiti-removal from a Fischer-Tropsch derived wax coated surface comprises the following steps:

10

- (a) heating the coated surface in water at a temperature below the congealing point of the Fischer-Tropsch wax used for coating the surface;
- (b) Cleaning the surface with the abrasive side of a kitchen sponge ;
- 15 (c) Repeating steps (a) and (b) to obtain a Fischer-Tropsch derived wax coated surface without graffiti coating.

The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

20

### Examples

#### Example 1

##### Wax impregnation

25

The following waxes were used to impregnate a tile:

- 1) Beeswax (refined) (Aldrich)
- 2) Carnauba wax No. 1 yellow (Aldrich)
- 3) SX50 Fischer-Tropsch wax
- 30 4) SX70 Fischer-Tropsch wax
- 5) SX105 Fischer-Tropsch wax

DSC analysis on the above waxes was performed with a TA Instruments Q2000 DSC. The samples were measured in the

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temperature range where the transition occurred with heating/cooling rates of 10 K/min. In figure 1, the thermal behavior of the waxes can be found.

The Fischer-Tropsch derived waxes SX50 having a congealing point of 50°C, SX70 having a congealing point of 70°C and SX105 having a congealing point of 105°C are prepared according to a Fischer-Tropsch derived process as for example described in WO2002/102941, EP 1 498 469 and WO2004/009739. In order to obtain a flat smooth porous surface, the backside of a ceramic tile (Dry-pressed ceramic tiles for interior wall (15x15 cm)) was sanded down using sand paper (see Figure 3). The tile was then weighed and placed on a hotplate (front side facing down) and heated to 130°C. 6.8g of a wax was molten at the sanded surface and equally distributed using tissue paper. After wax impregnation, the tile was weighed again to determine the exact amount of wax absorbed at the surface. The tile was cut into 9 smaller 4x5 cm tiles before further testing.

#### Example 2

##### Graffiti coating

One coat of paint (Montana Gold G-5080 Ultramarine aerosol spray can) was applied to the surface of the 4x5 cm tiles and left to cure for five days.

#### Example 3

##### Graffiti removal

The coated tile was first submersed in water at 75°C for one minute, followed by cleaning using the abrasive side of a kitchen sponge. For the following 3 minutes, the tile was repeatedly heated in water and cleaned. The experiment is performed 3 times for every wax. In Figure 2 the

- 8 -

results of the graffiti removal of the wax coated tiles can be found.

#### Results and discussion

Figure 2 shows that most paint left after cleaning was is  
5 at the surface of the control sample (no wax). The samples impregnated with wax have less paint at the surface and therefore show anti-graffiti properties. The best results were obtained with tiles coated with SX105 Fischer-Tropsch wax, where the most graffiti could be removed.

10 One possible reason for the improved anti-graffiti performance of SX105 could be the significantly higher melting point. This was illustrated by DSC measurements. In Figure 1, the thermal behavior during second heating of all waxes are plotted.

15 All the waxes melt over a broad temperature range, having two distinguishable melting peaks. The waxes can be ordered from highest to lowest melting point as follows:

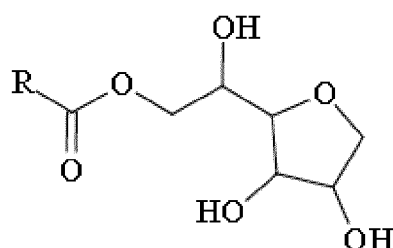
SX105 > Carnauba wax > SX70 > Beeswax > SX50. melting wax is  
20 SX50 < Beeswax

The DSC results indicate that when cleaning at 75°C, SX50, SX70 and Beeswax will be fully, and carnauba wax partly molten layers. SX105 on the other hand will remain as a solid  
25 layer between the surface of the substrate and paint, offering the best protection as opposed to a molten or softened wax layer.

Another possible added benefit could be that SX105 will remain at the surface after graffiti removal (as opposed to  
30 low melting waxes), and continue to protect the surface without the need to re-apply.

### CLAIMS

1. Anti-graffiti composition comprising Fischer-Tropsch derived wax, wherein the Fischer-Tropsch derived wax has a congealing point of at least 105°C and at most 130°C.
- 5 2. Anti-graffiti composition according to claim 1, wherein the composition also comprises a surfactant and water.
3. Anti-graffiti composition according to claim 2, wherein the surfactant has the formula I

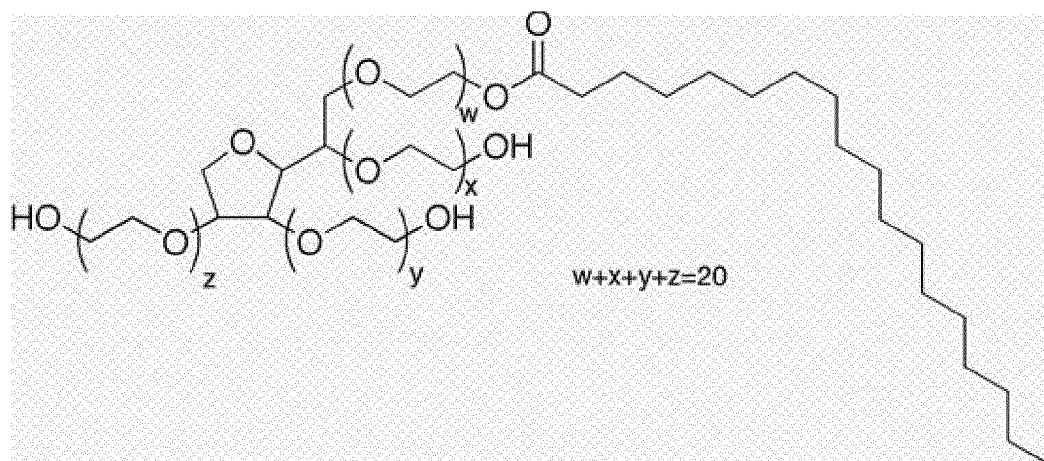


10

wherein R is in a range between 10 and 20 carbon atoms, R is preferably 17 carbon atoms, and wherein R is a saturated or unsaturated carbon chain

15

or the formula II



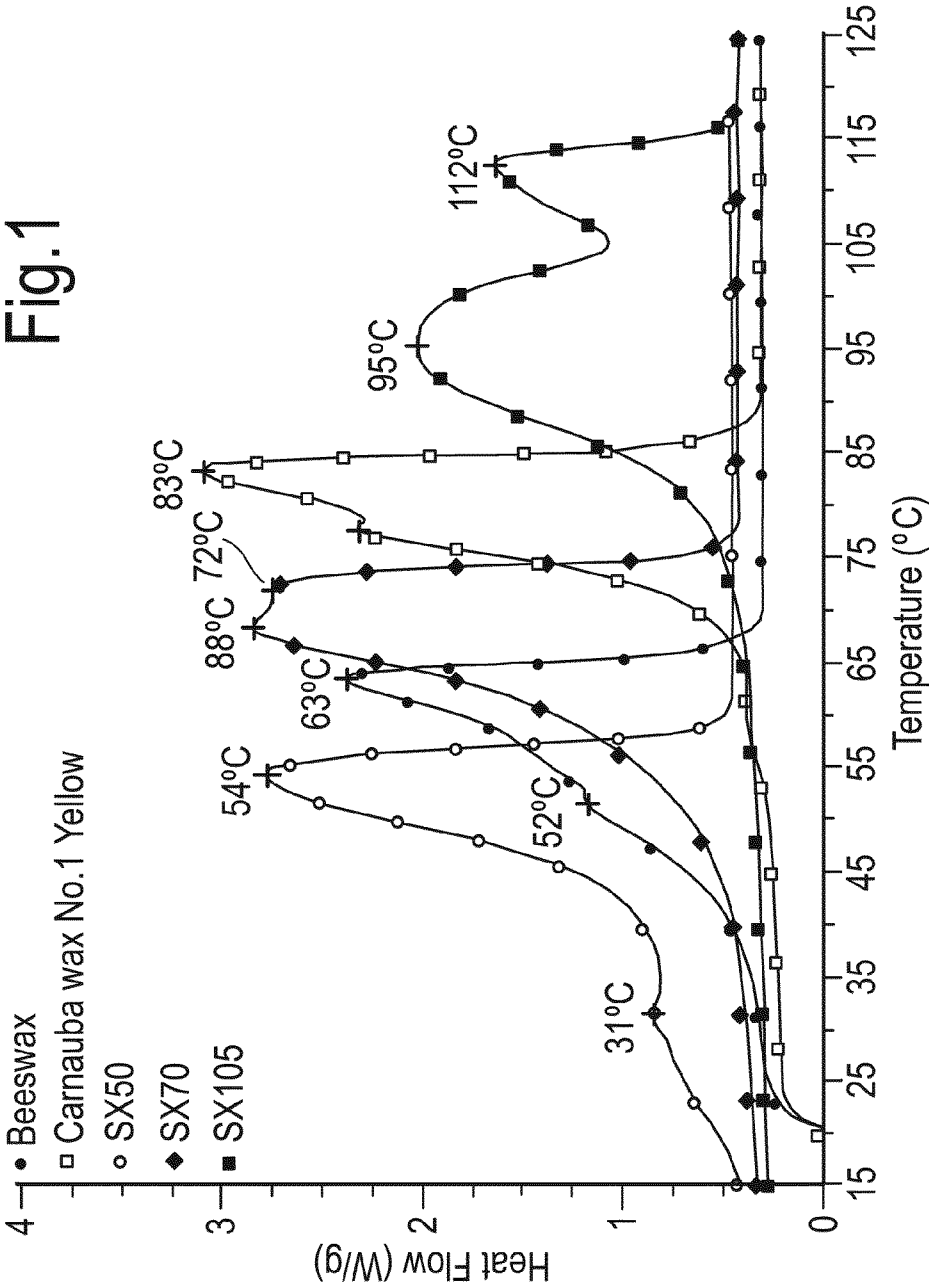
Wherein R is in a range between 10 and 20 carbon atoms,  
 5 preferably 11 carbon atoms and  $x+y+z+w=20$ , and wherein R  
 is a saturated or unsaturated carbon chain  
 or a mixture of the surfactants having formula I and  
 formula II.

4. Anti-graffiti composition according to claim 2 or 3,  
 10 wherein the ratio of surfactant to Fischer-Tropsch derived  
 wax is in a range between 20 to 200 wt.%, preferably in a  
 range between 30 and 80 wt.% based on the amount of the  
 anti-graffiti composition.
5. Anti-graffiti composition according to any one of claims 2  
 15 to 4, wherein the ratio of Fischer-Tropsch derived wax to  
 water is from 25:75 to 5:95, preferably 1 to 25.
6. Process to prepare anti-graffiti composition as defined  
 according to one or more of the preceding claims 2 to 5,  
 wherein the Fischer-Tropsch derived wax is emulsified with  
 20 surfactant and water.
7. Use of anti-graffiti composition as defined according to  
 one or more of the preceding claims 1 to 6, for coating a  
 surface.

- 11 -

8. Use of anti-graffiti composition according to claim 7,  
wherein the surface is masonry, concrete, natural stone,  
mortar, brick work, cement composites or artificial stone.

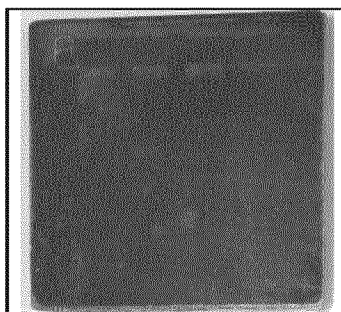
Fig.1



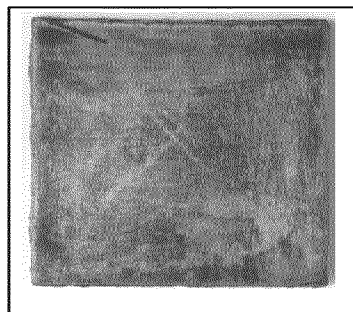
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Fig.2

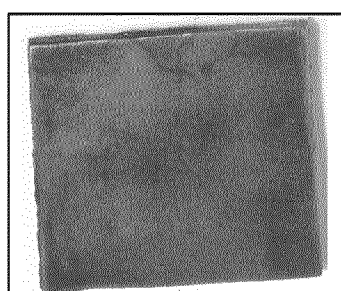
Control



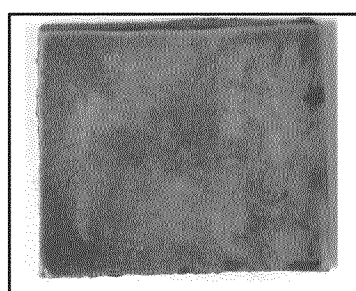
Beeswax



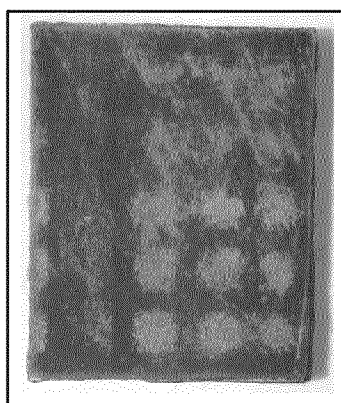
Carnauba



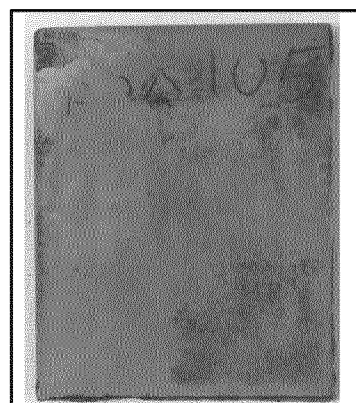
SX50 Fischer-Tropsch wax



SX70 Fischer-Tropsch wax

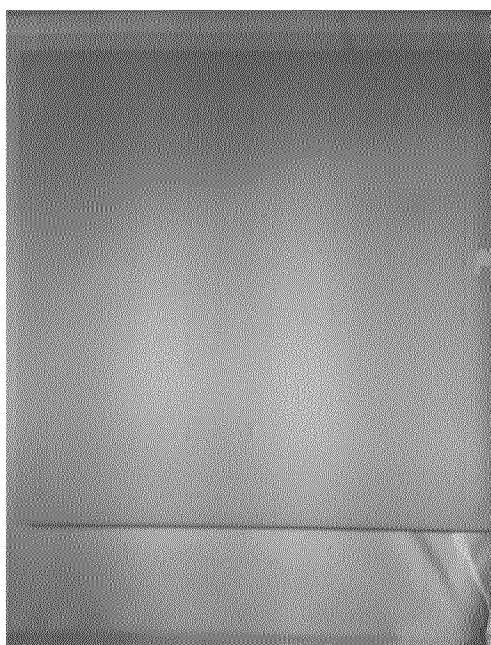


SX105 Fischer-Tropsch wax



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**Fig.3**  
Clean Tile



## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2016/082303

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C08L91/08 C09D5/00  
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)  
C08L C09D

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

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                         | Relevant to claim No. |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | US 5 387 434 A (BLACK ROBERT H [US])<br>7 February 1995 (1995-02-07)<br>examples 3,4<br>the whole document<br>-----                                                                                                        | 1-8                   |
| A         | US 5 773 091 A (PERLMAN DANIEL [US] ET AL)<br>30 June 1998 (1998-06-30)<br>column 1, line 51 - column 2, line 15<br>column 3, line 53 - line 61<br>column 9, line 15 - line 45; claims 1-18<br>the whole document<br>----- | 1-8                   |
| A         | US 6 033 736 A (PERLMAN DANIEL [US] ET AL)<br>7 March 2000 (2000-03-07)<br>column 2, line 5 - line 12<br>column 3, line 23 - line 26<br>column 7, line 9 - line 23<br>claims 1-28<br>the whole document<br>-----           | 1-8                   |



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

28 March 2017

Date of mailing of the international search report

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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

olde Scheper, Bernd

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/082303

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date     |
|-------------------------------------------|---------------------|----------------------------|-------------------------|
| US 5387434                                | A                   | 07-02-1995                 | NONE                    |
| -----                                     |                     |                            |                         |
| US 5773091                                | A                   | 30-06-1998                 | AU 734600 B2 21-06-2001 |
|                                           |                     | BR 9702349 A               | 28-12-1999              |
|                                           |                     | CA 2231615 A1              | 22-01-1998              |
|                                           |                     | DE 19717035 A1             | 15-01-1998              |
|                                           |                     | EP 0912260 A1              | 06-05-1999              |
|                                           |                     | JP H11514036 A             | 30-11-1999              |
|                                           |                     | NZ 329912 A                | 29-11-1999              |
|                                           |                     | US 5773091 A               | 30-06-1998              |
|                                           |                     | WO 9802257 A1              | 22-01-1998              |
| -----                                     |                     |                            |                         |
| US 6033736                                | A                   | 07-03-2000                 | AU 4705299 A 17-01-2000 |
|                                           |                     | CA 2336779 A1              | 06-01-2000              |
|                                           |                     | EP 1098939 A1              | 16-05-2001              |
|                                           |                     | US 6033736 A               | 07-03-2000              |
|                                           |                     | WO 0000556 A1              | 06-01-2000              |
| -----                                     |                     |                            |                         |