(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 952 266 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
09.12.2015 Bulletin 2015/50

(51) Int Cl.:
B05D 5/00 *(2006.01)* ***B05D 5/08*** *(2006.01)*
E04D 1/00 *(2006.01)*

(21) Application number: **14171043.4**

(22) Date of filing: **03.06.2014**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

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(54) Method for treating surfaces, particularly surfaces of tiles or the like, and tiles produced according to such method

(57) A method for treating surfaces, particularly for producing tiles having decreased permanence of water thereon after wetting, comprises the application of a coating so that such coated surfaces present alternate predetermined zones having different degree of hydrophobic properties.

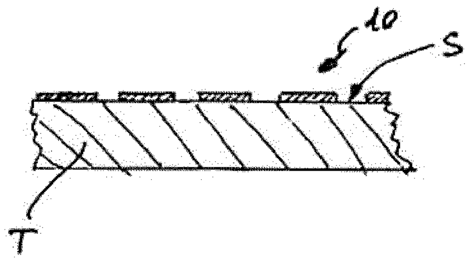

Fig. 2

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Description

[0001] The present invention relates to a method for coating surfaces, particularly for coating tiles which have a decreased permanence of water thereon after wetting.

[0002] With the term "tile" we mean whatever manufactured piece of hard-wearing material such as ceramic or stone, generally used for covering roofs, floors, showers, or other objects such as tabletops. Tiles are often used to form floor coverings, and their more common shape is a simple square. Tiles are most often made of ceramic, typically glazed for internal uses and unglazed for roofing, but other materials are also commonly used, such as concrete and other composite materials, and stone. Tiling stone is typically marble, onyx, granite or slate.

[0003] When tiles are applied for external purpose, they have the tendency, after raining, of keeping water droplets thereon. In other words water remains on tiles surfaces, and this can get the tiles surface dirty mainly due to the slow evaporation. This problem does exist also for tiles used inside, for instance when a floor is washed. When tiles are used outside, in the winter the water on tiles surface can freeze over becoming very dangerous for people's safety. The ice formation could lead also to cracks inside tiles.

[0004] The above problem is currently addressed by using organic or inorganic compound coatings (or mixture thereof) which cover the entire tile surface. These coatings can be either hydrophobic or hydrophilic. The main property for discriminating these two coating families is given by the contact angle value which is strictly connected to the surface energy according to the Young's theory. In Figure 1 is reported a schematic of a liquid drop showing the quantities in Young's equation.

[0005] The theoretical description of contact arises from the consideration of a thermodynamic equilibrium between the three phases as shown in figure1: the liquid phase (L), the solid phase (S), and the gas/vapor phase (G) (which could be a mixture of ambient atmosphere and an equilibrium concentration of the liquid vapor). The "gaseous" phase could also be another (immiscible) liquid phase. If the solid vapor interfacial energy is denoted by γ_{SG}, the solid-liquid interfacial energy by γ_{SL}, and the liquid-vapor interfacial energy (i.e. the surface tension) by γ_{LG}, then the equilibrium contact angle θ_C is determined from these quantities by Young's Equation:

$$0 = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos \theta_C$$

[0006] The contact angle can also be related to the work of adhesion via the Young-Dupré equation:

$$\gamma(1+\cos \theta_C)=\Delta W_{SLV}$$

where ΔW_{SLV} is the solid - liquid adhesion energy per unit area when in the medium V.

[0007] Generally, if the water contact angle θ_c is smaller than 90°, the solid surface is considered hydrophilic and if the water contact angle is larger than 90°, the solid surface is considered hydrophobic. Many polymers exhibit hydrophobic surfaces. Highly hydrophobic surfaces made of low surface energy (e.g. fluorinated) materials may have water contact angles as high as ~120°.Some materials with highly rough surfaces may have a water contact angle even greater than 150°, due to the presence of air pockets under the liquid drop. These are called superhydrophobic surfaces.

[0008] Some of the hydrophobic coatings can be based on fluorinated polymers like PTFE (polytetrafluoroethylene) and PFPE (perfluoropolyether) or on methyl groups (-CH3) like PP (polypropylene) or on silicone and fluoride resin. Super-hydrophobic coatings can be made from many different materials. The following are known as possible bases for the coating:

- manganese oxide polystyrene (Mn02/PS) nano-composite
- zinc oxide polystyrene (ZnO/PS) nano-composite
- precipitated calcium carbonate
- carbon nano-tube structures
- silica nano-coating

[0009] Hydrophilic coatings exhibit water-loving characteristics. Chemically, this means they participate in dynamic hydrogen bonding with surrounding water. Some of the hydrophilic coatings can be based on Nylon 6.6, PET (polyethylene terephthalate), PVC (poly vinyl chloride) or inorganic material such as alumina, titanium dioxide (titania), involving silica and zirconium dioxide (zirconia).

[0010] The current coatings and process are not able to ensure the right water flow from the tiles surface and moreover they have very low durability, low scratch resistance (due to the low hardness) and they can be damaged (yellowing, cracks) by UV radiation which is able to break polymeric chain bonds. Finally, the organic coating thickness is very high (around 30-50 microns) and this could modify the tiles appeal, changing for example the gloss.

[0011] An object of the present invention is to provide a method for producing or treating tiles which can overcome the above drawbacks. Such object is reached tanks to a method and a tile having the features listed in the appended claims.

[0012] The solution according to the invention comprises a deposition process which can be carried out downstream the furnace used for producing tiles. Such process provides an alternation of hydrophobic and hydrophilic areas on the tiles surface in order to guarantee the right water flow along the hydrophilic areas. The applicant has discovered that by having hydrophobic stripes on tiles surface, preferably in a parallel pattern, alternated to hydrophilic stripes, permits the right water flow which come from the hydrophobic stripes comprised between hydrophilic stripes. For achieving the fastest water flow from the surface it would be useful to coat the tiles thickness (side borders) using the hydrophilic coating (the same used for the hydrophilic stripes). In this way the liquid meniscus is easily broken and water can flow away. It is also advantageous to provide the surface of the tiles with an edge portion of hydrophilic coating as a sort of frame around the central area of the tile.

[0013] Even with a very low inclination angle of the tiles (lower than 1 °) it is possible to avoid stagnation of water which leads to ice formation in winter times and to stains which are formed due to the slow water evaporation.

[0014] The method according to the invention does not depend on the material of the tiles and on the specific hydrophilic or hydrophobic coating. Moreover it is not critical if hydrophobic stripes are applied directly on an already hydrophilic surface of the tile or on a previously applied hydrophilic coating covering the entire surface of the tile, or if hydrophilic stripes are applied on a hydrophobic substrate; what really matters it is the surface energy gap between the hydrophilic and hydrophobic areas which should be as highest as possible. The applicant observed that water goes from the hydrophobic areas to hydrophilic areas, where the evaporation is high because of the very low water meniscus height; the energy level required for water evaporation is low if the amount of water is low too. In a preferred embodiment of the invention, a hydrophilic coating is applied on the entire surface of the tiles before applying stripes of hydrophobic coatings. The applicant has also discovered that the dimension of hydrophilic and hydrophobic stripes is quite critical, the width of the hydrophilic stripes being preferably comprised between 1 and 10 mm, more preferably between 2 and 8 mm, with a most preferred value around 5 mm. Similarly, the width of the hydrophobic stripes is preferably comprised between 10 and 50 mm, more preferably between 20 and 30 mm.

[0015] Further advantages and features of the method according to the present invention will become clear from the following detailed description, with reference to the attached drawings, in which:

- Figure 1 is a schematic side view of a liquid drop showing the quantities in Young's equation;
- Figure 2 is a sectioned view of a tile according to the invention;
- Figure 3 is a sectioned view similar to figure 2 and referring to a second embodiment of the invention;
- Figure 4 is a perspective view of a stainless steel mask used in the method according to the invention;
- Figure 5 is a top view of a tile with a coating obtained by using the mask of figure 4, where the hydrophobic coating has been highlighted;
- Figure 6 is a top view of a tile with a hydrophilic coating applied according to a further embodiment of the invention;
- Figure 7 is a cylinder used in a continuous process for producing tiles where the coating obtained on tiles has the same pattern of figure 5;
- Figure 8 is a perspective view of a tile coated according to the method of the invention, where the tile borders coated with hydrophilic coating are highlighted; and
- Figure 9 is a perspective view of a tile where the inclination angle (lower than 1 °) of the tiles is highlighted

[0016] The hydrophobic coating 10 shown in figure 2 (where the thickness of coating layer is enlarged for clarity purpose) is directly applied on a upper surface S of a tile T. One of the coating used by the applicant is a hydrophobic coating produced by Diasen. Such coating 10 is applied by spray coating deposition using a stainless steel mask 12 (figure 4) where cut area 12a of the stainless steel sheet correspond to hydrophobic areas of the tile T. Figure 4 is a photo of the stainless mask placed on a tile T. Of course the use of such mask was mainly for experimental purpose, and the applicant has also applied the hydrophobic coating by means of a roll R (figure 7) in the production line of tiles T, for instance after the production furnace, in a zone downstream the furnace where temperature of the tiles is around 120°C. The roll R may have on its surface some helicoidally porous area R1 which can release on the tiles a predetermined amount of coating composition which, due to the movement of the tiles on the conveyor belt of the production line, leaves on the tiles a plurality of stripes inclined by 45° with respect to the advancing direction of the conveyor belt. The 45° inclination of the hydrophobic stripes is the best compromise for having the water flow along hydrophilic stripes independent on how tiles are placed on the ground. Of course the best solution would be to have hydrophilic and hydrophobic stripes parallel to the water flow direction on the tiles due to gravity, which is dependent on the inclination of tiles on ground. But such solution could be problematic for the tiler, since stripes are not visible. It is also possible to indicate a preferred direction of installation by indicating, for instance on the rear surface of the tiles or on an edge thereof, the direction of the stripes so that the tiler can install them in a correct configuration.

[0017] Independently on which method has been used for applying the stripes of hydrophobic coating 10 (spray coating, serigraphy, physical vapor deposition PVD, chemical vapor deposition CVD, plasma, etc.) the thickness thereof is preferably comprised between 0,1 and 2,5 micron, more preferably between 0,25 and 1 micron.

[0018] For achieving the fastest water flow from the surface it would be useful to coat the tiles thickness (border) using the hydrophilic coating (the same used for the hydrophilic stripes). In this way the liquid meniscus is easily broken and water can flow away.

[0019] Figure 3 shows the case in which a hydrophilic primer 14 is applied to the entire surface S of the tile T, and a plurality of hydrophobic stripes 10 are then applied on such first coating 14. Such hydrophilic coating 14 is preferably based on sol-gel inorganic nano-coatings material such as alumina, titania, involving silica and zirconia, produced by Sumitomo Osaka Cement (SOC). The total thickness of both coatings 14 and 10 is preferably comprised between 0,2 and 5 micron, more preferably between 0,5 and 2 micron. Higher thickness of the coating can lead to problems in terms of aestetichal changes (gloss alteration and undesired visibility of stripes).

[0020] Tiles treated with a method according to the invention, and particularly with the double coating of figure 2, have been tested by putting 200 ml of tap water on the surface S and by inclining the tile T of 0,5°. The pattern of tested coating is shown in the following table:

Stripes inclination angle	Coating type for hydrophilic areas	Coating type for hydrophobic areas	Hydrophobic stripes dimension	Hydrophilic stripes dimension	Tiles inclination for total water flow
Degree	Company	Company	mm	mm	Degree
45	SOC-zirconia based	Diasen BKK eco	20	2	0,5
45	SOC-zirconia based	Diasen BKK eco	20	3	0,5
45	SOC-zirconia based	Diasen BKK eco	20	4	0,5
45	SOC-zirconia based	Diasen BKK eco	20	5	0,5
45	SOC-zirconia based	Diasen BKK eco	20	10	0,5
45	SOC-zirconia based	Diasen BKK eco	20	20	0,5
45	SOC-zirconia based	Diasen BKK eco	20	30	0,5
45	SOC-zirconia based	Diasen BKK eco	30	2	0,5
45	SOC-zirconia based	Diasen BKK eco	30	3	0,5
45	SOC-zirconia based	Diasen BKK eco	30	4	0,5
45	SOC-zirconia based	Diasen BKK eco	30	5	0,5
45	SOC-zirconia based	Diasen BKK eco	30	10	0,5
45	SOC-zirconia based	Diasen BKK eco	30	20	0,5
45	SOC-zirconia based	Diasen BKK eco	30	30	0,5

(continued)

Stripes inclination angle	Coating type for hydrophilic areas	Coating type for hydrophobic areas	Hydrophobic stripes dimension	Hydrophilic stripes dimension	Tiles inclination for total water flow
45	SOC-zirconia based	Diasen BKK eco	40	2	0,5
45	SOC-zirconia based	Diasen BKK eco	40	3	0,5
45	SOC-zirconia based	Diasen BKK eco	40	4	0,5
45	SOC-zirconia based	Diasen BKK eco	40	5	0,5
45	SOC-zirconia based	Diasen BKK eco	40	10	0,5
45	SOC-zirconia based	Diasen BKK eco	40	20	0,5
45	SOC-zirconia based	Diasen BKK eco	40	30	0,5

[0021] All the treated tiles have shown a better behavior in terms of quick evaporation/elimination of water if compared to untreated tiles.

[0022] According to the following table and from the surface energy measurements, the Diasen BKK Eco hydrophobic coating offers good properties and the SOC-zirconia based coating offers good performances as hydrophilic coating.

Coating type	Contact angle [°]
Daisen BKK Eco	90-150
Uncoated	40-45
SOC-silica based	20-25
SOC-zirconia based	5-10

[0023] Even if the above results are referred to a spray deposition of coatings, other methods can be used, for instance PVD and CVD. The plasma technology can be applied either for providing the tiles with a coating or for treating the surface of tiles in order to create hydrophilic functional groups (as -OH) on the surface of the tiles.

[0024] Moreover, even if the above description is focused on production and coating of tiles, nevertheless the method according to the invention has been successfully tested with other kinds of surfaces where a quick draining of water is requested, for instance refrigerator liners, washing chambers of dishwashing machines, sinks, glass windows (particularly of skyscrapers where it is impossible to open windows), swimming pool areas, car and motorcycle bodies, solar panels, sport equipments etc.

Claims

1. Method for treating surfaces, particularly for producing tiles (T) having decreased permanence of water thereon after wetting, **characterized in that** at least one coating is applied on a surface (S) so that such surface presents alternate predetermined zones (10) having different degree of hydrophobic properties.

2. Method according to claim 1, wherein said zones have the shape of parallel stripes (10).

3. Method according to claim 1 or 2, wherein said predetermined zones (10) are coated with a hydrophobic coating.

4. Method according to claim 2 and 3, wherein said parallel stripes of hydrophobic coating (10) have a width comprised

between 10 and 50 mm, preferably comprised between 20 and 30 mm.

5. Method according to claim 4, wherein the distance between said stripes (10) is comprised between 1 and 10 mm, preferably comprised between 2 and 8 mm.

6. Method according to any of claims 3 to 5, wherein the surface is firstly coated with a hydrophilic coating (14).

7. Method according to any of claims 3 to 6, wherein the coatings are applied at a temperature comprised between 70 °C and 150 °C, more preferably between 100 °C and 120 °C.

8. Method according to any of claims 3 to 7, wherein the coatings are applied by spray coating, roll coating, PVD, CVD or plasma.

9. Method according to any of the preceding claims, wherein the hydrophobic coating (10) is selected in the group consisting of fluorinated polymers like PTFE (polytetrafluoroethylene) and PFPE (perfluoropolyether), polymers with methyl groups like PP (polypropylene), silicone and fluoride resins, manganese oxides - polystyrene (Mn02/PS) nano-composite, zinc oxide polystyrene (ZnO/PS) nano-composite, precipitated calcium carbonate, carbon nanotube structures, silica nano-coatings or mixture thereof.

10. Method according to claim 6 and 9, wherein the hydrophilic coating is selected in the group consisting of nylon 6.6, PET (polyethylene terephthalate), PVC (polyvinylchloride), inorganic compounds such as alumina, titanium dioxide (titania), silica and zirconium dioxide or mixture thereof.

11. Tile (T), particularly tile for external use and having a decreased permanence of water thereon after wetting, **characterized in that** its surface (S) presents alternate zones (10) having different degree of hydrophobic properties.

12. Tile (T) according to claim 12, wherein said zones have the shape of parallel stripes (10).

13. Tile (T) according to claim 13, particularly having a quadrangular shape, wherein said stripes (10) are inclined of about 45°.

14. Tile (T) according to claim 14, wherein said predetermined zones of the tile are coated with a hydrophobic coating (10) having a width comprised between 10 and 50 mm, preferably comprised between 20 and 30 mm.

15. Tile (T) according to any of claims 11 to 14, wherein the side borders (B) of tiles (T) are coated with a hydrophilic coating.

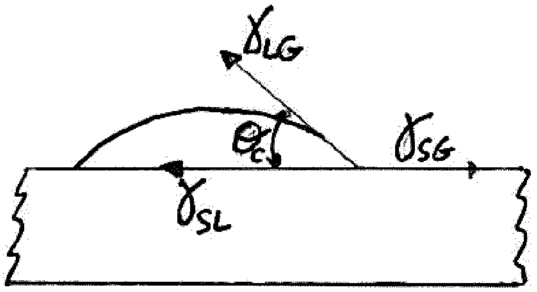

Fig. 1

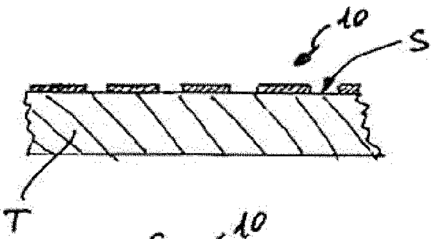

Fig. 2

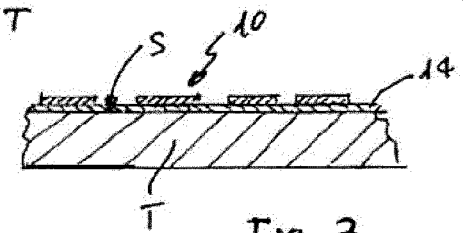

Fig. 3

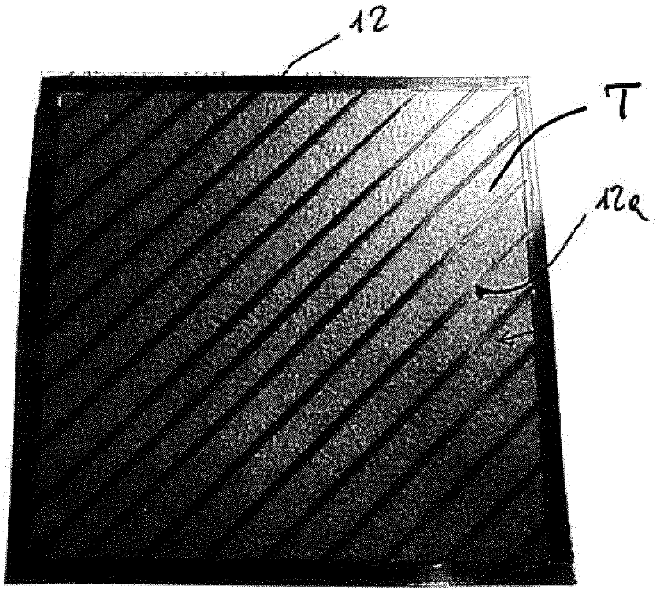

Fig. 4

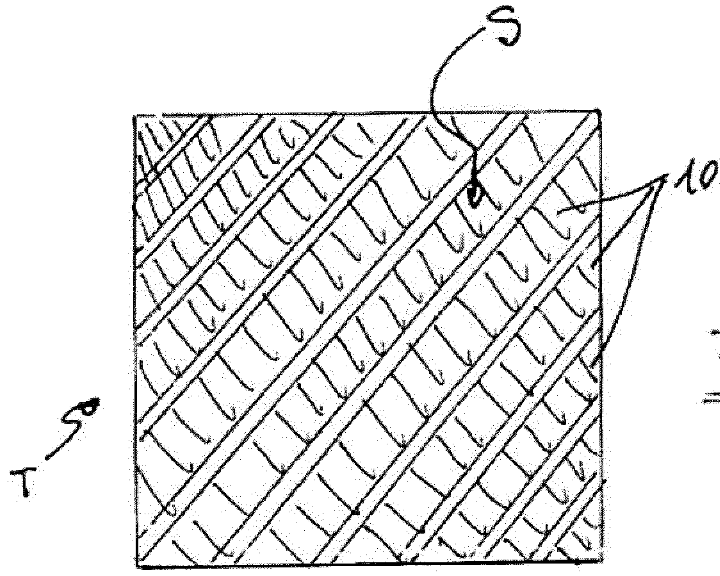

Fig. 5

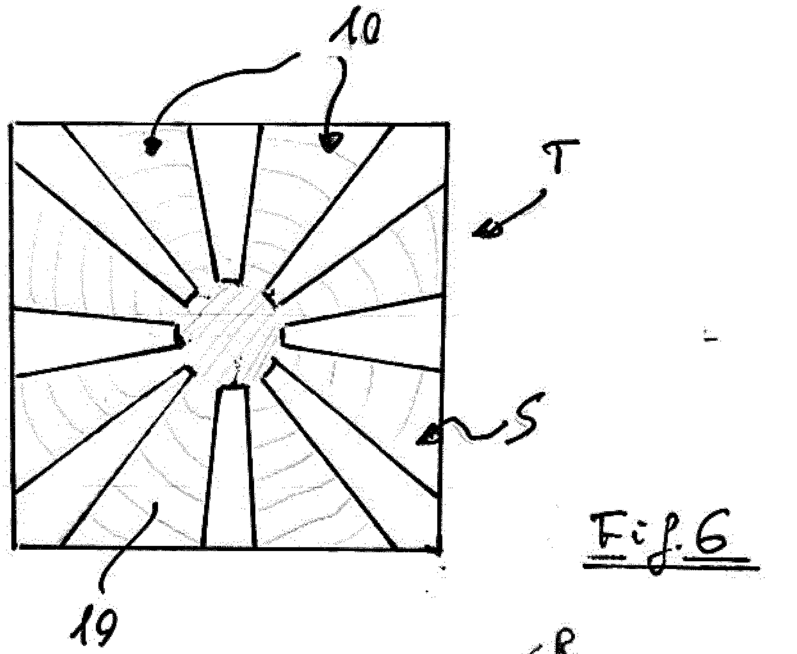

Fig. 6

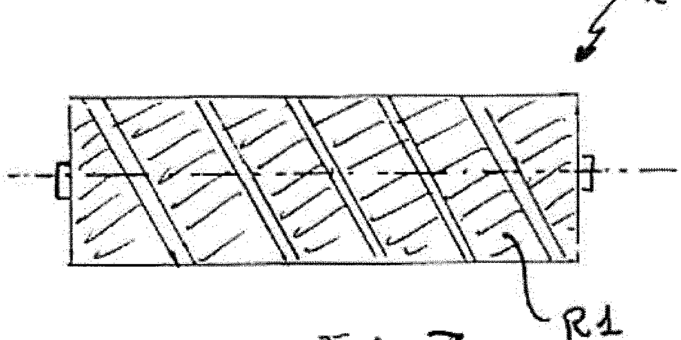

Fig. 7

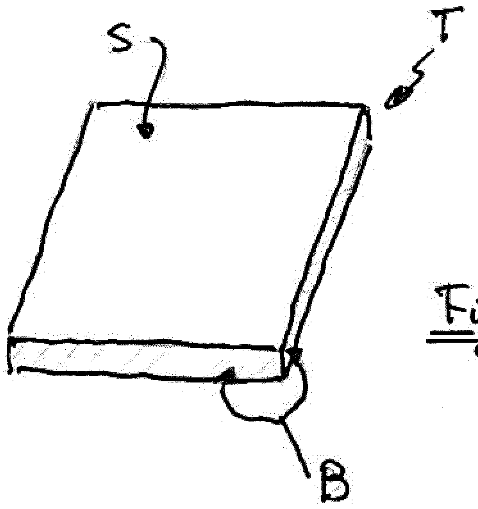

Fig. 8

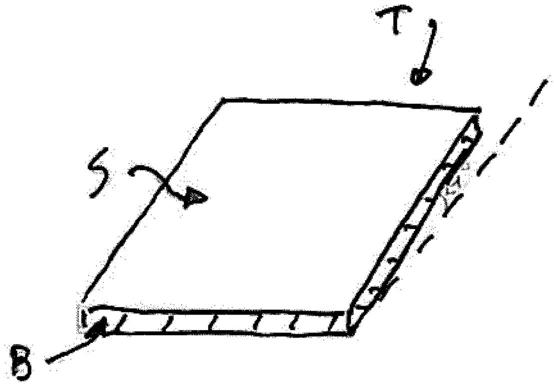

Fig. 9

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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
The Hague	18 November 2014	Slembrouck, Igor

CATEGORY OF CITED DOCUMENTS

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