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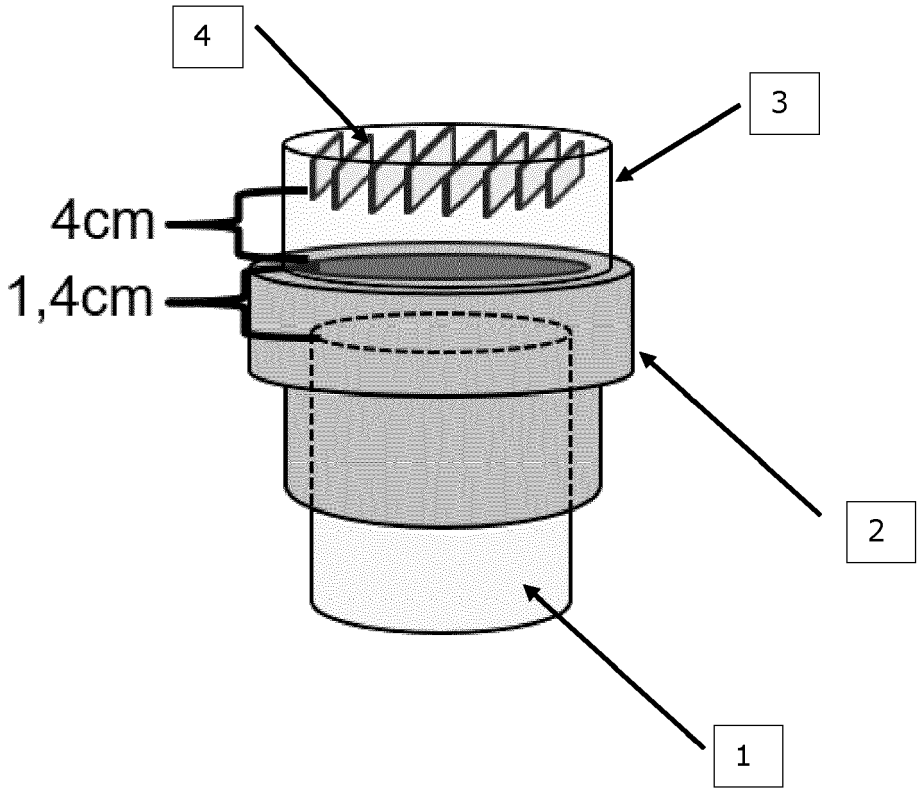
(54) **COATING APPARATUS**

(57) The present invention is directed to an apparatus and a respective process, which can be used in the production of exhaust catalysts. In particular, the present apparatus is used for supplying the liquid coating slurry to substrates, like honeycomb monoliths.

Fig. 1:



EP 4 299 194 A1

Description

[0001] The present invention is directed to an apparatus and a respective process, which can be used in the production of exhaust catalysts. In particular, the present apparatus is used for supplying the liquid coating slurry to substrates, like honeycomb monoliths.

[0002] Automotive exhaust abatement is of great importance as numbers of cars are growing tremendously, especially in East Asian countries. Several clean air acts around the world try to keep the pollution of the air by automobiles at respective low levels. Hence, more and more stringent legislation forces car manufacturers and suppliers to apply techniques for abatement of noxious pollutants stemming from internal combustion engines of vehicles. One area of techniques concerns the catalytic combustion of exhaust pollutants on or in so-called honeycomb monoliths either of the flow-through or the wall-flow type.

[0003] Normally such monolith bodies - called substrates - are made out of e.g. metal or cordierite and have to be coated with a layer being active in catalytically destroying the noxious pollutants in the exhaust under driving conditions. A great improvement has been achieved by chemically modifying the catalytically active layers with respect to the main reactions of the pollutants under stoichiometric, oxidative or reductive exhaust environment. A second approach is to apply certain coating strategies in order to gain an activity as high as possible with the materials at hand. Hence, several patent applications already deal with standard processes and devices/tools to coat said monolithic carriers. E.g. the following selection of patent publications, respectively, highlight aspects of such processes, like coating apparatus, methods for coating, or special units of a coating station etc. (WO9947260A1; US4550034; US4039482; WO9748500A1; US6478874B1; US20020178707A1; DE19781838T1; WO2011080525A1; US4191126; US6627257B1; US6548105B2; US20080107806A1; US6149973; US6753294B1).

[0004] In principle the coating techniques can be divided in two general classes. A first class is concerned with a coating strategy in which the liquid coating slurry is subjected to the vertically orientated substrate (i.e. support body or monolith carrier) from below. The second class of coating techniques discusses the application of the liquid coating slurry to the top of the vertically orientated substrate.

[0005] In WO9947260A1 a top-down coating technique is disclosed in which a substrate coating apparatus comprises means for dosing a pre-determined quantity of a liquid component, said quantity being such that it is substantially wholly retained within the intended support, liquid component containment means locatable on the top of a substrate to receive said quantity of liquid component, and pressure means capable of withdrawing the liquid component from the containment means into at least a portion of the substrate. Further techniques working this way can be found in US9144796B1, WO2015145122A2, EP1900442A1 or EP2415522A1.

[0006] In particular, the EP1900442A1 and the EP2415522A1 are concerned with the problem of applying an even liquid washcoat slurry on the top end of the substrate monoliths. This is important because an uneven distribution of the liquid slurry (washcoat) leads to an uneven distribution of the washcoat within the channels of such substrates after the suction step. This problem is said to be solved in these patent applications by rotating the substrate monolith or by applying a special nozzle technique.

[0007] The present invention is also concerned with the problem of metering a liquid coating slurry on the top end face of a monolith substrate in a way that the liquid coating slurry is distributed evenly over an area of the top end face of the substrate before it is going to be sucked and/or pressed into the substrate by applying a pressure difference across the channels of the respective substrate. The apparatus and the process involved should be advantageous in view of the prior art techniques from an economical and/or ecological point of view.

[0008] These objectives are solved by providing an apparatus as mentioned in claim 1. Preferred devices are proposed in claims dependent from claim 1. In claims 8 et seq. methods for performing the coating according to the invention are suggested.

[0009] In that an apparatus for coating substrates with a catalytically active liquid coating slurry, wherein the substrates have two end faces, a circumferential surface and an axial length and are traversed from the first end face to the second end face by a multiplicity of channels, said apparatus comprises

- a holding unit for reversibly holding the substrate vertically;
- a dosing unit for supplying a liquid coating slurry, which finally provides the catalytic activity to be submitted to the substrate;
- a unit for applying a pressure difference versus the substrate to introduce the liquid coating slurry into it;
- a containment means located at a distance above the substrate top end face for collecting the liquid coating slurry supplied by the dosing unit,

wherein the containment means has a bottom plate comprising flaps for reversible opening and closing, is established, the objectives of the present invention have been solved. The present apparatus allows the even distribution of a liquid coating slurry over an area of the top end face of a substrate. When introducing the slurry into the substrate by applying a pressure difference versus the substrate the liquid coating slurry does evenly enter the substrate channels, which leads to an even distribution of the slurry within the substrate, both in terms of length and in terms of concentration gradients. It is furthermore advantageous that with this equipment also liquid coating

slurries with low viscosities can be coated on the substrate in a sufficient manner, e.g. to provide excellently in-wall coated wall-flow filters.

[0010] The apparatus according to the invention comprises a containment means. This containment means is to hold the liquid coating slurry (i.e. washcoat) supplied by the dosing unit for a certain while and instantaneously supply substantially all of the washcoat slurry on the top end face of the substrate. This serves for a good distribution of the washcoat over this end face which in turn leads to an even distribution of the washcoat in the substrate channels upon establishing a pressure difference versus the substrate channels.

[0011] For this purpose, the containment means preferably has a pot-like design with a collar and a bottom plate, the latter being able to reversibly open and close as stipulated above. In a further preferred manner, the present apparatus is designed such that the distance between the substrate top end face and the bottom plate of the containment means is between 2 - 20 cm (measured from bottom plate with closed flaps to top end face of the substrate; see Fig. 1). If the distance is too large the velocity of the falling washcoat will be too high and it would already by hitting the top end face of the substrate intrude into the channels leading finally to an uneven distribution of the washcoat within the substrate. If the distance is too low the flaps may not be able to open accordingly because they may hit the top end face of the substrate.

[0012] To open and close the flaps it is preferred if they are arranged such that they can rotate around an axis of rotation. The flaps at the endpoints of this rotational axis are fixed to the collar of the containment means in such a way that they can be rotated around the axis of rotation. The rotation can be rendered by means know to the skilled worker, e.g. pneumatic, electric or mechanic triggers.

[0013] In a further preferred fashion mentioned flaps have a wing-like profile with a length (L) and can be flipped around an axis laying parallel to the length (L). It is more preferred if the axis of rotation of the flaps is positioned such that in an open mode operation point most of the profile of each flap perpendicular to the axis of rotation is located between the axis of rotation and the top end face of the substrate (see Fig. 1). This serves for a better pouring of the washcoat slurry over the top end face of the substrate without having much washcoat being slingshot away by flaps opening rapidly. Instead the liquid coating slurry within the containment means preferably shall just fall onto the top end face of the substrate with other momentums being minimized as much as possible.

[0014] It is advantageous if substantially all the liquid coating slurry which resides within the containment means is supplied to the top end face of the substrate. This aspect can be enhanced if the surface of the flaps at least partially has a hydrophobic surface. The liquid coating slurry normally is based on a water suspension. With a hydrophobic surface substantially no water and insoluble constituents of the suspension will adhere to the flaps. Even better waterrepelling surfaces may be achieved using the so called lotus effect on the surface of the flaps (https://de.wikipedia.org/wiki/Lotoseffekt). Hence, it is considered very advantageous if the flaps at least partially comprise a surface showing said lotus effect.

[0015] The coating of a substrate normally starts with engaging the substrate in a holding unit, i.e. a coating chamber in a vertical orientation, the substrate now having a top end face and a bottom end face. The holding unit can be any known to the skilled worker. Some examples are shown in the cited literature. Normally, the holding unit comprises an inflatable bladder to engage the substrate as described. The dosing unit supplies the liquid coating slurry into the containment means having the flaps closed. The dosing unit can be any known to the skilled worker, like a shower head, a nozzle, or those mentioned in cited literature. The containment means are located right above the substrate. After the slurry has been filled into the containment means the flaps open fast and the slurry falls onto the top end face of the substrate. Finally, a unit for applying a pressure difference versus the substrate is used to force the slurry into the channels of the substrate. After having been coated the substrate is removed from the holding unit by deflating the bladder and is further processed e.g. by drying and optionally calcining it. In very preferred cases the slurry in the containment means can be leveled out by vibration or agitation through a gas stream or an ultrasound.

[0016] It has to be acknowledged that, as the case may be, the introduction of the slurry into the substrate starts when the falling slurry hit the substrate. This is advantageous especially for thin washcoats having a low viscosity of 1 - 1000 mPas, preferably 10 - 600 mPas at 20 °C, respectively at a shear rate of 20 s-1 (measured according to DIN ISO 1652 - as valid at the application date). In these cases, the pressure difference versus the substrate is advantageously already established before the slurry hits the top end face of the substrate. On the other hand, it may well be that for slurries having a higher viscosity of 600 - 10000 mPas, preferably 600 - 2000 mPas at 20 °C, respectively at a shear rate of 20 s-1 that the washcoat may first be submitted to the top end face of the substrate in total and only afterwards the unit for applying a pressure difference versus the substrate is used to force the slurry into the channels of the substrate. The skilled worker will find the best mode for his coating problem.

[0017] The apparatus of the invention can be further equipped with a means to turn the substrates upside down within said apparatus. After a first coating step the substrate can be flipped around and can be coated again in the same manner and with the same apparatus from the other side being the top end face now. Preferably, when turning around the substrate this can be done with means known to the skilled worker, like robot arms etc.

or even manually. In an even further preferred way, the holding unit of the apparatus of the invention is arranged in a rotatory turntable device. The substrates thus can be moved towards and away from the dosing unit and the containment means by moving the turntable around an axis of rotation. Several process steps like flipping the substrates, providing the slurry onto the top end face and introducing the slurry into the substrates can be performed in parallel by preferably using the apparatus with a turntable comprising several holding units.

[0018] The unit for applying a pressure difference versus the substrate is preferably a suction unit. Hence, having submitted the liquid coating slurry on the top end face of the substrate the slurry is introduced by sucking it from the bottom end of the substrate through its channels. In a preferred embodiment no liquid coating slurry leaves the substrate, meaning that the amount of washcoat and the vacuum applied is such that all washcoat is retained in the substrate.

[0019] In a further aspect, the present invention is directed to a method for coating substrates with a liquid coating slurry providing the catalytic activity, wherein the substrates have two end faces, a circumferential surface and an axial length and are traversed from the first end face to the second end face by a multiplicity of channels, wherein each substrate is vertically orientated and a dosing unit supplies the liquid coating slurry into a containment means, and applying a pressure difference versus the substrate, wherein an apparatus as defined above is used.

[0020] It is conceivable that layers of washcoat may be put onto each other, preferably without any drying or calcination in between. This is possible by adopting certain viscosities of the slurries in use (EP3648885A1). In a further preferred embodiment the method according to the invention is performed twice with on substrate. Here, the method comprises the steps of:

- performing a first coating step according to the invention;
- turning the substrate upside down within that apparatus;
- performing a second coating step according to the invention.

[0021] Said processes can be done with or without any drying of the substrate in between. In view of a better cycle time no drying step is performed in between the coating steps. The skilled worker knows how to establish the respective devices to perform this process. The information given for the apparatus can be applied mutatis mutandis for the processes of the invention.

[0022] Preferably, for one or both coating steps the washcoat can be introduced as a slurry under conditions that are predetermined to form a washcoat layer along a length of the channels of the substrate that is up to but preferably less than 100% of the total length of the monolith carrier; more preferably a length equal to or greater than about 50% and less than 80%; and yet more preferably a length equal to or greater than about 55% and equal to or less than about 70%, although any length less than 100% may be desirable based on application. Targeting less than 100% of the total length of the carrier also provides further benefits including, though not limited to, mitigating the unintended leakage of washcoat slurry through the opposite end face of the substrate; and suppressing particle size and compositional drift issues (e.g., formation of a gradient), thereby promoting a uniform surface of the applied catalyst layer.

[0023] Preferably, the substrate coated according to the present invention is a flow-through or a wall-flow monolith. Flow-through substrates have fine, parallel gas flow passages extending from an inlet to an outlet face of the substrate, such that passages are open to fluid flow there through. The passages, which are essentially straight paths from their fluid inlet to their fluid outlet, are defined by walls on which or in which the catalytic material is coated as a washcoat so that the gases flowing through the passages contact the catalytic material. The flow passages of the monolithic substrate are thin-walled channels, which can be of any suitable cross-sectional shape and size such as trapezoidal, rectangular, square, sinusoidal, hexagonal, oval, circular, etc. Such structures may contain from about 400 - 900 or more gas inlet openings (i.e., cells) per square inch of cross section (62 - 140 cells/cm^2). The wall thicknesses, i.e. the thickness of the walls which separate the channels of the substrate from one another, are usually from about 0.005 cm to about 0.25 cm.

[0024] The substrate to be coated according to the invention may preferably also be a honeycomb wall-flow filter. Wall-flow substrates useful for supporting the coating compositions have a plurality of fine, substantially parallel gas flow passages extending along the longitudinal axis of the substrate. Typically, each passage is blocked at one end of the substrate body, with alternate passages blocked at opposite end-faces. Specific wall-flow substrates for use in the inventive process include thin porous walled honeycombs through which the fluid stream passes without causing too great an increase in back pressure or pressure drop across the article. Normally, the presence of a clean wall-flow article will create a back pressure of 0.036 psi to 10 psi.

[0025] The above-mentioned substrates are preferably metal or ceramic-like monoliths, the latter are made out of any suitable refractory material, e.g., cordierite, cordierite-alumina, silicon nitride, zircon mullite, spodumene, aluminasilica magnesia, zircon silicate, sillimanite, a magnesium silicate, zircon, petalite, alumina, an aluminosilicate and the like. In view of flow-through monoliths, which are e.g. suitable for the production of exhaust gas catalysts for motor vehicles according to the present process, they preferably have a porosity of more than 20%, generally from 20% to 70%, in particular from 35% to 65% prior to coating [measured according to DIN 66133 as of the application date]. The mean pore size is

at least 1 μm, e.g. from 1.5 μm to 25 μm, preferably more than 3 μm, in particular from 5 μm to 18 μm prior to coating [measured according to DIN 66134 as of the application date]. Finished substrates suitable for the exhaust gas catalysis of motor vehicles which originally have a mean pore size of 5 to 18 μm and a porosity of 25% to 65% are particularly advantageous. In view of ceramic wall-flow filter substrates, which are e.g. suitable for the production of exhaust gas filters for motor vehicles according to the present process, they preferably have a porosity of more than 40%, generally from 40% to 75%, in particular from 45% to 70% [measured according to DIN 66133 as of the application date]. The mean pore size is at least 7 μm, e.g. from 7 μm to 34 μm, preferably more than 10 μm, in particular from 10 μm to 20 μm or from [measured according to DIN 66134 as of the application date]. Finished substrates suitable for exhaust gas catalysis of motor vehicles have a mean pore size of 10 to 33 μm and a porosity of 45% to 65% are particularly advantageous.

[0026] When substrates with the aforementioned porosities and mean pore sizes are coated with a washcoat, adequate levels of the coating compositions can be loaded onto and/or into the pores of the substrates to achieve excellent pollutant conversion efficiency and, in view of filters, burning off of soot. These substrates are still able to retain adequate exhaust flow characteristics, i.e., acceptable back pressures, despite the catalyst loading. In a very preferred embodiment the substrate is a wall-flow filter.

[0027] The expression "coating / to coat" is to be understood to mean the application of catalytically active materials and/or storage components for noxious exhaust pollutants on a substantially inert substrate which may be constructed in the manner of an above-described wall-flow filter or flow-through monolith. After drying and calcining the established coating performs the actual catalytic function and contains storage materials and/or catalytically active metals which are usually deposited in highly dispersed form on temperature-stable, large-surface-area metal oxides (see below). The coating is carried out usually by means of the application of a liquid coating slurry of the storage materials and/or catalytically active components - also referred to as a washcoat - onto and/or into (into the pores of) the wall of the inert substrate. After the application of the liquid coating slurry, the support is dried and, if appropriate, calcined at elevated temperatures. The coating may be composed of one layer or constructed from a plurality of layers which are applied to a substrate one above the other (in multilayer form) and/or offset with respect to one another (in zones).

[0028] The liquid coating medium/slurry is, for example, a suspension or dispersion ("washcoat") for coating exhaust gas catalysts (flow-through monoliths or filters) for motor vehicles which contains the storage materials and/or catalytically active materials or precursors thereof and/or inorganic oxides such as zeolites, like CHA, AEI, AFX or similar 8-ring zeolites, or refractory oxides like aluminum oxide, titanium dioxide, zirconium oxide or a combination thereof, it being possible for the refractory oxides to be doped with silicon or lanthanum, for example. The zeolites can be exchanged with metal cations like Fe and/or Cu. Oxides of vanadium, chromium, manganese, iron, cobalt, copper, zinc, nickel or rare earth metals such as lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium or combinations thereof can be used as catalytically active components. Noble metals such as platinum, palladium, gold, rhodium, iridium, osmium, ruthenium and combinations thereof can also be used as catalytically active components. These metals can also be present as alloys with one another or with other metals or as oxides. The metals can also be present as precursors, such as nitrates, sulfites or organyls of said noble metals and mixtures thereof, and, in particular, palladium nitrate, palladium sulfite, platinum nitrate, platinum sulfite or $Pt(NH_3)_4(NO_3)_2$ can be used in the liquid coating medium. By calcination at about 400°C to about 700°C, the catalytically active component can then be obtained from the precursor. To coat a substrate for the production of automotive exhaust gas catalysts, a suspension or dispersion of an inorganic oxide can initially be used for coating, after which, in a subsequent coating step, a suspension or dispersion which contains one or more catalytically active components can be applied. However, it is also possible for the liquid coating medium to contain both components. In a very preferred embodiment the liquid coating slurry has a viscosity of from 10 - 2000 mPas at 20°C and a shear rate of 20 s-1.

[0029] In view of the described processes the preferred embodiments of the initial apparatus apply mutatis mutandis and vice versa. In a further preferred aspect, the present invention may encompass a coating station which comprises the apparatus according to the present invention. Also here, the preferred embodiments of the process and/or the apparatus disclosed apply mutatis mutandis to the coating station. This is the case, in particular, for the more mechanical aspects discussed in connection with the above-mentioned process and/or apparatus, like e.g. rotatory turntable, robot arm for loading and unloading or turning around the substrate within the holding unit and the possibility to coat the substrate monoliths from both end sides.

[0030] The present invention allows to perform an advantageous top-down coating process. The invention can be applied with liquid coating slurries for exhaust gas catalyst production, the slurries having a broad range of viscosity. Low viscous as well as high viscous washcoats can be extremely evenly coated either on flow-through or wall-flow substrates (Fig. 2). The even distribution of the washcoat within such substrates leads to optimized back-pressure, filtration efficiency and catalytic performance. This was not apparent to the skilled worker before the invention was made.

Figures:

[0031]

Fig. 1: Shows the holding unit (2) and the containment means (3) comprising the flaps (4) and the substrate to be coated (1).

Fig. 2: Opened monolith after having been coated according to the present invention, showing little variance of coating lengths from channel to channel.

Experimental Part:

Example 1:

[0032] A flow through substrate (Cordierite, 4.66" diameter*4.5" length, 600/4 cells per square inch/mils) was coated using the dosing unit with an alumina containing washcoat with a viscosity of 1200 mPas at 20 s-1 . The monolith was engaged into a coating station vertically and a respective amount of washcoat was submitted to the top end face by an apparatus with containment means according to the invention. After submission of the washcoat it was sucked from below into the monolith, which was then dried and calcined under normal conditions.

Claims

1. Apparatus for coating substrates with a catalytically active liquid coating slurry, wherein the substrates have two end faces, a circumferential surface and an axial length and are traversed from the first end face to the second end face by a multiplicity of channels,
said apparatus comprises

- a holding unit for reversibly holding the substrate vertically;
- a dosing unit for supplying a liquid coating slurry to be submitted to the substrate;
- a unit for applying a pressure difference versus the substrate to introduce the liquid coating slurry into it;
- a containment means located at a distance above the substrate top end face for collecting the liquid coating slurry supplied by the dosing unit,

characterized in that
the containment means has a bottom plate comprising flaps for reversible opening and closing.

2. Apparatus according to claim 1,
characterized in that
the distance is 2 - 20 cm (measured from bottom plate to top end face with closed flaps).

3. Apparatus according to claim 1 and/or 2,
characterized in that
the flaps have wing-like profile with a length (L) and can be flipped around an axis laying parallel to the length (L).

4. Apparatus according to one of the preceding claims,
characterized in that
the surface of the flaps at least partially have a hydrophobic surface.

5. Apparatus according to one of the preceding claims,
characterized in that
said apparatus comprises a means to turn the substrates upside down within said apparatus.

6. Apparatus according to one of the preceding claims,
characterized in that
the holding unit is arranged in a rotatory turntable device.

7. Apparatus according to one of the preceding claims,
characterized in that
the unit for applying a pressure difference versus the substrate is a suction unit.

8. Method for coating substrates with a liquid coating slurry, wherein the substrates have two end faces, a circumferential surface and an axial length and are traversed from the first end face to the second end face by a multiplicity of channels, wherein each substrate is vertically orientated and a dosing unit supplies the liquid coating slurry into a containment means, and applying a pressure difference versus the substrate, wherein an apparatus as defined in one of the preceding claims is used.

9. Method according to claim 8 comprising the steps:

- performing a first coating step according to claim 8;
- turning the substrate upside down within that apparatus;
- performing a second coating step according to claim 8.

10. Method according to one of claims 8 - 9,
characterized in that
the substrate is a wall-flow filter.

11. Method according to one of claims 8 - 10,
characterized in that
the liquid coating slurry has a viscosity of from 0,01 - 10 Pa*s at 20°C and a shear rate of 20 s^{-1}.

Fig. 1:

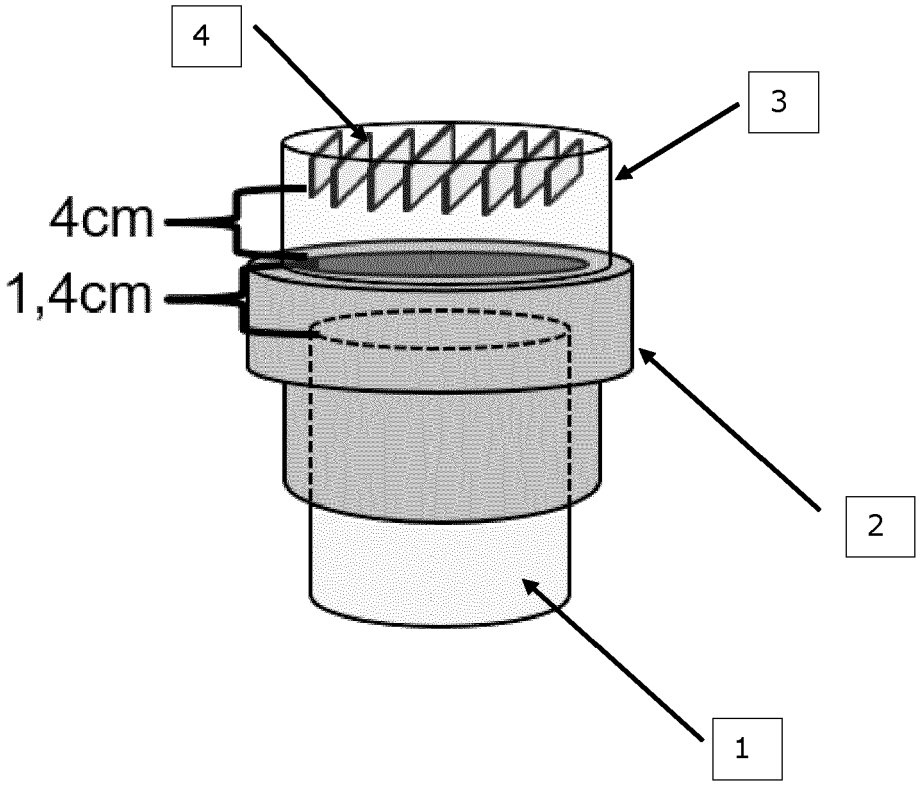
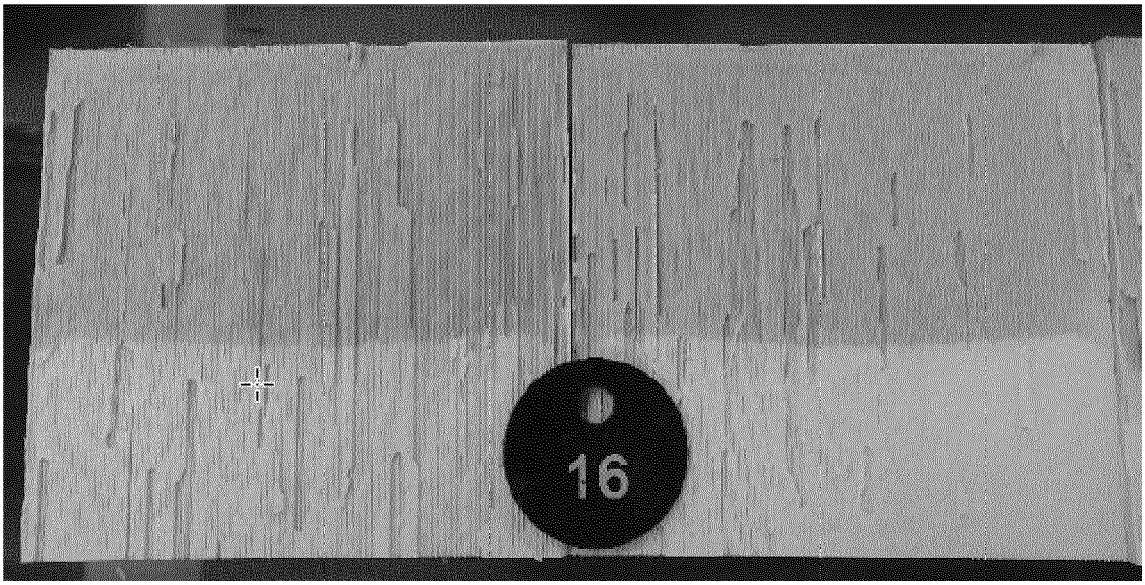


Fig. 2:



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EUROPEAN SEARCH REPORT

Application Number
EP 22 18 1902

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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TECHNICAL FIELDS SEARCHED (IPC)

B05C
B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	18 January 2023	Barré, Vincent

CATEGORY OF CITED DOCUMENTS

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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