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(12) # EUROPEAN PATENT SPECIFICATION

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(54) **Method for applying a thermoplastic adhesive layer to a body.**

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Description

The invention relates to a method for applying an adhesive layer consisting substantially of thermoplastic plastic to a body, for example a honeycomb plate which can serve as core of a sandwich panel with thermoplastic covering sheets.

Known from membrane technology is a method whereby a thermoplastic plastic is deposited from a solution onto a body by bringing the solution to saturation using artificial means. With the correct choice of process parameters the surface of the body can be given a porous structure, as a result of which the process attains a great depth of penetration.

This known art is used for instance in the manufacture of semi-permeable membranes, which can be used as filters for a specific particle size or for the separation of two phases.

For the manufacture of sandwich panels consisting of a substantially plate-like core and for example fibre reinforced thermoplastic sheets as skin layers, an adhesive layer is applied from a solution to the core material and integrated with the skin layers by fusing or diffusion. Such a method is described in EP-A-0 274 789 published after the present application's priority date, which defines a state of the art according to Article 54(3) EPC. Described in this patent application is a method according to which the solvent is partially removed by evaporation.

High quality thermoplastics which can be used for fibre reinforced materials usually require solvents with a high boiling point. The evaporation of the solvent therefore requires a treatment at a high temperature.

So for example n-methylpyrrolidone (NMP), a suitable solvent for thermoplastics, has a boiling point of above 200 degrees C. Heating to temperatures of this order demands large investment, while moreover much attention must be paid to fire safety. Furthermore, not all reinforcing fibres and core materials can withstand the high temperatures necessary to remove solvents with a high boiling point.

The invention has for its object to propose a method which does not have the said drawbacks of the known art and moreover has a starting point known processes from the field of membrane technology.

In order to achieve this object the invention provides a method as described in claim 1.

Use can advantageously be made of a method as claimed in claim 2. With the use of a body in the form of a honeycomb plate, closing of the honeycomb cells by the solution can occur. By applying the steps as claimed in claim 3, cells that may have been closed will spring open.

In preference the method as in claim 4 is employed. This results in the forming of a porous structure on the surface of the adhesive layer. This structure gives the adhesive layer a stability such that it cannot drip and can remain fixed for example on the end wall portions of the honeycomb cells.

As already described in the aforementioned EP-A-0 274 789, for the assembly of a sandwich structure with a core plate and fibre reinforced thermoplastic skin layers, a certain percentage of the first solvent has to remain present in the adhesive layers. This can be achieved in particular by employing the method as claimed in claim 5. Occurring as a result during the diffusion process in accordance with step (4) is a state of equilibrium at the selected content of the first solvent.
This content can be controlled very accurately.

Particular advantages are offered by the method of claim 6. It will be apparent that through application thereof the second solvent can be removed in very simple manner. A method as according to claims 7 and/or 8 may for example be chosen. With respect to these choices the invention is now elucidated briefly and in general. Subsequent to application of the solution of NMP as according to step (3) to the body, the surface treated in this way is exposed to water by submersion in a water bath, which results in the NMP being dissolved by the water and being transported to the surface by means of a diffusion process. This transport continues as long as there exists a difference in concentration between the water bath and the NMP still present on the surface. Through the exchange reaction small channels are created in the solution of the plastic in NMP, whereby the plastic concentration gradually increases, these channels penetrating more and more deeply into the layer. These channels also possess porous walls themselves, so that the exchange takes place rapidly and homogeneously. This latter is a fact established on the basis of extensive laboratory tests. It has also been found thereby that for the applying of adhesive layers on core materials the reaction depth is great enough to bridge the thickness of the material.

The invention will now be elucidated with reference to the annexed two figures, in which:

Fig. 1 shows a highly schematic view of a continuous operating device, in which the method according to the invention is implemented; and

Fig. 2 is a partly broken away, perspective view of a part of a simpler, intermittently operating device.

Fig. 1 shows a device 1 for applying an adhesive layer consisting substantially of thermoplastic plastic to a honeycomb plate 2 which can serve as core of a sandwich panel with thermoplastic cover-

ing sheets.

Plate 2 is transported through coating rollers 3, which rollers 3 transfer the solution 6 present in the supply trays 5 therefrom via rolls 4 onto the end wall surfaces of the honeycomb plate 2. The solution 6 consists of the thermoplastic plastic for application in n-methylpyrrolidone (NMP). Plate 2 is conveyed further in the direction of the arrow 7 by the coating rollers 3.

It passes through a heat treatment station 8 in which heat lamps 9 are present.

Thereafter the plate 2 passes through a steam chamber 10 wherein steam coming from a source (not drawn) is introduced into steam chamber 10 via steam inlets 11.

Situated between the trays 5, in the heat treatment station 8 and in the steam chamber 10 is a slot-like passage through which the honeycomb plate 2 can pass.

The honeycomb plate 2 is then trained through a container 12 in which is placed a mixture 13 containing water with a predetermined quantity of NMP.

After leaving the water bath the honeycomb plate 2 runs through an after treatment station 14 wherein the formed adhesive layer is further dried by having air passed along it, as is indicated symbolically with arrows 15.

Located downstream relative to the after treatment station 14 are two conveyor rolls 16 which, as a result of an appropriate drive speed, convey plate 2 at the same speed as the coating rollers 3.

Subsequent to leaving the conveyor rolls 16 the finished plate is guided between two pressure/conveyor belts 17 with the interpositioning of protective foils 18 which are carried along by the honeycomb plate 2 and unrolled from supply rolls 19.

After leaving the pressure/conveyor belts 17 the honeycomb plate 2 is provided on both end wall surfaces with an adhesive layer consisting substantially of thermoplastic plastic which is covered in turn by the protective foil.

A short description of the operation of the device 1 now follows. The honeycomb plate 2 is in this case fed to the coating rollers in a continuous form. These coating rollers 3 are driven by non-drawn means at a preselected speed. The peripheral velocity of coating rollers 3 corresponds with the peripheral velocity of the conveyor rolls 16 and the speed of the pressure/conveyor belts 17. The transporting speed of the honeycomb plate 2 hereby selected corresponds with a required submersion time of the plate 2 in the mixture 13 present in container 12.

Coating rollers 3 receive this solution 6, consisting of NMP and the thermoplastic plastic to be applied, via the transfer rolls 4 which roll through the solution 6 present in trays 5.

Closing off of cells of the honeycomb plate 2 may occur as a result of the coating treatment. The treatment in the heat treatment station 8 is carried out in order to reopen such cells.

The subsequent treatment in the steam chamber 10 stabilizes the adhering layer which has partially penetrated into the material of the honeycomb plate 2.

In the following washing cycle, that is, the passage through container 12, washing out of the NMP takes place in the mixture present in the container. If only water were to be found in container 12, the NMP can then be for the most part removed so that there is virtually no longer any NMP present in the adhesive layer present on the honeycomb plate 2. For reasons to be indicated briefly hereinafter it is recommended that some NMP is still present in the adhesive layer to be formed. It is for this reason that the mixture 13 consisting of water and a desired quantity of NMP is preferably used.

Additional drying takes place in an after treatment station 14 at a temperature above 100 degrees C, the boiling point of water, in order to remove any water still present from the plate 2. The conveyor rolls 16 transport the plate further.

From this moment the treatment of the plate is completed and a semi-manufacture is obtained consisting of a honeycomb plate 2, the end wall surfaces of which are provided with an adhesive layer consisting of the thermoplastic plastic and some NMP. This plate can be immediately used to form a sandwich panel by laying an optionally fibre reinforced thermoplastic covering sheet against the plate on both sides and, using a suitable treatment, for example a heat treatment, an ultrasonic treatment and/or a treatment under pressure, by removing the NMP still present through diffusion, and joining the sheet to the honeycomb core.

In the device 1 as in fig. 1 however the semi-manufacture is finished by arranging a protective foil on the sides provided with an adhesive layer. The thus finished plate can be transported to a user who makes further use thereof in the manner described.

Fig. 2 shows a device 20. Parts corresponding to those as in fig. 1 are designated in this figure with the same reference numerals.

Steam chambers 21 comprise here an in-feed portion 22 and a discharge portion 23, which results in the steam passing along the coated surface in the manner indicated with the arrow 24.

After leaving steam chambers 21 the honeycomb plate 25 drops into a container 26 in which is to be found the mixture 13 as described above. After submersion for a sufficiently long period the plate is taken out of the container 26 and if re-

quired subsequently treated further. Such an after treatment may comprise a drying process and if desired a finishing as described with reference to fig. 1.

Use is made for internal parts of aircraft of a honeycomb formed from Nomex paper, which is drenched in phenol resin and subsequently cured. The weight of this type of honeycomb is 48 kg per cubic metre.

A honeycomb panel of this material is provided on both sides with a coating of polyetherimide dissolved in n-methylpyrrolidone. The concentration of thermoplastic in the solution is 25%. The coating is applied with a weight such that the amount of thermoplastic in the solution has a weight of 100 grams per side. The coating is predried for thirty minutes at a temperature of 240 degrees Celsius. Approximately 25% solvent will then be found in the coating. The skin sheets are joined to the core in a flat press at a temperature of 170 degrees C and a pressure of one bar for a duration of ten minutes. In a peel test with a panel manufactured in this manner it is the core material that disintegrates and not the adhesive layer.

Claims

1. Method for applying an adhesive layer consisting substantially of thermoplastic plastic to a body, for example a honeycomb plate which can serve as core of a sandwich panel with thermoplastic covering sheets,
   comprising the following steps:
   (1) the providing of a body to which said adhesive layer has to be applied;
   (2) the making of a solution of the thermoplastic plastic in a first solvent;
   (3) the applying of said solution to the surface of the body for coating;
   (4) the at least partial removal of said first solvent by insertion of said body in a second solvent, wherein the thermoplastic material is substantially non-soluble, and wherein said first solvent is soluble, and the holding of said body therein for a long enough period of time such that said first solvent is removed to a sufficient extent from said surface of said body.

2. Method as claimed in claim 1, **characterized by** the following step:
   (5) the exposing after step (3) of the relevant surface of the body to an increased temperature for a period of time.

3. Method as claimed in claim 2, **characterized in that** step (5) is performed using heat radiation.

4. Method as claimed in claim 2 or 3, **characterized in that** step (5) is performed using steam.

5. Method as claimed in claims 1-4, **characterized by** the following step:
   (6) the addition prior to step (4) of a chosen quantity of the first solvent to the second solvent such that a desired concentration of said first solvent is left in the resulting adhesive layer on the body.

6. Method as claimed in claims 1-5, **characterized by** the following steps:
   (7) the selection of a first solvent that has a higher boiling point than the second solvent;
   (8) the at least partial removal of said second solvent by subjecting the relevant surface of the body to a temperature that is minimally in the order of magnitude of the boiling point of said second solvent.

7. Method as claimed in claims 1-6, **characterized by** the following step:
   (9) the selecting of n-methylpyrrolidone as first solvent.

8. Method as claimed in claims 1-7, **characterized by** the following step;
   (10) the selecting of water as second solvent.

Patentansprüche

1. Verfahren zum Aufbringen einer im wesentlichen aus thermoplastischem Kunststoff bestehenden Adhäsionsschicht auf einen Körper, beispielsweise eine bienenwabenförmige Gitterplatte, die als Kernschicht einer Verbundplatte mit thermoplastischen Deckschichten dienen kann, mit den folgenden Schritten:
   (1) das Bereitstellen eines Körpers, auf den die Adhäsionsschicht aufzubringen ist;
   (2) das Zubereiten einer Lösung des thermoplastischen Kunststoffes in einem ersten Lösungsmittel;
   (3) das Aufbringen der Lösung auf die Oberfläche des zu beschichtenden Körpers;
   (4) das wenigstens teilweise erfolgende Entfernen des ersten Lösungsmittels durch Einführen des Körpers in ein zweites Lösungsmittel, wobei das thermoplastische Material im wesentlichen unlösbar ist und wobei das erste Lösungsmittel lösbar ist, und der Körper in dem zweiten Lösungsmittel für eine entsprechend lange Zeitdauer gehalten wird, so daß das erste Lösungsmittel in ausreichendem Maß aus der Oberfläche

des Körpers entfernt wird.

2. Verfahren nach Anspruch 1, gekennzeichnet durch den folgenden Schritt:
(5) das Aussetzen der relevanten Oberfläche des Körpers einer erhöhten Temperatur für eine Zeitdauer nach dem Schritt (3).

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß der Schritt (5) mithilfe von Wärmestrahlung ausgeführt wird.

4. Verfahren nach Anspruch 2 oder 3, dadurch gekennzeichnet, daß der Schritt (5) mithilfe von Dampf ausgeführt wird.

5. Verfahren nach den Ansprüchen 1-4, gekennzeichnet durch den folgenden Schritt:
(6) das Hinzufügen einer ausgewählten Menge des ersten Lösungsmittels zu dem zweiten Lösungsmittel vor dem Schritt (4), derart, daß eine gewünschte Konzentration des ersten Lösungsmittels in der resultierenden Adhäsionsschicht an dem Körper zurückbleibt.

6. Verfahren nach den Ansprüchen 1-5, gekennzeichnet durch die folgenden Schritte:
(7) das Auswählen eines ersten Lösungsmittels mit einem höheren Siedepunkt als das zweite Lösungsmittel;
(8) das wenigstens teilweise erfolgende Entfernen des zweiten Lösungsmittels durch Aussetzen der relevanten Oberfläche des Körper einer Temperatur, die mindestens in der Größenordnung des Siedepunktes des zweiten Lösungsmittels liegt.

7. Verfahren nach den Ansprüchen 1-6, gekennzeichnet durch den folgenden Schritt:
(9) das Auswählen von N-Methylpyrrolidon als erstes Lösungsmittel.

8. Verfahren nach den Ansprüchen 1-7, gekennzeichnet durch den folgenden Schritt:
(10) das Auswählen von Wasser als zweites Lösungsmittel.

Revendications

1. Procédé d'application d'une couche adhésive consistant substantiellement en une matière plastique thermoplastique sur un corps, par exemple une plaque à nid d'abeilles qui peut constituer le coeur d'une structure sandwich avec des feuilles recouvrantes thermoplastiques,
comprenant les étapes suivantes :
(1) la fourniture d'un corps sur lequel ladite couche adhésive doit être appliquée;
(2) la confection d'une solution de la matière plastique thermoplastique dans un premier solvant;
(3) l'application de ladite solution sur la surface du corps comme revêtement;
(4) l'élimination au moins partielle dudit premier solvant par introduction dudit corps dans un second solvant, dans lequel le matériau thermoplastique est substantiellement non soluble, et dans lequel ledit premier solvant est soluble, et le maintien dudit corps dans ce second solvant pendant une période suffisamment longue de sorte que ledit premier solvant soit éliminé en proportion suffisante de ladite surface dudit corps.

2. Procédé tel que revendiqué dans la revendication 1, caractérisé par l'étape suivante :
(5) l'exposition après l'étape (3) de la surface concernée du corps à une température accrue pendant une certaine durée.

3. Procédé tel que revendiqué dans la revendication 2, caractérisé en ce que l'étape (5) est réalisée en utilisant de la radiation de chaleur.

4. Procédé tel que revendiqué dans la revendication 2 ou 3, caractérisé en ce que l'étape (5) est réalisée en utilisant de la vapeur.

5. Procédé tel que revendiqué dans les revendications 1 à 4, caractérisé par l'étape suivante :
(6) l'addition préalable à l'étape (4) d'une quantité choisie du premier solvant au second solvant de sorte qu'une concentration désirée dudit premier solvant est retenue dans la couche adhésive résultante sur le corps.

6. Procédé tel que revendiqué dans les revendications 1 à 5, caractérisé par les étapes suivantes :
(7) la sélection d'un premier solvant qui a un point d'ébullition supérieur à celui du second solvant;
(8) l'élimination au moins partielle dudit second solvant en soumettant la surface concernée du corps à une température qui est au moins de l'ordre de grandeur du point d'ébullition dudit second solvant.

7. Procédé tel que revendiqué dans les revendications 1 à 6, caractérisé par l'étape suivante :
(9) le choix de la n-méthylpyrrolidone comme premier solvant.

8. Procédé tel que revendiqué dans les revendications 1 à 7, caractérisé par l'étape suivante :

(10) le choix de l'eau comme second solvant.

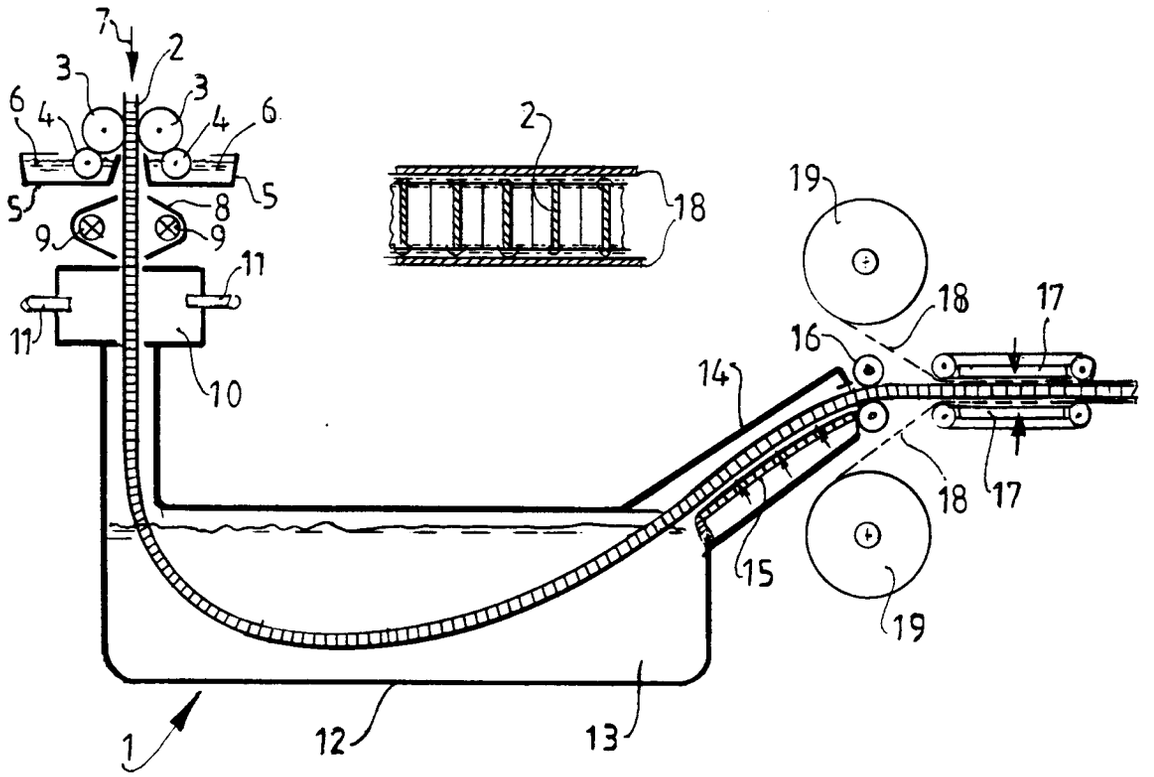

FIG.1

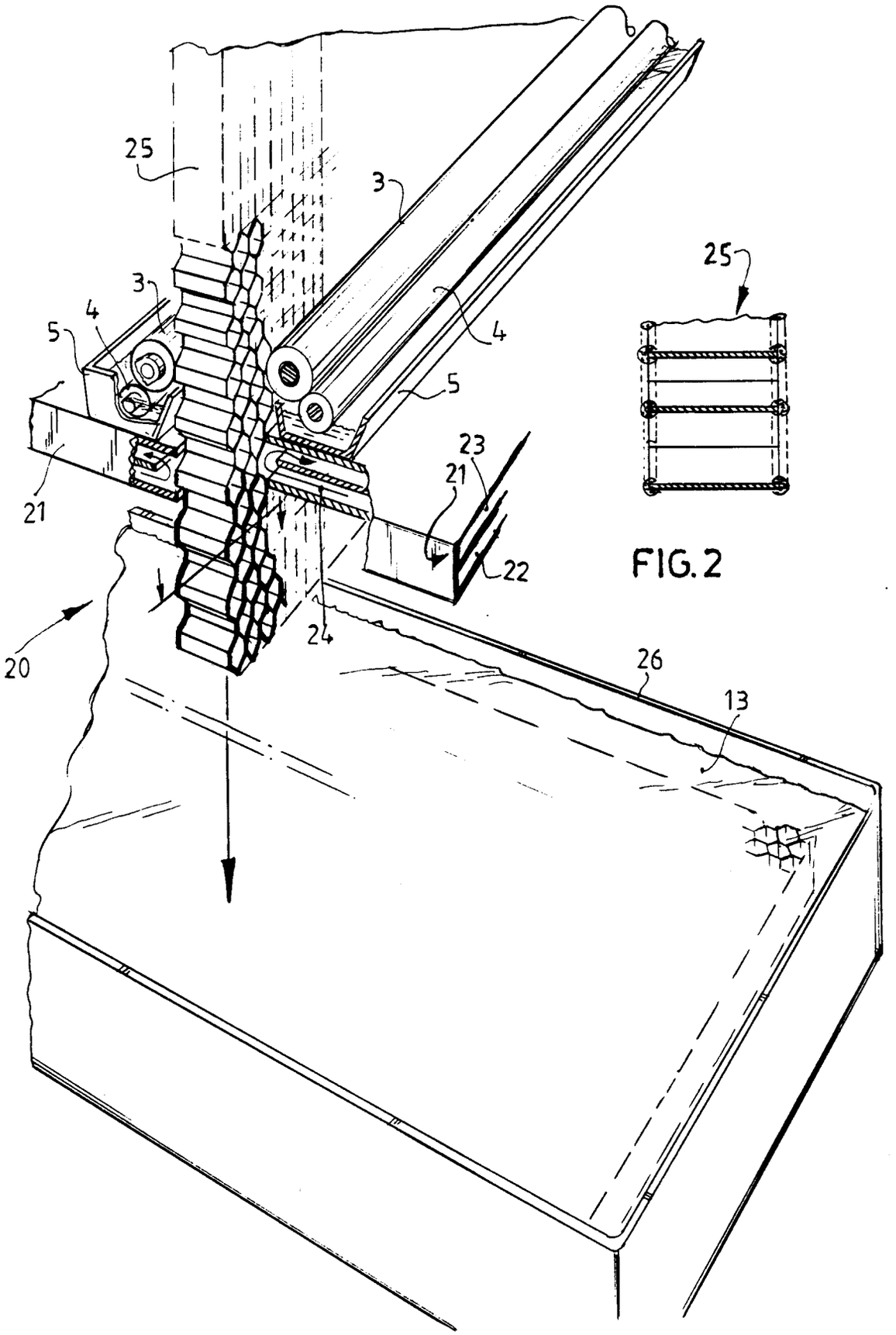

FIG. 2