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(54) Title: METHOD FOR TREATING A FILM WITH A COMPOSITION

(57) Abstract: Method for treating a film with a composition, whereby the film is folded along a fold line dividing the film into two parts of substantially equal weight, a support bar is positioned under the fold line to allow the film to be suspended and the bar is placed in a vessel containing the composition so as to bring the film into contact with the composition.



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Method for treating a film with a composition

The invention relates to a method for treating a film with a composition and to a device for carrying out this method.

In numerous film-treatment methods the issue of bringing the film into contact with a composition arises.

5 In case of liquid compositions, it is known practice to place the film in suspension in the liquid without using any supporting means. In this method, the film may sometimes crumple and fold in on itself under the effect of its own weight, and this may adversely affect the morphology (e.g. the flatness, the surface uniformity) of the film after treatment. In this case, it is also difficult to
10 place a large area of film in the treatment vessel while at the same time maintaining uniform contact between the film and the composition and preventing the film from sticking to the walls of the vessel.

 In an attempt to alleviate these problems, it is known practice to use a device known as a "jigger" comprising one or more sets of winding and
15 unwinding rolls, the film to be treated passing alternately from one roll to the other through a region in which it is brought into contact with the treatment composition. A device of this kind is described in particular in WO 90/12913.

 Film treatment methods using devices employing rolls are, however, very complicated and expensive, it being necessary for the control of the rotational
20 speed of the rolls to be very sophisticated in order to ensure that the film is correctly tensioned while it is being treated. The Applicant company has noticed that when, following treatment, the dimensions, both lateral and longitudinal, of the film alter, the use of rollers is even more difficult because of the risk of undesirable wrinkles appearing on the film after treatment.

25 The Applicant company has also noticed that certain, simpler, support means, comprising for example grippers and/or hooks supposed to support the film are also liable to introduce localized stresses which may locally and irreversibly deform the film, especially when the surface area and the weight of the film used are relatively high.

30 The invention aims to provide a method for treating films with a composition which allows the film to be brought uniformly into contact with the composition avoiding any risk of deformation, said method being, notably,

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effective from a technical standpoint, simple, economical, and suitable for being extrapolated on an industrial level.

In consequence, the invention relates to a method for treating a film with a composition, whereby the film is folded along a fold line dividing the film into
5 two parts of substantially equal weight, a support bar is positioned under the fold line to allow the film to be suspended and the bar is placed in a vessel containing the composition so as to bring the film into contact with the composition.

The Applicant company has found that the method according to the invention, on the one hand, allows the film to be supported while at the same
10 time preventing it from crumpling and/or sticking to the walls of the vessel and, on the other hand, makes it possible to prevent the film, the weight of which is spread uniformly along the fold line, from being able to be subjected to localized stresses liable to cause it to deform.

The method according to the invention also allows a large area of film to
15 be placed in the vessel encouraging uniform contact with the treatment composition.

As a preference, the film comprises at least one plastic consisting of a polymer or of an organic copolymer and as a more particular preference it is made of at least one plastic.

20 The plastic of the film may for example be polyethylene (PE), polypropylene (PP), a partially fluorinated (co)polymer such as polyvinylidene fluoride (PVDF) or polyethylene tetrafluoroethylene (ETFE), a completely fluorinated (co)polymer such as a copolymer of tetrafluoroethylene with a perfluorovinyl ether containing fluorosulphonyl groups, for example.

25 The composition generally comprises at least one and preferably several chemical components liable to react with the film. The chemical components may be in the gaseous, vapour and/or liquid state. As a preference, they are in the vapour and/or liquid state. As a more particular preference they are liquids. These compositions may, for example, be in the form of a solution or of an
30 emulsion.

If the treatment composition is liquid, its density is preferably less than that of the film.

As a preference, the method according to the invention is aimed at manufacturing an ionic membrane precursor and/or an ionic membrane.

35 An ionic membrane is to be understood as meaning a sheet comprising at least one organic polymer and/or copolymer comprising ionic functional groups.

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Thanks to these ionic functional groups and according to their nature, an ionic membrane has the ability to selectively exchange cations (cationic membrane) or anions (anionic membrane).

5 An ionic membrane precursor is to be understood here as meaning a sheet comprising at least one organic polymer and/or copolymer comprising one or more nonionic functional groups capable of being transformed, by a subsequent treatment, into ionic functional groups.

10 As a particular preference, the method according to the invention is used for the large-scale manufacture of ionic membrane precursors and/or of ionic membranes. The expression "large-scale manufacture" is used here to denote manufacture generally involving the production of a batch of at least 1 m² of ionic membrane and/or of precursor, preferably a batch of at least 50 m² ionic membrane and/or of precursor and as a more particular preference, a batch of at least 100 m² of ionic membrane and/or of precursor.

15 From a chemical standpoint, the manufacture of an ionic membrane or of an ionic membrane precursor by the treatment of a film generally comprises several treatments involving chemical reactions of different natures.

20 The treatments in question are, for example: (a) a chemical or radiochemical grafting treatment using a grafting agent which may or may not comprise nonionic functional groups capable of being transformed into ionic functional groups; (b) a treatment with a cross-linking agent; (c) a functionalization treatment aimed at incorporating into the film nonionic functional groups capable of being transformed, in a subsequent step (for example a hydrolysis step) into ionic groups; (d) a hydrolysis treatment
25 hydrolysing the nonionic functional groups with a view to transforming them into ionic functional groups; (e) a hot maturing treatment aimed at dimensionally stabilizing the finished membrane.

30 Grafting agents comprising no functional group capable of being transformed in a later step into an ionic functional group are, for example, styrene or α,β,β -trifluorostyrene.

Grafting agents having a functional group capable of being transformed in a later step into an ionic functional group are, for example, chloromethylstyrene (by amination) and acrylic acid or its esters (by hydrolysis).

35 When the method according to the invention is aimed at the manufacture of an ionic membrane or of an ionic membrane precursor, the treatment of the film is preferably a chemical or radiochemical grafting, cross-linking,

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functionalization and/or hydrolysis treatment.

The vessel that can be used to implement the method according to the invention is advantageously of parallelepipedal shape.

For preference, the vessel has internal dimensions H (height), L (width)
5 and P (depth) such that $H > L > P$.

As a preference, the vessel is made of metal, for example titanium or stainless steel. As a preference, it is able to withstand a partial vacuum and, as a particular preference, an absolute vacuum. A partial vacuum is to be understood here as meaning a vacuum corresponding to a pressure of less than 1 bar and at
10 least 50 mbar. An absolute vacuum is to be understood here as meaning a vacuum corresponding to a pressure below 50 mbar.

It is also preferable for the vessel to be able to withstand raised pressures, generally a raised pressure of at least about 2 bar and, as a particular preference, a raised pressure of at least about 3 bar.

15 The support bars for suspending the film are in turn supported inside the vessel by support means. The support means that can be used for implementing the method according to the invention are preferably removable metal plates fixed to the upper part of the vessel and exhibiting notches in which the ends of the support bars may be placed.

20 These plates, which have the shape of combs, allow the support bars to be stored parallel to one another, just below the upper edge of the vessel.

By way of example, Fig. 8 schematically illustrates combs (13) positioned inside a vessel of parallelepipedal shape (25) near its upper edge.

The number of support bars described hereinabove that can be used
25 according to the method according to the invention depends, amongst other things, on the size of the vessel.

The vessel advantageously contains at least 5 bars, preferably at least 50 bars and as a particular preference, at least 80 bars. Furthermore, the vessel advantageously contains at most 400 bars and preferably 300 bars at most.

30 The support bar is preferably a metal batten of length L' where L' is slightly shorter than the internal width L of the vessel so as to allow it to be positioned in the upper part of the said vessel, parallel to the side L and perpendicular to the side P .

As a preference, several battens are placed in the upper part of the vessel
35 using support means such as the combs described above.

The thickness P' of the support batten is preferably as small as possible in

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order to limit the space occupied by the batten in the direction of the depth P of the vessel while at the same time maintaining good rigidity and enough mechanical strength to support the film.

5 The height H' is not particularly critical but, like the thickness P', needs to be such as to ensure good rigidity and sufficient mechanical strength.

Advantageously, the support bar is a metal batten with a thickness P' of at least 0.5 mm and at most 1.5 mm, a height H' of at least 5 mm and at most 25 mm. The length L' is advantageously at least 70 cm and preferably at least 80 cm. Furthermore, L' is advantageously at most 1.5 m and preferably at most 10 1.2 m. An example of a support bar (5) is illustrated in Fig. 3 and Fig. 5.

In the case of a parallelepipedal vessel having an internal height H and an internal width L, it is preferable to use rectangular plastic sheets of thickness P and having sides of length l and h, where $l < L$, $h/2 < H$.

By way of example, Fig. 1 schematically illustrates a reaction vessel (1) of 15 parallelepipedal shape, having an internal height H, an internal width L and an internal depth P, and a rectangular sheet (2) of height h and width l. Fig. 2 illustrates the rectangular sheet (2) folded along a fold line situated at mid-height h (3) and (4). Fig. 3 illustrates the folded rectangular sheet (4) and a support bar (5) of length L' ($L' > l$).

20 Sometimes, it may be beneficial to make holes in register with the fold line in order to facilitate the removal of the gas which may remain trapped under the sheet as the vessel is filled with a liquid composition.

Fig. 3 illustrates the folded rectangular sheet (4') placed over the support bar (5) and in which holes (6) have been made along the fold line.

25 Often, during certain treatments, especially, for example, certain grafting and functionalization treatments, the film has a tendency to swell, generally isotropically, following the massive incorporation of reactants.

The Applicant company has observed that, when the film, during treatment, is subjected to constraints that impede its swelling, it may exhibit 30 surface defects and/or deformations.

If the film swells, the suspension means according to the invention also has the advantage of allowing the film to be supported while at the same time preventing or considerably limiting any constraints liable to oppose its swelling, particularly in the direction defined by the fold line, given that the film is 35 generally free to slide along the support bar.

In the event of swelling, the size of the sheet at the end of the treatment

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may be an important aspect that needs to be taken into consideration when implementing the method.

In the case described above, of a sheet of rectangular shape, of height h , width l and thickness p , the swelling, when isotropic, occurs proportionately
5 identically in all three directions h , l and p , allowing the sheet to maintain its initial shape.

The swelling of the sheet in the direction of the thickness p , although proportionately identical to the dimensional variations that occur in the direction of the width l and of the height h is, unlike these variations, negligible in terms
10 of absolute value (typically ranging from a few microns to a few tens of microns in the case of sheets with an initial thickness of some one hundred microns). The space available around the suspended sheet as described previously is easily enough for its thickness p to be able to increase freely (i.e. without any element contained in the vessel opposing the swelling in this direction).

In general, the thickness p is at least one micron, preferably at least
15 5 microns and as a particular preference at least 20 microns. Furthermore, the thickness p is generally at most 1 mm, preferably at most 500 microns and as a particular preference 200 microns at most.

Contrary to the case with the thickness p , the swelling of the sheet in the
20 direction of the height h and the width l may be as much as several tens of centimetres when the initial h and l values are of the order of 1 metre.

The suspension means according to the invention allows the sheet to swell in these directions, particularly in the height and width direction, except when the height h and the width l become excessive and the sheet touches either the
25 bottom of the vessel and/or its side walls.

In the event of swelling, it is beneficial for the initial dimensions l and h of the sheet to be chosen as a function of the dimensions L and H of the vessel and of the dimensions that the sheet will have at the end of treatment.

In this respect we should note that, in general, the final dimensions of a
30 sheet subjected to treatment with a reactive composition are dependent not only on its initial dimensions but also on the coefficient of linear expansion of the film specific to the envisaged treatment.

This coefficient of expansion is in turn dictated by a series of experimental parameters (e.g. the type of film, the nature and concentration of the reactants,
35 the temperature, the duration of the treatment, etc.) and is generally very repeatable.

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Determining the coefficient of linear expansion of the film beforehand makes it possible to predict what the dimensions of the sheet will be at the end of treatment.

5 In the case of treatment with a liquid composition, this coefficient of linear expansion may be determined for example on a laboratory scale using a test specimen of film measuring a few centimetres squared placed in suspension in an excess of liquid composition.

10 If the sheet, following treatment, is liable to swell by Δl and Δh , the initial length l is advantageously chosen so that the final length $(l + \Delta l)$ is at most equal to L , L being the internal width of the vessel.

Furthermore, the initial length l is preferably chosen so that $(l + \Delta l)$ is at least 80% of L , as a particular preference so that $(l + \Delta l)$ is at least 90% of L , and as a more particular preference, so that $(l + \Delta l)$ is at least 99% of L .

15 Furthermore, the initial height h is advantageously chosen so that the final length $(h/2 + \Delta h/2)$ is at most equal to H , H being the internal height of the vessel.

Furthermore, the initial height h is preferably chosen so that $(h/2 + \Delta h/2)$ is at least 80% of H , as a particular preference so that $(h/2 + \Delta h/2)$ is at least 90% and as a more particular preference so that $(h/2 + \Delta h/2)$ is at least 99% of H .

20 This makes it possible, on the one hand, to prevent the final dimensions of the sheet at the end of treatment from exceeding the internal dimensions of the vessel, as this, as the Applicant company has observed, generally causes wrinkling and/or other morphological defects and, on the other hand, to prevent the final dimensions from being markedly smaller than the internal dimensions of the vessel, as this would lead to excessive and unjustified consumption of
25 reactants with respect to the area of film treated.

At the end of the treatment, a rectangular sheet of initial width l and initial height h as described previously, having swelled by Δl in the width-wise direction and by Δh in the height-wise direction, can be cut along its fold line,
30 thus yielding two smaller rectangular sheets of width $(l + \Delta l)$ and height $(h/2 + \Delta h/2)$.

When the film is in the form of a rectangular sheet of width l and height h , the width l is preferably at least 0.4 m, more particularly preferably at least 0.7 m, and as a more particular preference still, at least 0.9 m. Furthermore, the
35 width l is preferably at most 1.2 m and as a particular preference at most 1.0 m. According to this embodiment, the height h is preferably at most 2.5 m, as a

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more particular preference at most 2 m. Furthermore, the height h is preferably at least 1.5 m.

It is sometimes preferable for a separator grid to be positioned between the aforesaid two parts of the film.

5 One possible function of the separator grid is that of preventing the internal faces of the two parts of the sheet situated on either side of the fold line from being able to touch and stick during treatment, even locally and/or temporarily.

This phenomenon, as observed by the Applicant company, may sometimes adversely affect the quality of the sheet after treatment.

10 As illustrated by way of example in Fig. 4, the separator grid (7) may be attached directly to the support bar (5). The film (4') is then placed over the bar (5) afterwards. In this case, the dimensions of the separator grid are preferably almost equal to those of the cross section $H \times L$ of the vessel.

15 The grid may be attached to the support bar by any known fixing means (for example hooks, a string, grippers, etc.).

Fig. 5 illustrates by way of example a support bar (5) in which a series of holes have been made so that the separator grid can be fixed using, for example, hooks or strings.

20 In general, the mesh size of the separator grid and its thickness vary according to the conditions in which the method is implemented.

According to a preferred embodiment, the thickness of the separator grid may be at least 50 and at most 700 microns. Advantageously, the separator grid comprises a plastic. As a preference, the separator grid is made of one or more plastics. The plastic is preferably flexible and mechanically strong.

25 Furthermore, when use is being made of a liquid treatment composition, its density is preferably less than that of the grid material.

As a particular preference, the grid material is inert with respect to the component used for treatment and with respect to the film employed.

30 What this implies, amongst other things, is that this material does not react or reacts only negligibly with the chemical compounds used for the treatment (e.g. grafting, functionalization, hydrolysis and/or maturing agents) and/or that the said material is not soluble in any of the solvents that might be used for the treatment.

35 The plastic of the grid may for example be a partially fluorinated copolymer. Polyethylene tetrafluoroethylene (ETFE) is particularly suitable. It is also possible for the separator grid to be made of metal. Separator grids made of

titanium or of stainless steel may be appropriate according to the treatment conditions (e.g. duration, temperature) and the chemical compounds that make up the composition.

When the method intends to treat a very large surface area of film, several
5 folded films, each suspended from a support bar, may be positioned side by side in the vessel and grid inserts are also positioned between the adjacent films.

The grid inserts, so called in order to differentiate them from the separator
grids described hereinabove, are aimed at preventing the outer faces of two
adjacent sheets from being able to come into contact with and stick to one
10 another, even locally, during treatment.

The grid inserts have the same technical characteristics as the separator
grids described hereinabove, preferably in all respects.

The grid inserts are generally attached to bars positioned on either side of
each bar used to suspend a folded sheet and a separator grid.

15 The bars used to suspend the grid inserts generally meet the same technical characteristics as the bars that support the sheets and the separator grids.

These bars are supported by the same support means intended to support
the other bars, for example the "combs" described beforehand.

In order to maximize the number of sheets that can be loaded into the
20 vessel while at the same time limiting the phenomena of friction near the fold lines, the Applicant company has found that certain loading modes may prove particular effective.

For example, it may be beneficial for the support bars used to suspend
adjacent films to be positioned in the vessel alternately at different heights.

25 Another method of loading the sheets and the grids which may sometimes prove to be particularly effective is to place the bar supporting the grid insert just above the one supporting the sheet and the separator grid.

To do this, the bar intended to support the grid insert is preferably a
batten (8) like the one illustrated in Figs 5 and 6. The batten (8) is equipped at
30 its two ends with lugs that allow it to be placed on a support bar (5) of the same thickness and intended to support the sheet and the separator grid. A grid insert (10) and a separator grid (7) may be attached to the bars (8) and (5) respectively using fixing systems (9). The space between the two bars (Fig. 5) allows the sheet to pass and sit astride the support bar (5).

35 This method of loading the sheets and grids in particular makes it possible to increase the spacing between the bars (for the same number of bars) while at

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the same time preventing them from all being positioned at the same level, near the upper edge of the vessel.

It is sometimes preferable for the two modes of loading the sheets described hereinabove to be combined.

5 The Applicant company has found that sometimes, notwithstanding the use of the loading modes described hereinabove, the swelling of the sheet near the fold line may be impeded or completely obstructed by the presence of the adjacent sheets and/or grids.

10 That does not, however, prevent the sheet from swelling at locations remote from the fold line, particularly in the lower part of the vessel.

As illustrated in Fig. 7, this phenomenon may cause a sheet to be obtained at the end of treatment (e.g. an ionic membrane or a precursor) that has a bowed trapezoidal shape (11).

15 In this case, the sheet is also adversely affected by the presence of numerous especially transverse wrinkles (12) caused by compression of the film near the fold line.

Although located roughly more in the upper part of the sheet, the transverse wrinkles (12) often also spread towards the bottom of the sheet and irreversibly damage it.

20 During manufacture, for example, of ionic membranes, the lack of flatness and the presence of these wrinkles often render the membrane completely unusable.

25 As a result, in the event of swelling, it may be beneficial for stretching means to be applied to the fold line of the film to prevent the film from being in compression near the suspension means during treatment.

In general, the stretching means according to the invention comprise a mass the weight of which is transmitted by a filament to one of the ends of the fold line.

30 It is preferable for the stretching means according to the invention to be applied in such a way that the stretching force exerted on one of the ends of the fold line has no component orthogonal to the direction of the support bar.

Figs. 9-13 illustrate, by way of example, one possible embodiment of the invention comprising a stretching means.

35 In particular, Figs. 9-11 illustrate one of the two top corners of the sheet (4) which, according to the invention, is folded along the fold line (18) and placed straddling the support bar (5). A hole (15) is made in the sheet (4) near to the end

of the fold line (14). A second hole (15'), drawn in dotted line, is made in the sheet (4). The hole (15') lies facing the hole (15) on the other side of the fold line (18). A hole (16) is made at the end of the support bar (5). The sheet (4) is positioned straddling the bar (5) in such a way that the holes (15) (15') and (16)
5 are aligned. A metal pin (17) is inserted in the holes and fixes the end of the fold line (14) to the end of the bar (5) (Fig. 10). As illustrated in Fig. 11, the sheet (4) may also be fixed, for example, using a string (19) passing through the holes (15) (15') and (16). Fig. 12 illustrates the other top corner of the sheet (4).

A mass (20) is attached to the holes (24) and (24') situated at the end of the
10 fold line by a set of strings (22) and (22') passing through the eye (21).

By means of the eye (21) and the set of strings (22) and (22'), the stretching force T is uniformly distributed between the two faces of the sheet (4) on either side of the fold line (18). The stretching force T exerted on the fold line (18) near its end (23) makes it easier for the sheet (4) to slide along the bar (5), particularly
15 when there is significant friction between the film and the bar, preventing the film from being in compression near to the support bar when it has a tendency to swell during treatment.

The eye (21) is located more or less at the same height as the holes (15), (15'), (24) and (24'). This in particular makes it possible to prevent the stretching
20 force T from having a component orthogonal to the fold line.

As illustrated in Fig. 13, as the sheet (4) gradually swells, the mass (20) drops. Throughout the treatment, the stretching force T exerted on the end of the fold line (23) is constant because it is equal to the weight of the mass (20).

The mass (20) may for example be in the shape of a cylinder (e.g. made of
25 stainless steel or of titanium). Preferably, the mass (20) is chosen so that it exerts on the sheet a stretching force T that is at least strong enough to overcome all the stresses (for example friction forces) that may prevent the film from swelling and cause it to compress along the fold line.

In the case of the embodiment described above, it is sometimes preferable
30 to position eyelets, for example metal eyelets, in register with the holes (15) (15') (24) and (24') in order to limit the risk of the film being torn or cut by the strings (22) and (22') connected to the mass (20).

The strings may be made of plastic, polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF) are particularly suitable.

35 As illustrated in Fig. 14, when the mass (20') is too heavy, the stretching force T' may yield a sheet at the end of treatment (e.g. an ionic membrane) that is

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of trapezoidal shape (4'') (namely that is wider in the upper part near the support bar (5) than it is in the lower part) and lead to degradation in terms of the flatness by comparison with the starting sheet.

5 The Applicant company has observed that in general it is preferable for the strength of the stretching force T to be below the yield point of the film at the temperature and in the reaction medium used for the treatment.

The stretching means described in the preceding example are very effective and inexpensive. They also have the advantage of allowing a constant tensile force to be exerted on the fold line this being independently of the width that the
10 sheet attains during treatment.

They thus make it possible to avoid recourse to solutions that are particularly complex from a technical standpoint and very expensive, such as stretching and dewrinkling means controlled from outside the vessel for example, for example using motorized servomechanisms or manually, and acting
15 via dynamic seals.

What is more, the absence of dynamic seals enables a closed vessel to be produced that is perfectly sealed and particularly well suited to the carrying-out of certain manufacturing treatments, particularly those requiring the use of compounds that are toxic and/or corrosive at high temperature and pressure
20 and/or in the absence of oxygen.

The stretching means according to the preceding example also have the advantage of self-adapting to the rate at which each individual sheet swells.

This makes it possible, amongst other things, to treat, in the same manufacturing batch, sheets which have different expansion tendencies (for
25 example, when radiochemically grafting sheets irradiated at different doses).

On the basis of the foregoing, the invention can also be seen as a device for treating films with a composition comprising a vessel to contain the composition, support bars for suspending folded films, support bars for supporting grids, bar-support means, and stretching means to stretch the ends of the fold lines of the
30 films.

The support bars, the grids and the stretching means have the same technical characteristics as the support bars, the grids and the stretching means described previously, preferably in all respects.

The bar-support means, as described previously, are preferably metal plates
35 in the form of combs. The bar-support means are generally removable.

As a particular preference, the bar-support means need to allow the support

bars to be positioned in the vessel alternately at different heights.

The vessel advantageously has one or more of these characteristics:

- parallelepipedal shape
- metal structure
- 5 ▪ removable lid equipped with several tapplings intended in particular for inerting, evacuating, and venting operations and intended for connection to safety systems such as, for example, rupture discs;
- several orifices on the bottom intended in particular for loading, unloading and/or for circulating the composition before, during and/or after treatment;
- 10 ▪ several orifices in the upper part of the side walls and intended in particular for loading, unloading and/or circulating the composition before, during and/or after treatment;
- portholes made of transparent material situated in the upper part of the lid and/or on the side walls, so that the ends of the fold lines of the films and, if
- 15 necessary, the level of composition inside the vessel in particular can be seen;
- several pressure and temperature sensors for monitoring and regulating the pressurizing and heating of the installations;
- a layer of lagging on the external walls to limit heat loss phenomena;
- a system for heating the vessel, for example a heating coil.

20 As a preference, the vessel is of parallelepipedal shape and comprises orifices situated near its upper edge and orifices situated on the bottom, the said orifices being intended, amongst other things, to allow the composition to be loaded, unloaded and/or circulated during treatment.

25 When a liquid composition is kept circulating by a pump connected to the vessel by means of a looped network of pipes, the orifices situated near the upper edge of the vessel are preferably used to supply the liquid composition while the orifices situated on the bottom of the vessel are preferably used to remove the said composition.

30 As a preference, the vessel comprises transparent portholes so that the ends of the fold lines of the films in particular can be seen.

The presence of these portholes may prove beneficial not only for visually monitoring the level of swelling of the sheets during treatment but also, if necessary, for monitoring the level of liquid composition inside the vessel.

35 When using a liquid composition, the device according to the invention advantageously comprises a heat exchanger and/or a circulating pump which are connected to the vessel by a looped network of pipes.

As illustrated in Fig. 15, the support and stretching means according to the invention are very compact and take up very little space inside the vessel (25).

The method and the device according to the invention thus allow a great number of sheets to be treated with respect to the volume of the vessel and
5 therefore with respect to the volume of composition.

Given the sometimes very high cost of certain reactants used to treat films, particularly reactants involved in the manufacture of ionic membranes, particularly in the case of manufacturing methods using chemical or radiochemical grafting and/or functionalization, the reduction in the volume of
10 composition means that manufacturing costs can be reduced appreciably.

The number of sheets that can be employed according to the method and the device according to the invention depends amongst other things on the size of the vessel.

The vessel advantageously contains at least 5 sheets, preferably at least 50
15 sheets and as a particular preference at least 80 sheets. Furthermore, the vessel advantageously contains at most 400 sheets and preferably 300 sheets at most.

For the treatments aimed at manufacturing a number of sheets greater than about 400 it is preferable to use several vessels operating in parallel and/or in series rather than one single vessel operating individually.

20 Series operation implies in particular that the component, having been used to treat a first batch of sheets, is reused to treat a second batch and so on. Series operation is particularly preferred, in particular, when the cost price of the treated sheets (e.g. ionic membranes) is to be reduced.

In the case of a liquid composition circulating through the vessel from top
25 to bottom, parallel to the sheets suspended on the support bars as described previously, the method and the device according to the invention thus contribute to ensuring a highly favourable hydrodynamic regime limiting all gradients, amongst other things concentration and temperature gradients, particularly near the surface of the film.

30 In the case of the manufacture of ionic membranes, this also contributes to the obtaining of membranes that are flat with no surface defects, uniform from a mechanical and electrochemical standpoint and, in particular, which have highly uniform electrical resistance, exchange capacity and water content values.

The ionic membranes resulting from the method according to the invention
35 can be used in numerous applications such as, for example, electrolysis, electrodialysis, fuel cells.

- 15 -

The particular features of the invention will become apparent from the following description of the appended figures:

- Fig. 1 Reaction vessel of parallelepipedal shape and rectangular sheet;
Fig. 2 folded rectangular sheet;
5 Fig. 3 folded rectangular sheet placed over a support bar;
Fig. 4 folded rectangular sheet placed over a support bar with separator grid;
Fig. 5 support bars for the sheet, separator grid and grid insert;
Fig. 6 supported grid insert and separator grid;
Fig. 7 suspended sheet, deformed and wrinkled as a result of it being placed in
10 compression near the support bar;
Fig. 8 combs placed inside a parallelepipedal vessel;
Fig. 9 top corner of a folded sheet suspended from a support bar, attachment
by means of a pin;
Fig. 10 top corner of a folded sheet suspended from a support bar, attachment
15 by means of a pin;
Fig. 11 top corner of a folded sheet suspended from a support bar, attachment
by means of a set of strings;
Fig. 12 top corner of a folded sheet, suspended from a support bar, stretching
system using a mass connected to the end of the fold line via a set of
20 strings;
Fig. 13 sheet suspended from a support bar with separator grid and stretching
means;
Fig. 14 sheet deformed by excessive stretching force; and
Fig. 15 vessel containing a panoply of separator grids, grid spacers and
25 suspended sheets to which stretching means are applied.

Example

The example illustrates the large-scale manufacture of a batch of anionic membranes of rectangular shape with sides of the order of one linear metre long. The anionic membranes were manufactured according to the method according
30 to the invention starting from a film of polyethylene tetrafluoroethylene (ETFE).

Manufacture involved the steps of:

- (i) radiochemically grafting the film with chloromethylstyrene (CMS)
- (ii) aminating the grafted film with trimethyl amine (TMA)
- (iii) dimensionally stabilizing the aminated fuel with an aqueous saline solution
35 in the hot state.

The anionic membranes resulting from the manufacturing method were

characterized by determining their final dimensions and the dimensional variation experienced by the sheets following the series of treatments (i)-(iii), their final appearance (shape, level of flatness, surface finish) and the exchange capacity (EC), the water content (WC) and the electrical resistance (ER).

5 1. Analytical methods

1.1 – To determine the exchange capacity (EC) and water content (WC) of an anionic membrane

A test specimen of anionic membrane (measuring about 4×4 cm²) was first of all rinsed with demineralized water and then immersed in a beaker
 10 containing 250 ml of 1M HCl for 2 hours. The test specimen was extracted from the acid solution and rinsed several times using demineralized water (250 ml each time for 30 minutes) until pH neutral rinsing waters were obtained. The test specimen was then immersed in a flask containing a solution made up of 250 ml of 0.1M HNO₃ for about 12 hours with slow stirring. The test specimen was
 15 extracted from the flask and rinsed with demineralized water, adding the rinsing water to the solution contained in the flask. The total number of chloride ions present in the nitrous solution ($n_{(Cl^-)}$, in milliequivalents, meq) was determined by argentimetry. The test specimen of membrane was then immersed in water until its pH became constant. Having carefully blotted the test specimen between
 20 two sheets of filter paper it was weighed, by placing it in a sealed and precalibrated weighing bottle (w_w = weight of the wet test specimen of membrane). The membrane was then placed in an oven at 60°C, in the open weighing bottle, for about 12 hours. The weight of the dry membrane (w_d = mass of the dry test specimen of membrane) was determined by using a
 25 (prec calibrated) sealed weighing bottle in order to avoid rehydrating the membrane during the weighing operation. The EC was calculated using the following formula

$$EC = n_{(Cl^-)} / w_d \text{ (meq/g)}$$

30 The WC was calculated using the following formula

$$WC = (w_w - w_d) / w_d \text{ (%)}$$

1.2 – To determine the electrical resistance (ER) of an anionic membrane

A test specimen of anionic membrane measuring about 4×4 cm² was
 35 immersed in an aqueous solution containing 10 g/l of NaCl. The test specimen was conditioned in the measurement medium for at least 12 hours. The electrical

resistance measurement was taken, in the aqueous saline solution, using a conductivity measuring clip equipped with two platinum electrodes each having a surface area of 1 cm² situated in the bottom of two godet rolls to grip the sheet and enclose a given volume of solution. A first electrical resistance value was
5 determined by clamping the test specimen of anionic membrane between the two godet rolls ($R_{(\text{membrane} + \text{solution})}$). A second electrical resistance value was determined by slipping the test specimen of membrane out of the godet rolls ($R_{(\text{solution})}$) without in any way opening the clip and parting the electrodes. The difference between the values of $R_{(\text{membrane} + \text{solution})}$ and $R_{(\text{solution})}$ gave the
10 electrical resistance (ER) of the membrane (expressed in Ω or in $\Omega \cdot \text{cm}^2$).

2 – Description of the reaction vessel and of the peripheral installations

Manufacture was performed using a grade 2 titanium reaction vessel of parallelepipedal shape with an internal height H of 162.4 cm, an internal width L of 113 cm and an internal depth P of 70 cm. The vessel was lagged and equipped with a
15 removable lid, also made of titanium, and equipped with portholes in order to view the upper part of the sheets employed (particularly of fold lines). The lid was also equipped with several tappings and valves allowing it to be connected to venting, evacuating and inert gas (nitrogen) supply circuits. The vessel and its lid were capable of withstanding an absolute vacuum and a raised pressure of at most 4.5 bar. Near
20 the upper edge of the walls of the vessel identifiable by the dimensions $P \times H$ and on the bottom of the said vessel there were also several orifices of a diameter of 25 mm (on the side walls) or 50 mm (on the bottom) intended, amongst other things, to allow the liquid components in and out. The vessel was connected to a network of lagged Armylor® pipes connecting loopwise the upper orifices with its
25 lower orifices, the said network comprising, amongst other things, titanium manifolds external to the vessel for distributing the flow of the fluids, several cut-off valves, a titanium circulating pump (SGL Technics® S.H. 80-50-200, impeller diameter 210 mm, maximum delivery 118 m³/h, maximum speed 3 000 revolutions/min) to draw up the liquid contained in the vessel via the
30 orifices situated in the bottom and supply it via the orifices situated near the upper edge of the walls, a titanium plate-type heat exchanger (Alfa Laval® M10 BFG, 59 plates, maximum pressure 10 bar, exchange area 13.7 m², exchange capacity 2 415 W/m²K) and several storage tanks (for storing the reactants and the solvents, for preparing the liquid components, for unloading spent liquid
35 components). The entire installation described hereinabove was of course capable of withstanding the absolute vacuum and the same level of raised

pressure that the vessel/lid assembly was able to tolerate. Like the lid, the vessel was also equipped with portholes to allow the ends of the fold lines of the sheets adjacent to the walls to be seen, these portholes being situated near the upper edge of the side walls identifiable by the dimensions $L \times H$. The vessel also
5 contained removable support systems consisting of two identical combs (elements (13), Fig. 15) placed near the upper edge of the walls $H \times P$ just below the lid. Each comb consisted of a titanium plate 0.5 cm thick, 70 cm wide and 15 cm high. 85 notches each 1.7 mm wide had been made in each plate so that the ends of the sheet-support bars and grid-support bars could be slipped into
10 these notches. The notches alternately had heights of 7 cm and of 10 cm. The notches were situated about 6.5 mm apart, the first and the last notch being situated 4.5 mm from the ends of the plate. The two combs, placed one facing the other, were able to support and store, parallel to the walls $H \times L$ of the vessel, the 85 bars intended to support the sheets and the separator grids and the 85 bars
15 intended to support the grid inserts. The vessel via its network of Armylor[®] pipes was connected to a system of pumps in order to evacuate the installation (a Sihi[®] liquid ring pump K5216PPM b and a Leybold[®] vane pump Trivac D65B) to a cryogenic nitrogen tank (with a capacity of 10 m³), to automatic temperature and pressure control devices and to a system of scrubbers (acidic and basic) for
20 venting the gases, collecting toxic and/or corrosive vapours and venting the installation to the atmosphere.

3 – Means for supporting the film and the grids, means for stretching the film

The support means used for the sheets and the separator grids were titanium battens 112.8 cm long, 2 cm high and 1.5 mm thick (element (5),
25 Fig. 5). Under each batten had been attached a woven polyethylene tetrafluoroethylene (ETFE) grid of rectangular shape 500 microns thick and with sides measuring 110 cm and 141 cm respectively. The grid had an alternate square mesh 800 microns in size. The support means used for the grid inserts were titanium battens with the same dimensions as those described above and
30 also equipped at their ends with square lugs 2 cm high and 0.5 cm wide (element (8), Fig. 5). The weave of the grid inserts had the same technical characteristics as that of the separator grids. Each support bar (element (5), Fig. 12) was equipped at one of its ends with an eye (element (21), Fig. 12) to support the bundle of stretching strings (elements (22) and (22'), Fig. 12) connecting a metal
35 mass of cylindrical shape (element (20), Fig. 12) to the fixing points (24) and (24') of the sheet (5) (Fig. 12), the points (24) and (24') lying at the end of the

fold line of the sheet (elements (23) and (18), Fig. 12). Each sheet (5) was fixed to the other end of its support bar (element (16), Fig. 11) by a system of strings (element (19), Fig. 11). Each mass (20) weighed about 250 g.

4 – Liquid compositions used to treat the film

5 The monomers and more especially those containing substantial quantities of stabilizers such as divinylbenzene (DVB) and chloromethylstyrene (CMS) had been previously destabilized by washing in a 0.1M NaOH basic aqueous medium then rinsed to the pH-neutral state with demineralized water in glass installations of appropriate size. The destabilized monomers were kept at -18°C until they
10 were ready for use.

4.1 – Liquid composition C1

The liquid composition C1 was prepared in a stainless steel tank with a volume of 2.4 m³. The tank had been previously deoxygenated by a series of flushings with nitrogen. Thereafter, the following components were introduced:
15 (1) denatured ethanol (E), 1 040 litres (844.45 kg); (2) chloromethylstyrene (CMS), 260 litres (280.8 kg); (3) divinylbenzene (DVB), 7.8 litres (7.18 kg); (4) methylene blue (MB) acting to inhibit polymerization in solution, (0.312 kg).

The liquid composition C1 was purged with nitrogen for 24 hours until an oxygen concentration of below 10 ppm was obtained in the reactor overhead.
20 The liquid composition C1 thus deoxygenated was stored under a nitrogen atmosphere prior to use.

4.2 – Liquid composition C2

The liquid composition C2 was an aqueous solution containing 50% by weight of trimethyl amine (TMA).

25 4.3 – Liquid composition C3

The liquid composition C3 was an aqueous solution containing 0.1 mol/l of HNO₃.

4.4 – Liquid composition C4

The liquid composition C4 was an aqueous solution containing 10 g/l of
30 NaCl.

5 – Film

A polyethylene tetrafluoroethylene (ETFE) film in the form of a band 220 m long, 0.80 m wide and 100 microns thick had been previously irradiated in the presence of air under an electron beam at a voltage of 1.5 MeV and at a
35 dosage rate of 10 kGy/s. The dose deposited on the film was 100 kGy. The irradiated film was kept at a temperature of -18°C or below until it was ready to

be used.

At -18°C the irradiated film can be kept for at least 12 months with a negligible loss of reactivity. The web of film was cut into 85 rectangular sheets of a height h of 1.90 m and a width l of 0.80 m. Each sheet was folded at mid-height $h/2$ and placed over a support bar as described hereinabove. Small holes of a diameter of about 2 mm were made every 5-6 cm along the fold line of each sheet. Each sheet was then fixed to one of the ends of its own support bar (this support bar already being equipped with a separator grid (Fig. 13)) and connected to stretching means as described previously (Figs. 11-12).

10 6 – To load the sheets into the reaction vessel

The 85 sheets, each sheet having been placed as described previously straddling its own support bar (equipped with a separator grid and with stretching means) were all placed in the vessel by inserting the ends of each support bar in the combs. The bars intended to support the grid inserts were positioned just above the bars supporting the sheets, by sliding their ends into the notches of the combs in such a way as to make them rest via the square lugs on the underlying support bars. At the end of this operation, 170 bars, 85 of them supporting the sheets and the separator grids and 85 of them supporting the grid inserts, were arranged in the vessel parallel to the walls identifiable by the dimensions $H \times L$ (Fig. 15).

20 7 – Sequence of treatment operations

Once the vessel had been closed with the lid, the vessel, the pipes and the peripheral installations (plate-type heat exchanger, circulating pump, etc.) were depressurized to a vacuum of about 10 mbar. Thereafter, nitrogen was introduced until a raised pressure of about 1 bar was reached. The raised pressure of nitrogen was then discharged via the orifices situated at the inlets and outlets of the vessel and via the venting valves and the lid and the peripheral network until a residual raised pressure of about 0.1 bar was reached. This nitrogen purging operation was repeated several times until practically all the residual oxygen both in the vessel and in the pipework and the peripheral installations had been eliminated (< 10 ppm).

30 7.1 – To treat the sheets with the liquid composition C1 (to graft CMS)

The liquid composition C1 was transferred from the stainless steel tank (mentioned at item 4.1) to the vessel by introducing it through the orifices in the bottom, initially under gravity and then driven by nitrogen. Once enough liquid to cover the entire surface of the sheets employed had been transferred to the

35

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vessel, the circulating pump and the plate-type heat exchanger were switched on. The liquid component C1 was heated to a temperature of 75°C in about 25 minutes. After 30 minutes, the assembly consisting of the vessel and the peripheral network had reached the thermal equilibrium as indicated by the numerous temperature probes placed at various points on the installation. Treatment was continued at this temperature for 16 hours, ensuring that the sheets were constantly immersed in the mass of circulating liquid (with the pump rotating at 2 500 rpm). During the treatment, a significant shifting of the ends of the fold lines could be seen visually through the portholes placed in the walls of the vessel and in the lid. At the end of treatment, the spent liquid composition C1 was cooled to a temperature about 30°C and discharged through the orifices in the bottom of the vessel to storage tanks.

7.2 – To treat the sheets with the liquid composition C2 (to aminate using TMA) and the liquid composition C3 (to rinse)

The grafted sheets resulting from step 7.1 were rinsed with 1 500 litres of ethanol and subsequently treated with 1 500 litres of the liquid composition C2 for 24 hours at ambient temperature. The liquid composition C2 was not circulated at all during this time. During treatment, a significant shifting of the ends of the fold lines could be seen visually through the portholes placed in the walls of the vessel and in the lid. At the end of the amination step, the vessel was emptied and the sheets were rinsed with 1 500 litres of the liquid composition C3. After 4 hours, the liquid composition C3 was discharged.

7.3 – To treat sheets with the liquid composition C4 (to dimensionally stabilize)

After grafting, aminating and rinsing, the sheets were immersed in the liquid composition C4. The liquid was heated to 60°C and circulated for 16 hours using the shuttle pump. During treatment, a significant shifting of the ends of the fold lines could be seen visually through the portholes placed in the walls of the vessel and in the lid.

8 – To recover the membranes and results of the evaluation tests

At the end of the dimensional stabilization step, the 85 sheets were extracted from the vessel, disconnected from the stretching means, removed from the support means and stored at ambient temperature in an aqueous solution containing 10 g/l of NaCl. Each sheet was then cut along its fold line, thus yielding a batch of 170 anionic membranes practically identical in shape and size. All the membranes of the batch were characterized by a width of 98 cm

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(± 0.5 cm) and a height of 116 cm (± 0.5 cm). These dimensions corresponded to a mean linear variation ($\Delta l/l$, $\times 100$ of about + 22.5% (l being the initial width of the sheets employed) and a mean linear variation ($\Delta h/h$) $\times 100$ of about + 22.1% (h being the initial height of the sheets employed). All the anionic membranes

5 were flat and exhibited no surface defect. The manufacturing batch was sampled selecting 8 membranes (M1-M8), two from the ends of the stack (M1, M8) and the other six about every 10 cm (M2-M7); 64 square test specimens with side lengths of 4 cm were taken to start with from each of these membranes (for a total of 512 test specimens); the test specimens were taken about 9 cm apart in

10 the width-wise direction and about 10 cm apart in the height-wise direction so as to cover the entire area of each membrane as uniformly as possible.

The exchange capacity (EC), water content (WC) and electrical resistance (ER) of the 512 test specimens were determined. The values thus obtained are given in Tables 1-3.

15

Table 1 Exchange capacity (EC) values

Membrane	Position in stack	EC mean (meq/g)	EC maximum (meq/g)	EC minimum (meq/g)	Standard deviation *
M1	Left-hand end	1.327	1.30	1.36	$2 \cdot 10^{-4}$
M2	About 10 cm from left-hand end	1.321	1.31	1.33	$9 \cdot 10^{-5}$
M3	About 20 cm from left-hand end	1.324	1.30	1.35	$3.2 \cdot 10^{-4}$
M4	About 30 cm from left-hand end	1.321	1.31	1.34	$2.0 \cdot 10^{-4}$
M5	About 40 cm from left-hand end	1.329	1.32	1.34	$8.0 \cdot 10^{-5}$
M6	About 50 cm from left-hand end	1.333	1.32	1.36	$2.2 \cdot 10^{-4}$
M7	About 60 cm from left-hand end	1.319	1.30	1.35	$1.7 \cdot 10^{-4}$
M8	Right-hand end	1.316	1.31	1.33	$3.7 \cdot 10^{-5}$

* Standard deviation = $[\sum x^2 - (\sum x)^2 / n] / [n(n-1)]$, x = EC values

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Table 2 Water content (WC) values

Membrane	Position in stack	WC mean (%)	WC maximum (%)	WC minimum (%)	Standard deviation *
M1	Left-hand end	20.3	17.6	23.1	3.16
M2	About 10 cm from left-hand end	-	-	-	-
M3	About 20 cm from left-hand end	-	-	-	-
M4	About 30 cm from left-hand end	20.3	17.9	22.9	3.13
M5	About 40 cm from left-hand end	-	-	-	-
M6	About 50 cm from left-hand end	20.7	18.4	22.5	1.24
M7	About 60 cm from left-hand end	-	-	-	-
M8	Right-hand end	20.3	17.8	22.5	3.11

* Standard deviation = $[\frac{n\sum x^2 - (\sum x)^2}{n(n-1)}]^{1/2}$, x = WC values

Table 3 Electrical resistance (ER) values

Membrane	Position in stack	ER mean (Ohm.cm ²)	ER maximum (Ohm.cm ²)	ER minimum (Ohm.cm ²)	Standard deviation*
M1	Left-hand end	4.39	4.1	5.0	5.2 10 ⁻²
M2	About 10 cm from left-hand end	4.40	4.2	4.9	4.0 10 ⁻²
M3	About 20 cm from left-hand end	4.39	4.2	4.8	3.5 10 ⁻²
M4	About 30 cm from left-hand end	4.45	4.2	4.8	2.7 10 ⁻²
M5	About 40 cm from left-hand end	4.44	4.2	5.0	3.6 10 ⁻²
M6	About 50 cm from left-hand end	4.42	4.0	4.9	4.3 10 ⁻²
M7	About 60 cm from left-hand end	4.42	4.0	4.7	3.0 10 ⁻²
M8	Right-hand end	4.45	4.2	4.8	2.9 10 ⁻²

* Standard deviation = $[\frac{n\sum x^2 - (\sum x)^2}{n(n-1)}]^{1/2}$, x = ER values

5 These EC, ER and WC values demonstrate the extreme uniformity from an electrochemical standpoint of each membrane and of the manufacturing batch overall.

- 25 -

CLAIMS

1. Method for treating a film with a composition, whereby the film is folded along a fold line dividing the film into two parts of substantially equal weight, a support bar is positioned under the fold line to allow the film to be
5 suspended and the bar is placed in a vessel containing the composition so as to bring the film into contact with the composition.
2. Method according to the preceding claim, characterized in that a separator grid is placed between the aforesaid two parts of the film.
3. Method according to the preceding claim, characterized in that several
10 folded films, each suspended from a support bar, are positioned side by side in the vessel and grid inserts are also positioned between the adjacent films.
4. Method according to the preceding claim, characterized in that the support bars used to suspend adjacent films are positioned in the vessel alternately at different heights.
- 15 5. Method according to any one of the preceding claims, characterized in that stretching means are applied to the fold line of the film to prevent the film from being in compression near the suspension means during treatment.
6. Method according to the preceding claim, characterized in that the stretching means comprise a mass the weight of which is transmitted by a
20 filament to one of the ends of the fold line.
7. Method according to Claims 5 or 6, characterized in that the stretching means are applied in such a way that the stretching force exerted on one of the ends of the fold line has no component orthogonal to the direction of the support bar.
- 25 8. Method according to any one of the preceding claims, characterized in that the film comprises at least one plastic.
9. Method according to any one of the preceding claims, characterized in that it is aimed at manufacturing an ionic membrane precursor and/or an ionic membrane.

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10. Method according to the preceding claim, characterized in that the treatment is a chemical or radiochemical grafting, cross-linking, functionalization and/or hydrolysis treatment.

5 11. Device for treating films with a composition comprising a vessel to contain the composition, support bars for suspending folded films, support bars for supporting grids, bar-support means, and stretching means to stretch the ends of the fold lines of the films.

10 12. Device according to the preceding claim further comprising a heat exchanger and/or a circulating pump which are connected to the vessel by a looped network of pipes.

13. Device according to Claims 11 or 12, characterized in that the vessel comprises transparent portholes so that the ends of the fold lines of the films in particular can be seen.

15 14. Device according to any one of Claims 11 to 13, characterized in that the vessel is of parallelepipedal shape and comprises orifices situated near its upper edge and orifices situated on the bottom, the said orifices being intended, amongst other things, to allow the composition to be loaded, unloaded and/or circulated during treatment.

20 15. Device according to the preceding claim, characterized in that the orifices situated near the upper edge of the vessel are used to supply the liquid composition while the orifices situated on the bottom are used to remove the said composition.

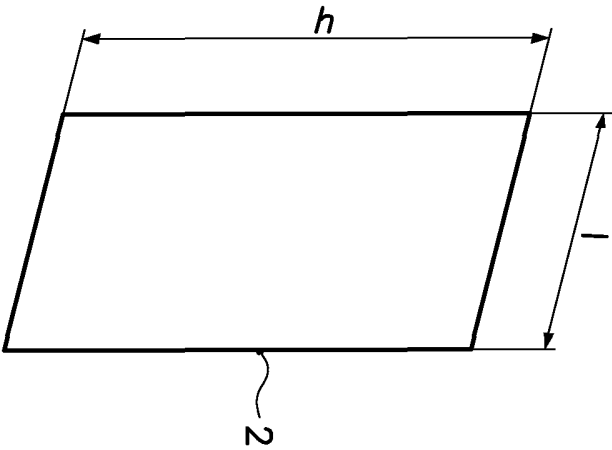
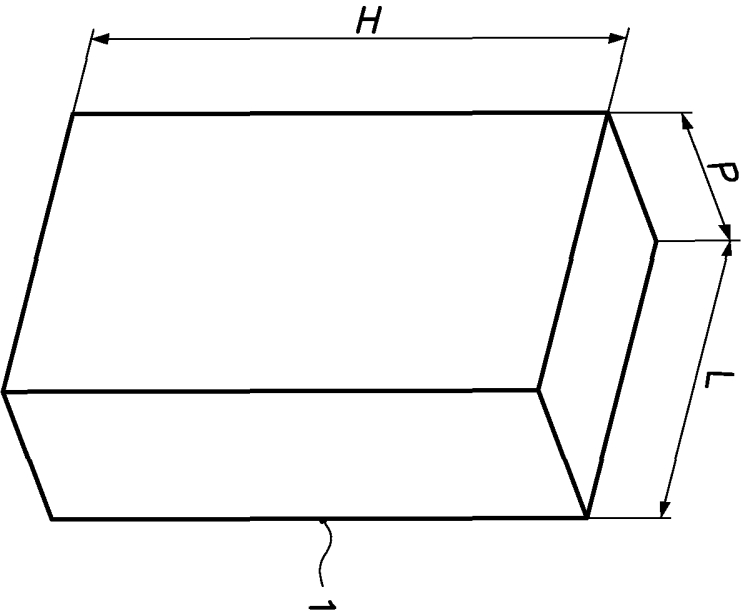


Fig. 1

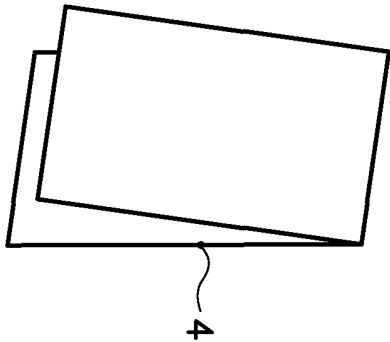
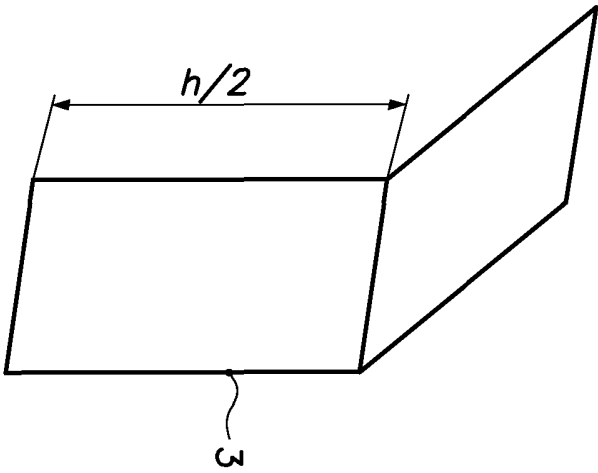
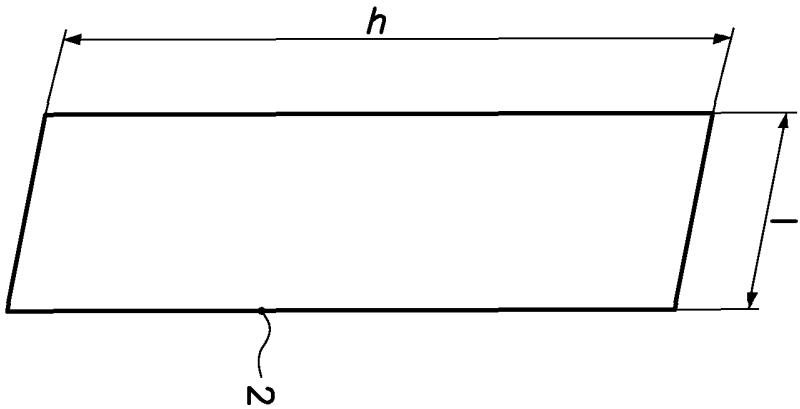


Fig. 2

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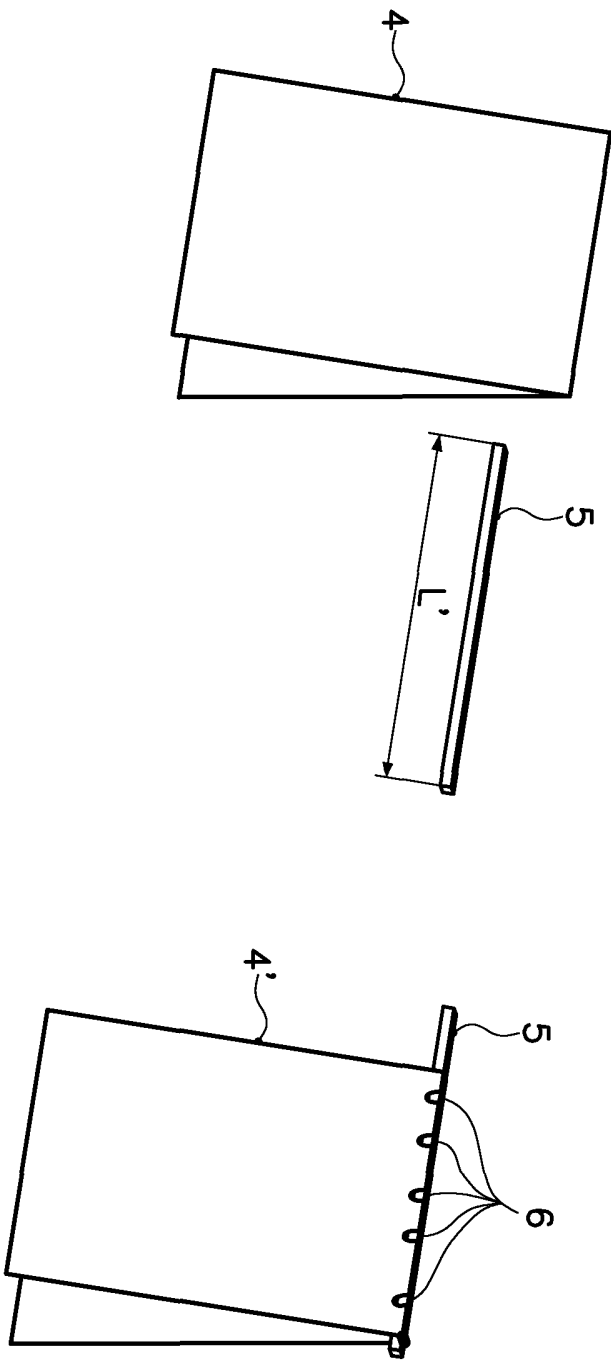


Fig. 3

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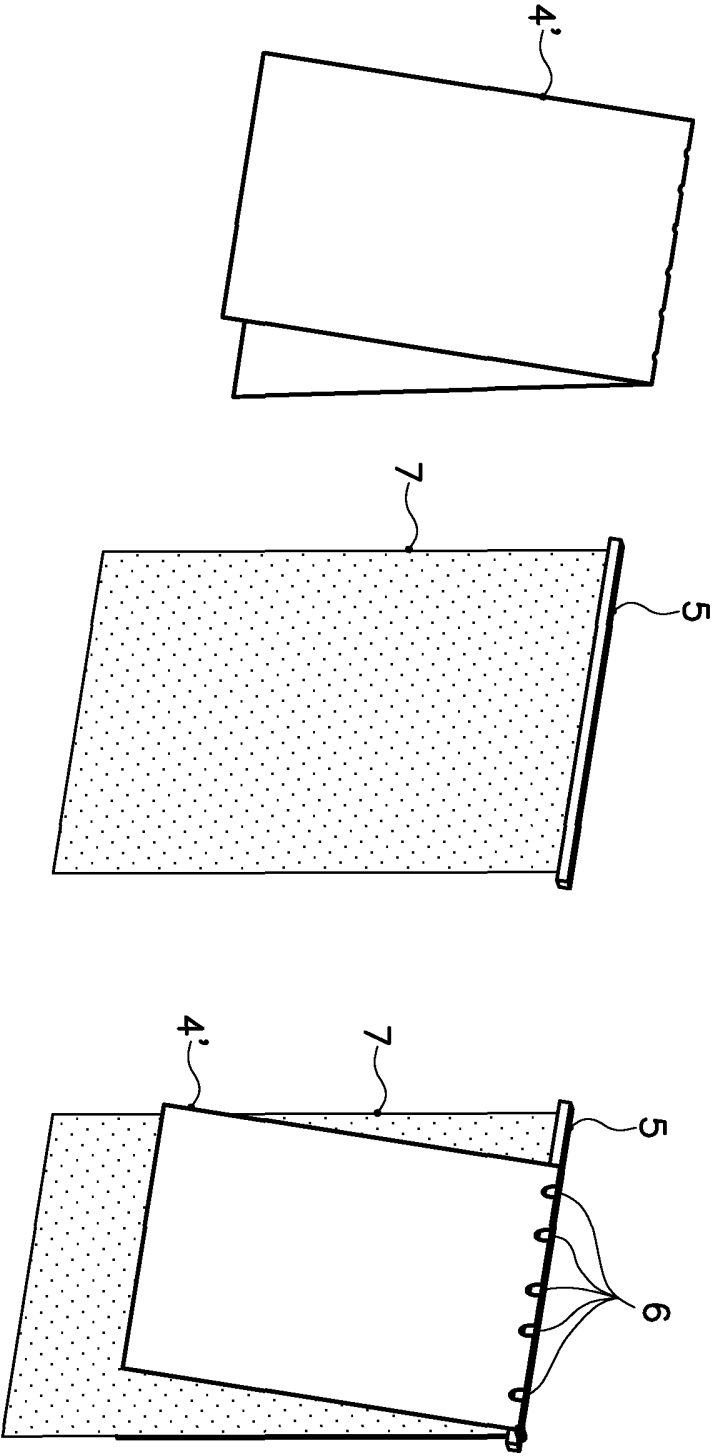


Fig. 4

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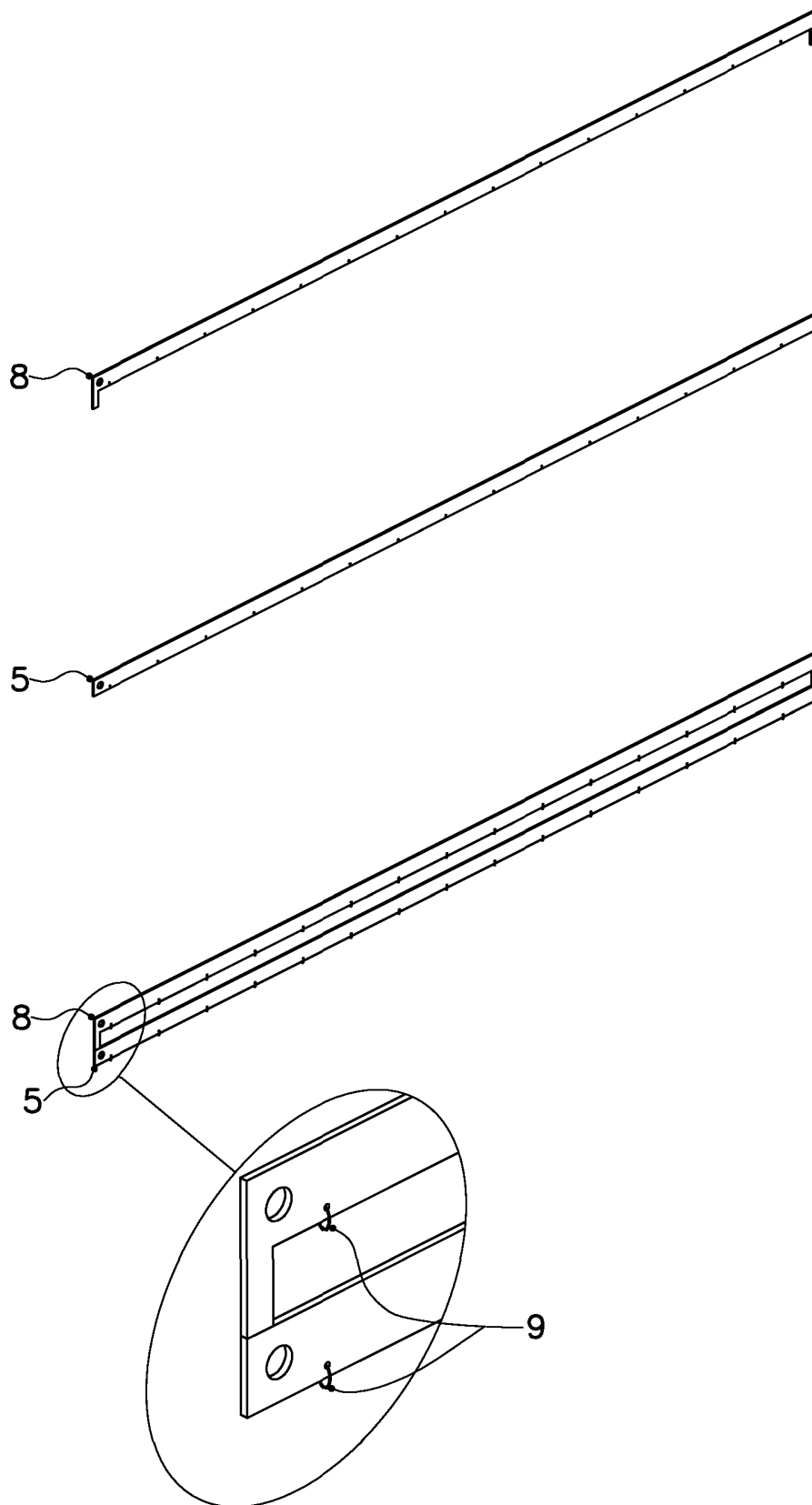


Fig. 5

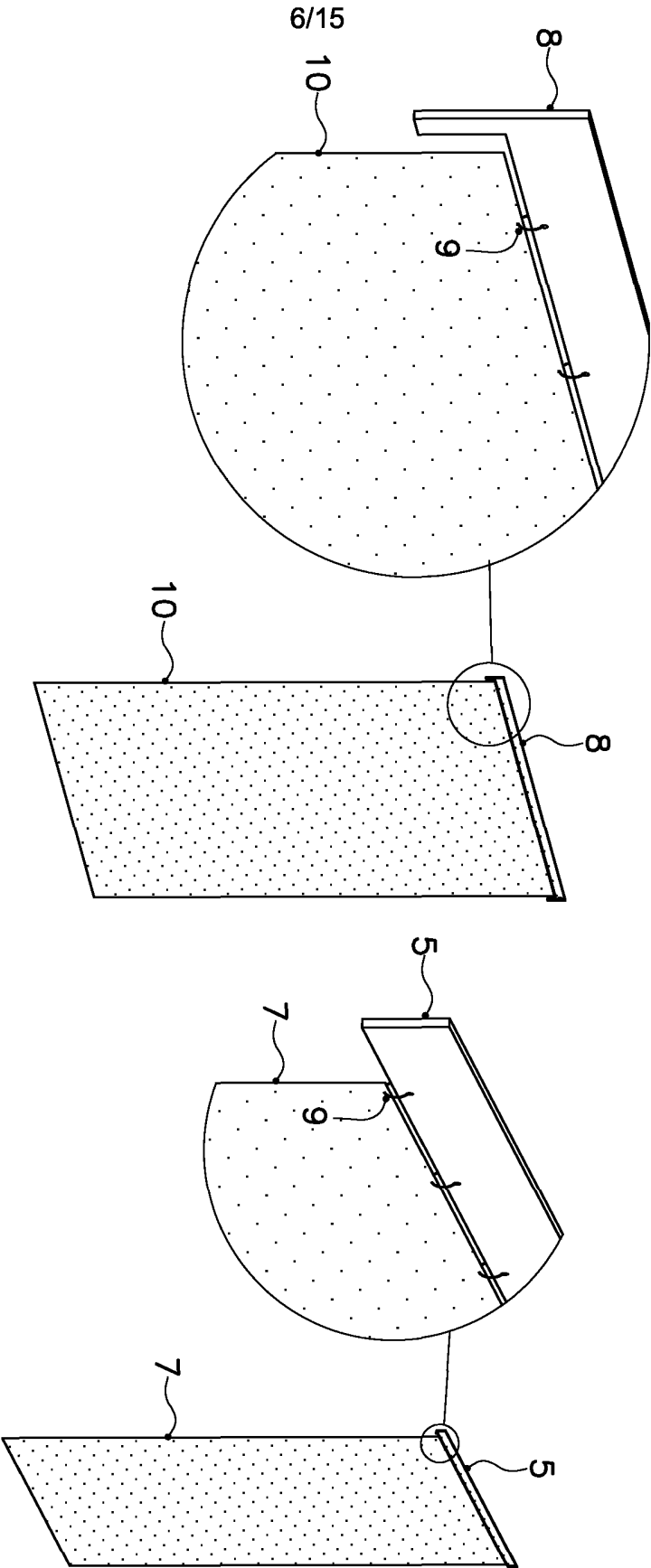


Fig. 6

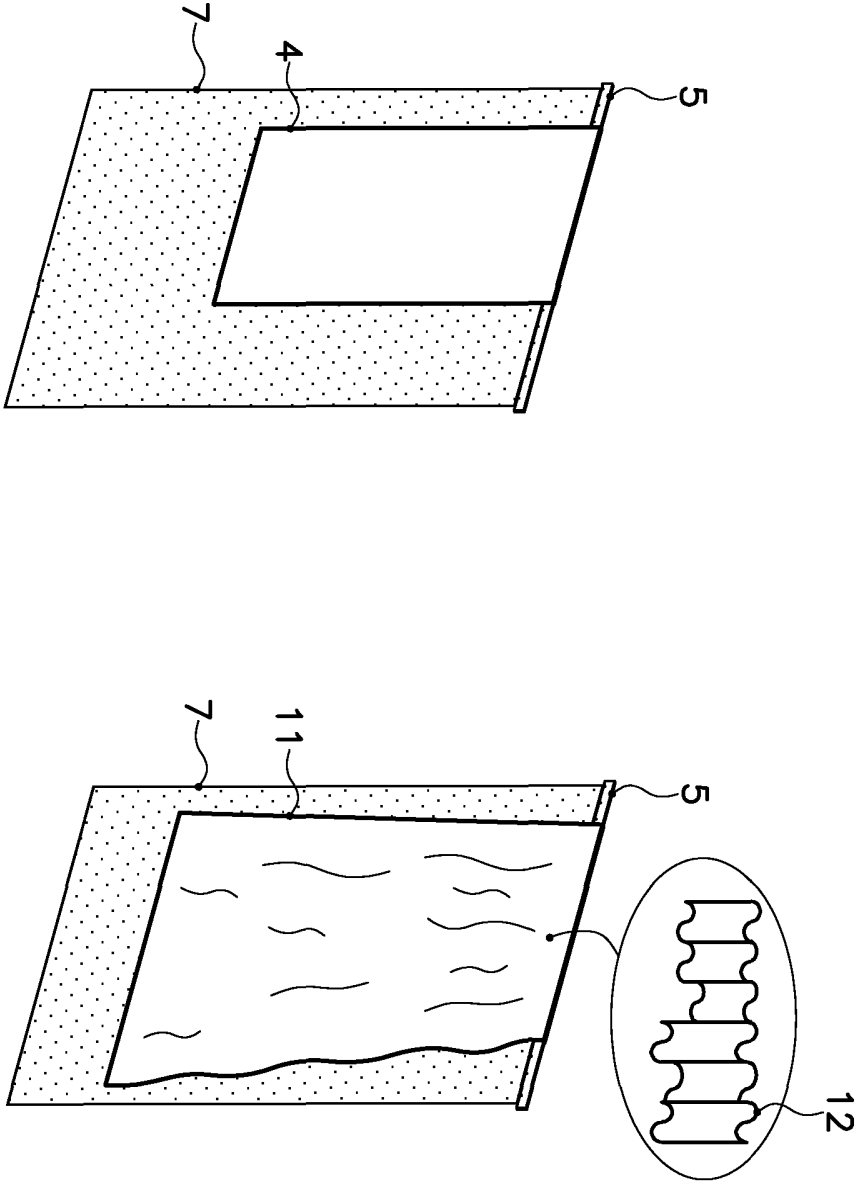


Fig. 7

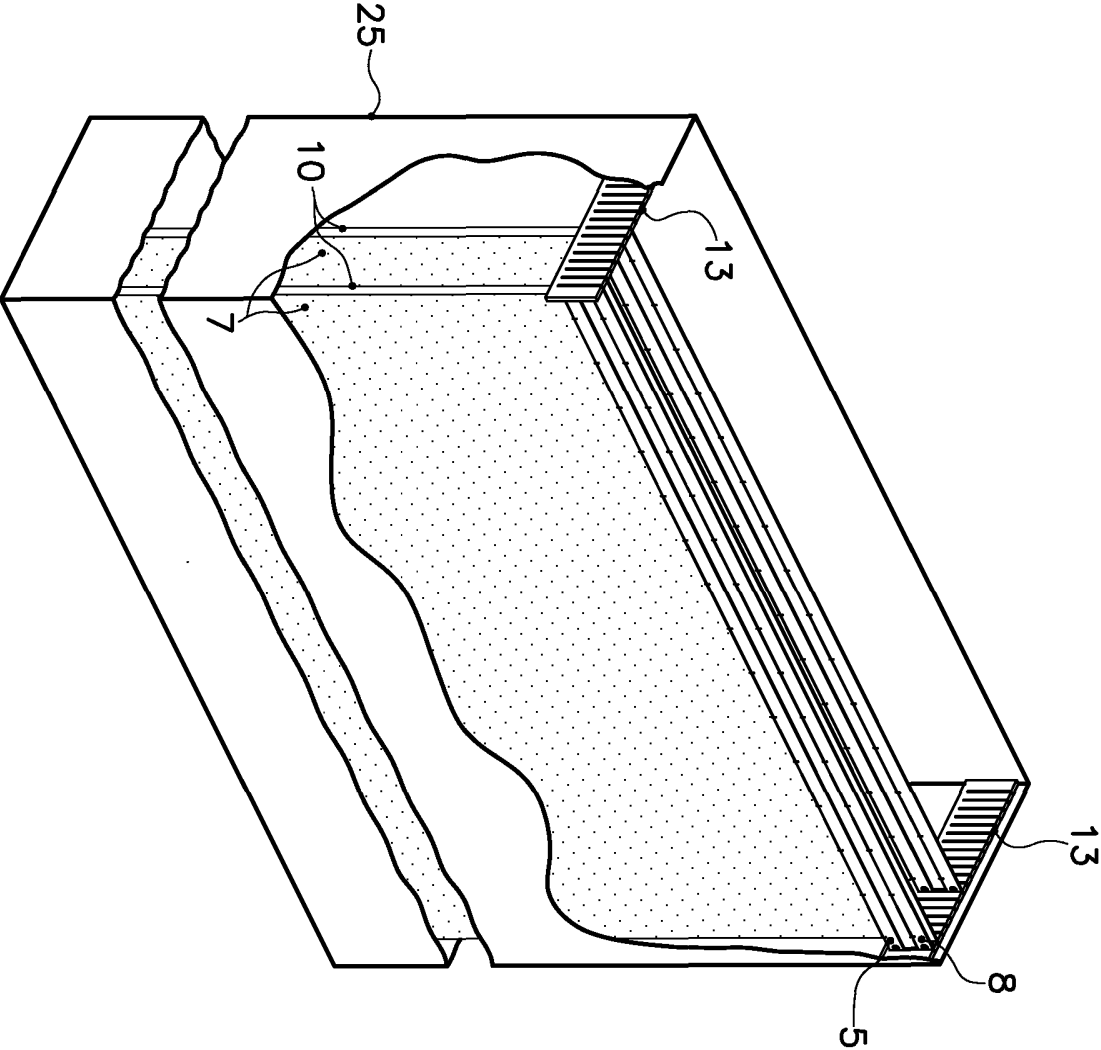


Fig. 8

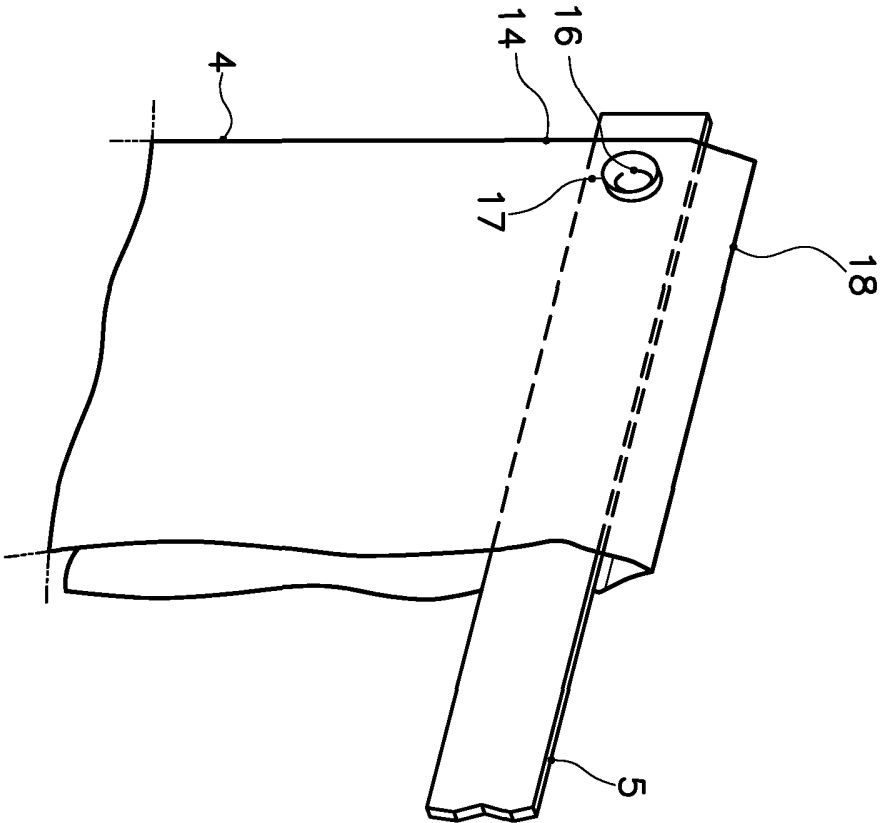


Fig. 10

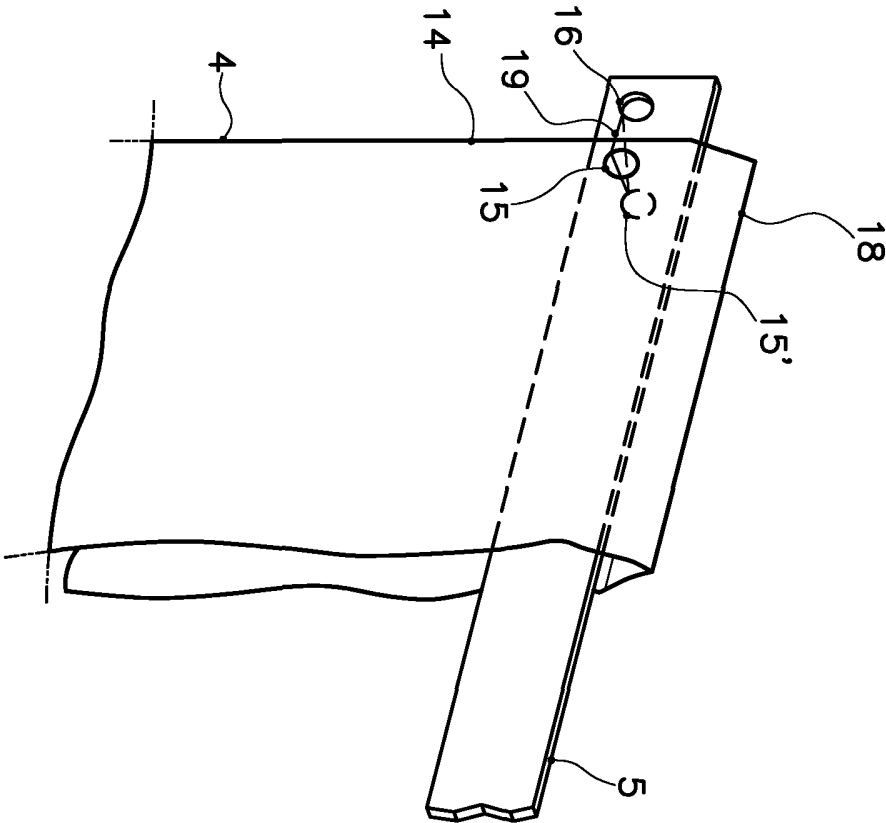


Fig. 11

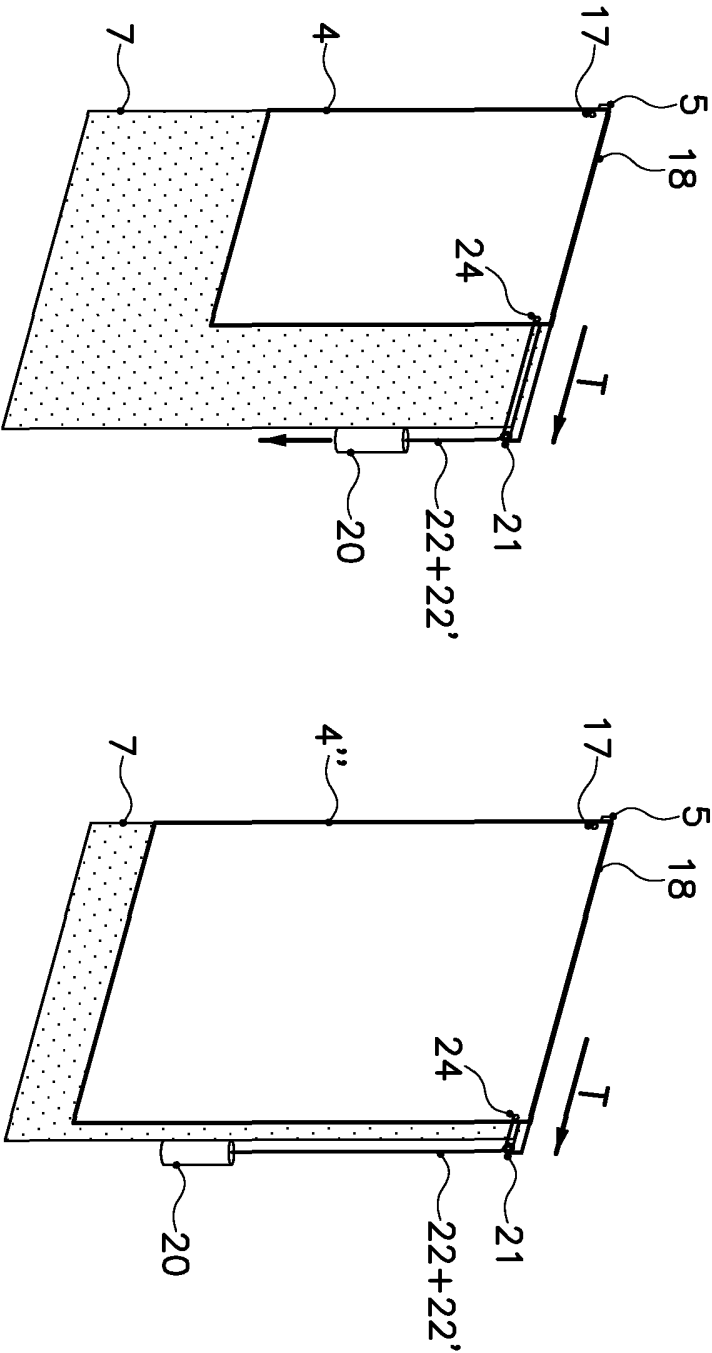


Fig. 13

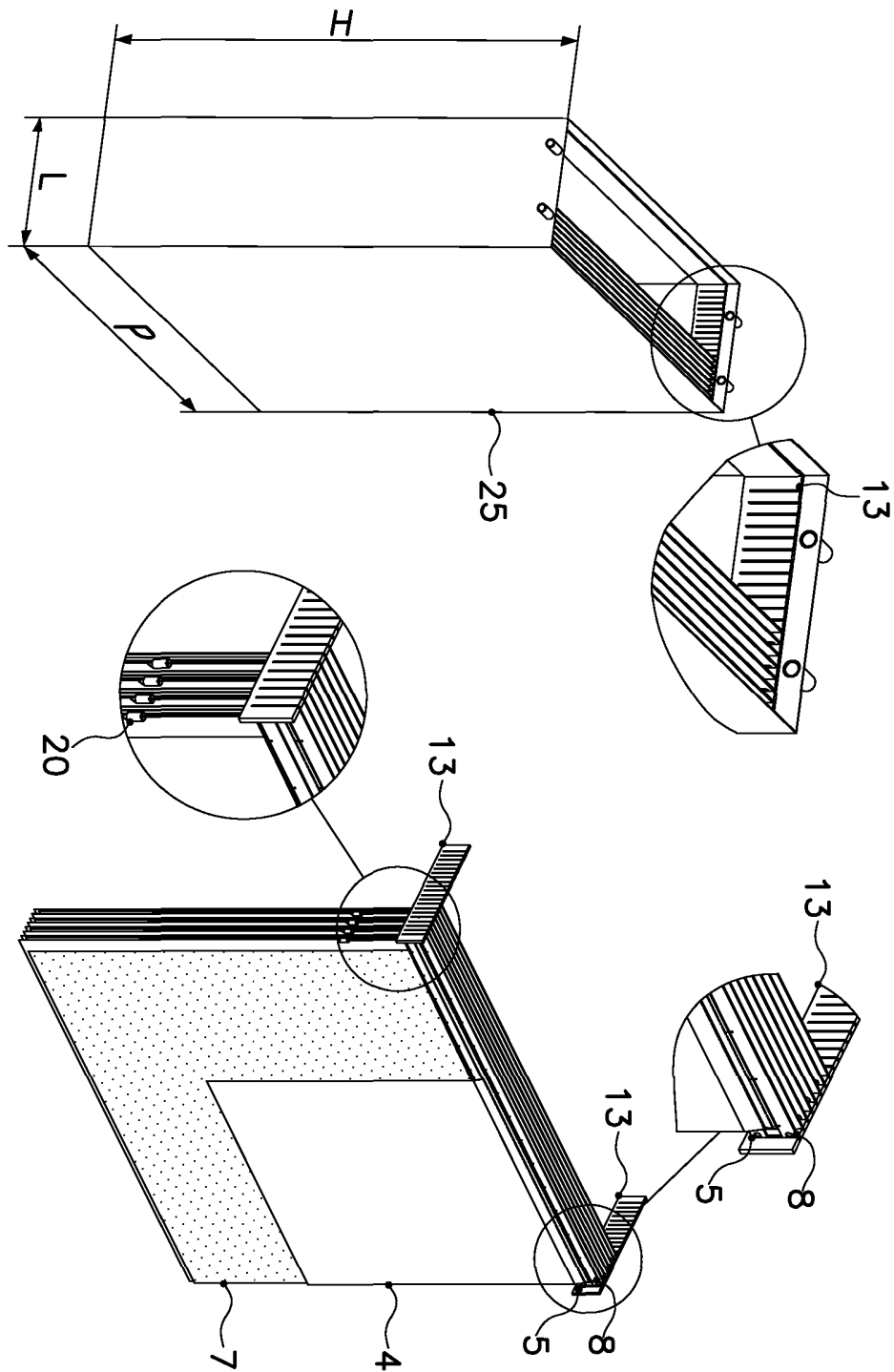


Fig. 15