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(54) **NON-STICK PHOTORESIST LAMINATE**

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Related U.S. Patent Documents

Reissue of:

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(52) **U.S. Cl. 430/273.1; 430/271.1**
(58) **Field of Search 430/273.1, 271.1**

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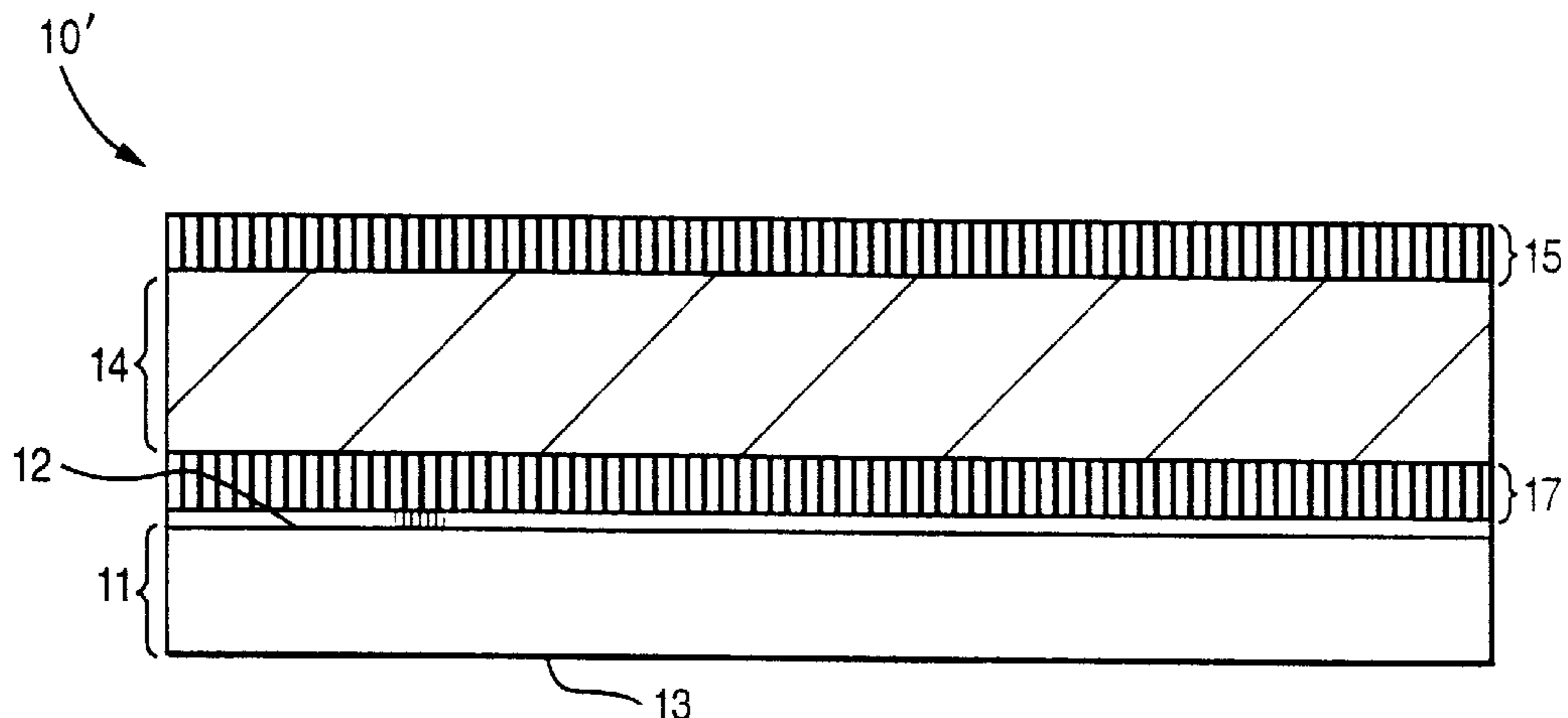
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(57) **ABSTRACT**

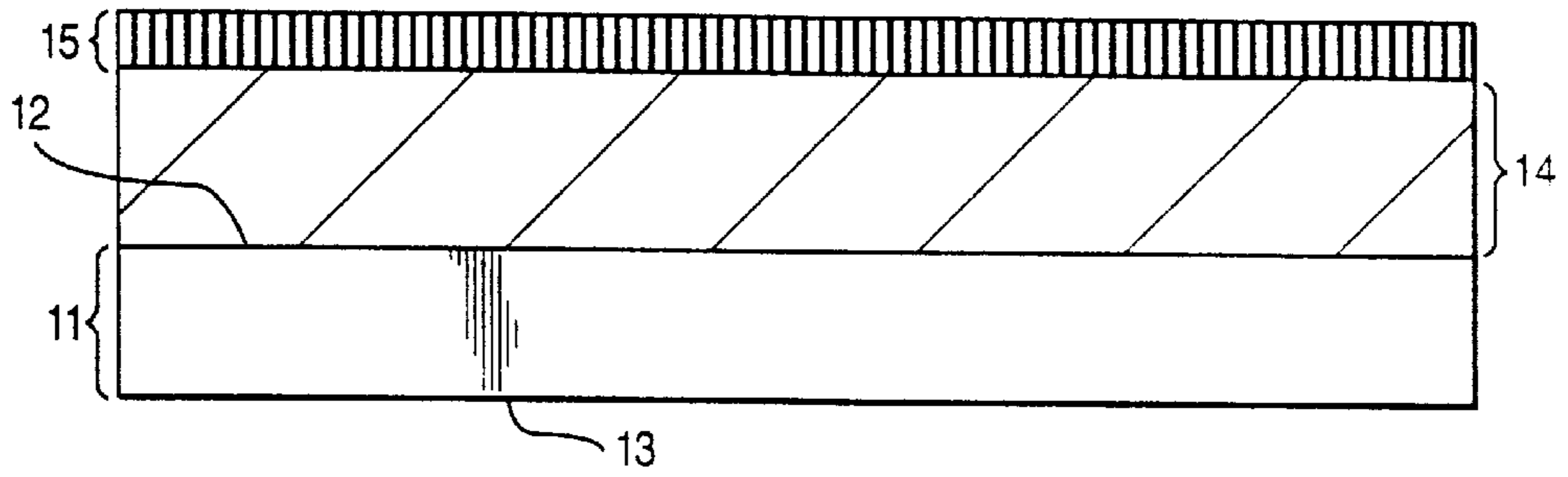
A photoresist laminate includes a substrate (such as PET film having a thickness of between about 0.002–0.003 inches) with first and second faces, a first film layer, and a second layer. The first film layer is a photoresist material (radiation sensitive) which is soluble or dispersible in water but which will harden upon sufficient exposure to radiation so as to become substantially insoluble or non-dispersible. The first film layer may be of any conventional photoresist material (e.g. having a thickness of about 0.002–0.009 inches) and is operatively disposed on the substrate first face (either directly connecting it or connected to a membrane support layer which in turn is directly connected to the substrate first face). The second layer is of a material and thickness so that it substantially prevents sticking of the first film layer to other surfaces, while not significantly interfering with the radiation sensitivity thereof. The second layer is on the opposite side of the first film layer from the substrate, and may comprise a mixture of polyvinyl alcohol solution and polyvinyl acetate emulsion, having a thickness of less than 0.0005 inches (e.g. about 0.0001–0.0002 inches). The laminate is used in a method of making a stencil for abrading or etching by exposing the laminate to radiation, processing a laminate by spraying water on the laminate to remove the soluble or dispersible portion, and then using the stencil so formed as a mask on the surface of an object to etch or abrade the surface.

4 Claims, 1 Drawing Sheet



10

Fig. 1



10'

Fig. 2

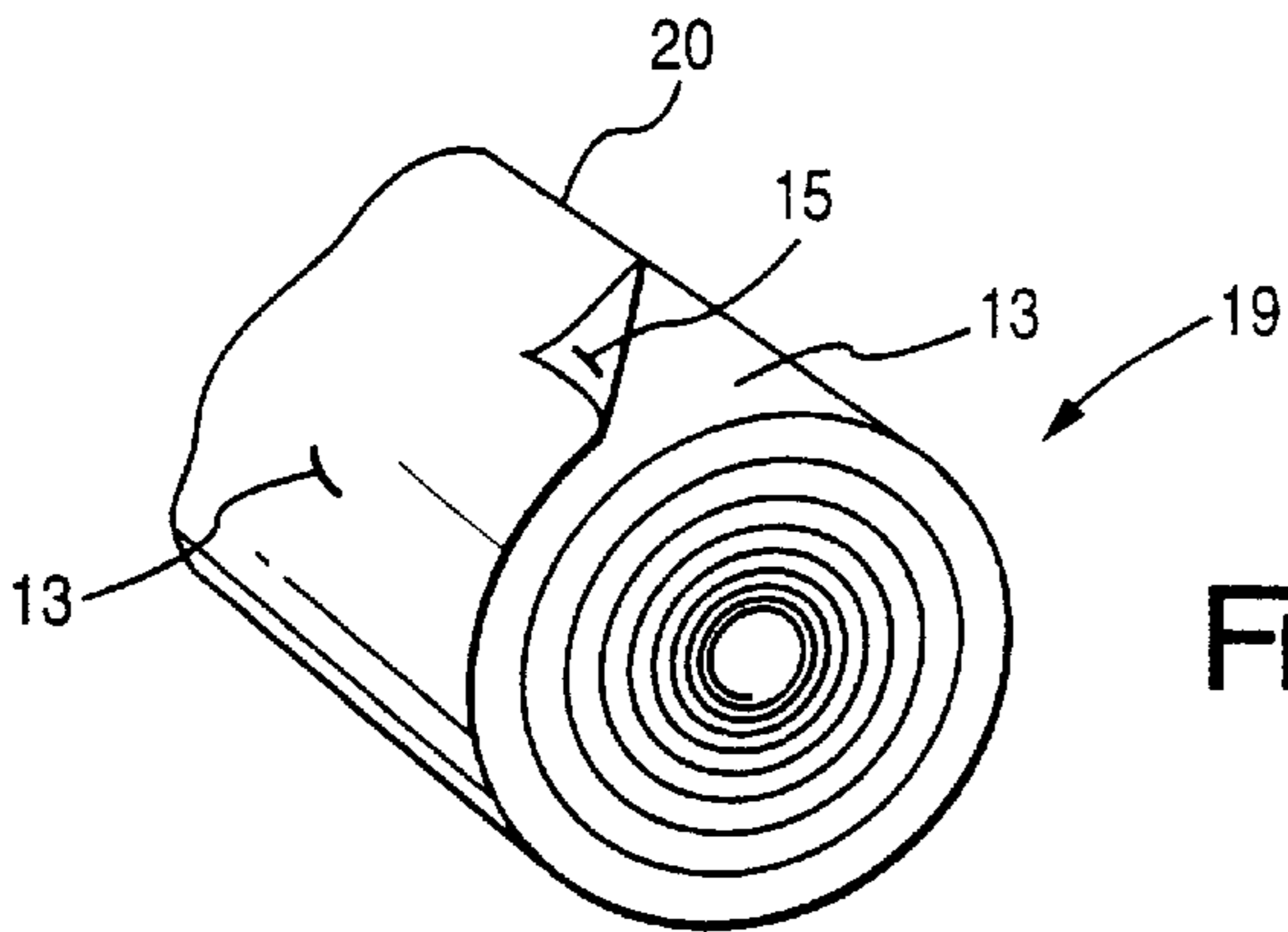
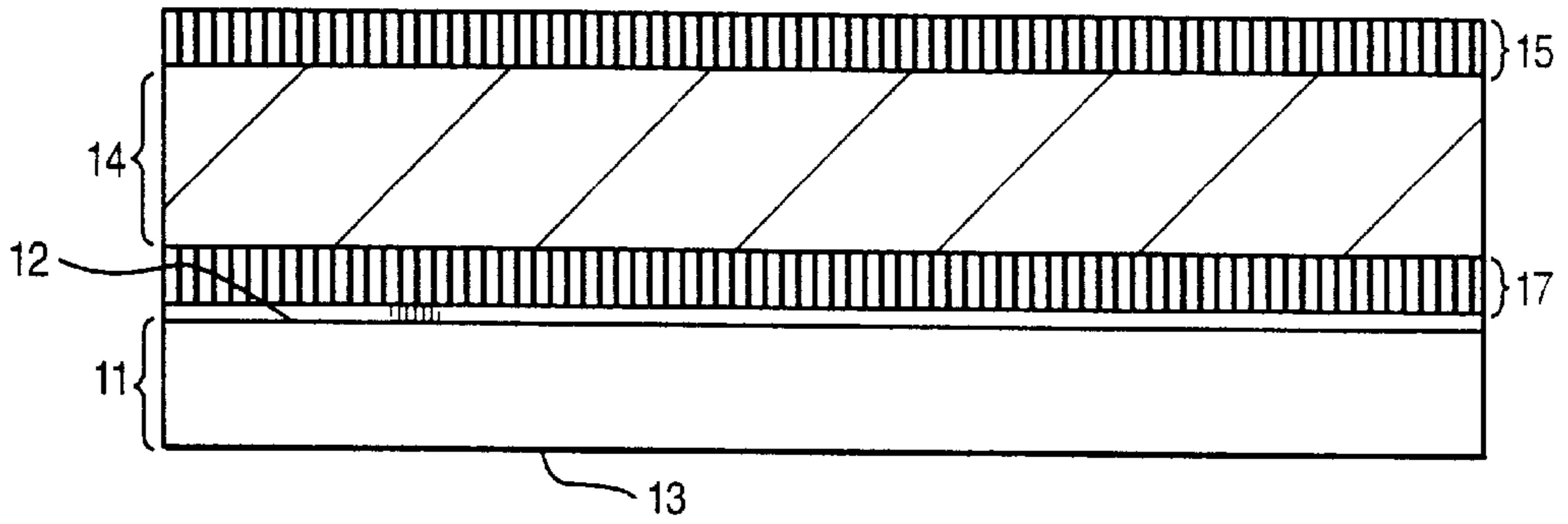
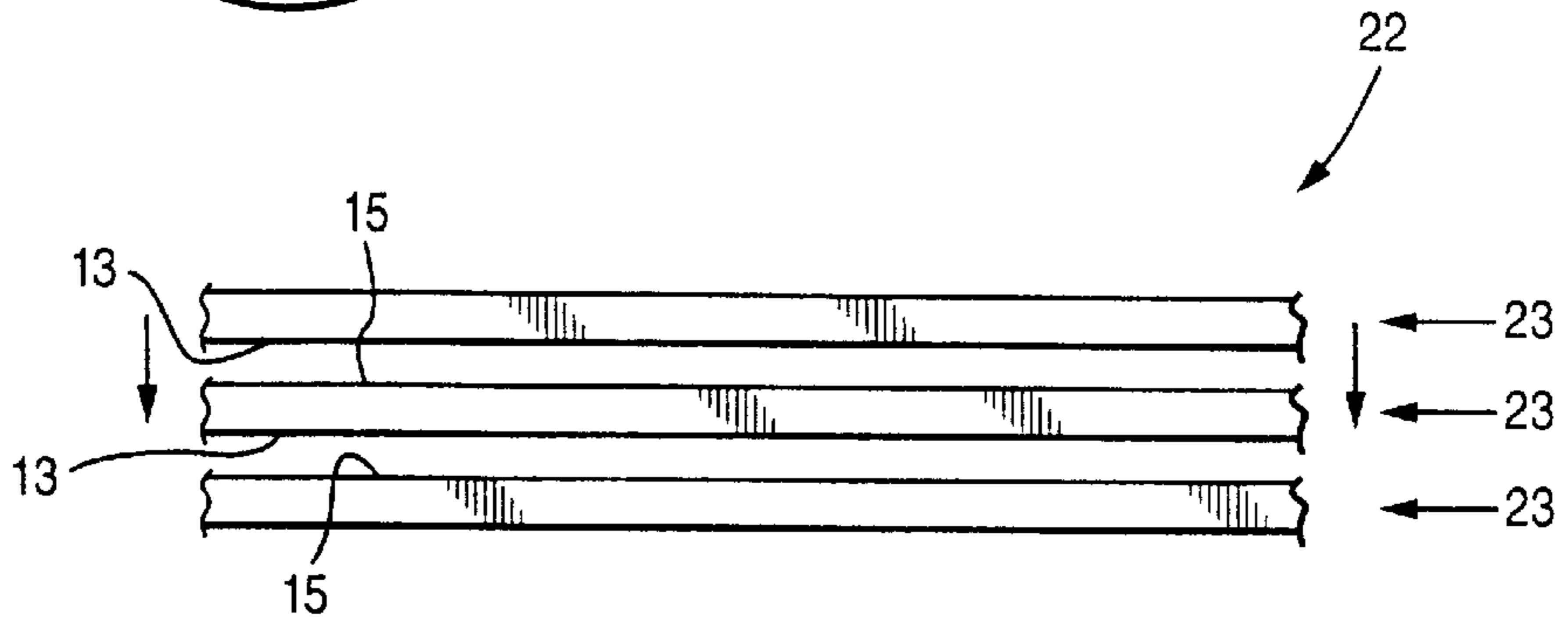


Fig. 3

Fig. 4



NON-STICK PHOTORESIST LAMINATE

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

BACKGROUND AND SUMMARY OF THE INVENTION

Products that have decorative patterns formed on the surface of the products by abrasion (typically sandblasting) or etching are becoming increasingly more popular. A wide variety of techniques have been developed to effectively produce masks to facilitate accurate production of such objects, such as shown in U.S. Pat. Nos. 5,370,762, 4,764,449, and 5,427,890 (the disclosures of which are hereby incorporated by reference herein), and various automated equipment has been developed to facilitate processing during production of such masks (such as shown in U.S. Pat. No. 5,366,584). The basic processes utilize a photoresist laminate which may have a variety of constructions, but includes a substrate and an outer layer of photoresist material (radiation sensitive material which is soluble or dispersible in water but will harden upon sufficient exposure to radiation so as to become substantially insoluble or non-dispersible) facing outwardly from the substrate. The photoresist laminate is typically provided in roll form where the radiation sensitive material of one part of the roll contacts a substrate on another part of the roll; or the laminate may be provided in sheet form with one sheet stacked upon another with the radiation sensitive material of one sheet contacting the substrate of another. Under some circumstances, especially where there is high humidity or products have been maintained in a roll or stacked configuration for a long period of time, a problem of sticking may occur. That is, the photoresist material sticks to the substrate of an engaged part of the roll, or of another sheet. This can be a significant problem since sticking may cause the photoresist material to be removed or separated from the substrate, and make it unusable for its intended purpose.

Another problem can occur when the photoresist is exposed to UV radiation. The pattern that creates the latent image is printed on a paper vellum or plastic film. This pattern is pressed onto the surface of the photoresist during its exposure to radiation. A sticky photoresist material can cause paper vellums to tear or pull off the ink that creates the pattern. The sticking can also cause delamination between the photoresist and the substrate film when the vellum is removed.

In order to overcome this problem, various types of substrates have been attempted to be utilized, with less than optimum success in preventing or minimizing the sticking problem. Also providing a release liner on top of the radiation sensitive material (photoresist material) which is removed prior to use significantly increases the costs of the laminate, makes the laminate bulkier to ship, and introduces another step for the utilization thereof.

According to the present invention a photoresist laminate, a stencil made therefrom and a method of utilization thereof for abrading or etching, are provided which substantially eliminate or minimize the sticking problem in a simple and effective manner, without significantly increasing the cost of the laminate, and without introducing another step for utilization thereof. According to the present invention, during manufacture the radiation sensitive material is provided with a very thin coating which is readily removed during

processing, and does not significantly interfere with the radiation sensitivity of the photoresist material, yet it substantially prevents sticking of the photoresist material to a substrate of an adjacent portion of the laminate in a roll, or of another sheet in the stack, or even to other materials that the photoresist material may inadvertently come into contact with.

According to one aspect of the present invention a photoresist resist laminate is provided comprising the following components: A substrate having first and second faces. A first film layer of radiation sensitive material which is soluble or dispersible in water but will harden upon sufficient exposure to radiation so as to become substantially insoluble or non-dispersible, and operatively disposed on the substrate first face. And a second layer of a material and thickness so that it substantially prevents or minimizes sticking of the first film layer while not significantly interfering with the radiation sensitivity thereof. The second layer is on the opposite side of the first film layer from the substrate.

The photoresist laminate may comprise other layers and constructions. For example, a membrane support layer may be provided between the substrate and the first film layer and engaging both the substrate and the first film layer. Also, or alternatively, the first film layer may comprise two clearly different colored portions, one atop the other, specifically as described in said copending application Ser. No. 09/137,702; and the laminate may consist of the recited elements above.

Typically, the second layer has a maximum thickness of about 0.0005 inches, e.g. about 0.0003 inches, and most desirably between 0.0001–0.0002 inches. While any material suitable for performing the non-stick, yet not interfering with the radiation sensitivity, functions may be provided, one particularly desirable material for forming the second film layer comprises a mixture of polyvinyl alcohol solution and polyvinyl acetate emulsion. The range may be 2–98% by weight of one and 98–2% of the other. If a water soluble formula is desired so as to facilitate wash-away of the second layer during processing, preferably about 80%–98% by weight polyvinyl alcohol solution with the remainder polyvinyl acetate solution (and perhaps some inert materials is provided). If a substantially water insoluble formulation is desired it comprises about 80–98% by weight polyvinyl acetate solution with the remainder polyvinyl alcohol solution (and perhaps inert ingredients).

The second layer may be applied in a conventional coating process (e.g. direct roll coating) after the rest of the laminate has been formed, or may be provided by spraying a fine spray of the second layer material on the first layer, to form a fine film, using conventional aerosol equipment.

A variety of thicknesses and materials may be utilized. For example the first film layer may have a thickness of between about 0.002–0.009 inches may be a conventional photoresist material such as described in said copending application Ser. No. 09/137,702, or a positive or a negative acting film such as described in U.S. Pat. No. 4,764,449, or of any other conventional construction such as shown in U.S. Pat. No. 5,427,890. The substrate typically has a thickness of about 0.002–0.003 inches and may comprise PET film, or Mylar® polyester film (e.g. type S-200 gauge), or any other conventional substrate. The membrane support layer, when utilized, may have a thickness of between 3–5 microns and also may comprise any suitable conventional material. Other layers are also possible depending upon the particular use or circumstances, again such as described in U.S. Pat. No. 4,764,449.

The laminate may be in a roll form with the second layer contacting the second face of the substrate in a substantially non-stick manner. Alternatively, the laminate may be in sheet form, and stacked with other substantially identical laminates so that the second layer of one sheet engages the second face of the substrate of another sheet.

The laminate as described above preferably is utilized in a method of making a stencil and ultimately an etched or abraded object, such as described in either the inventive or background portions of copending application Ser. No. 09/173,702. For example, by utilizing the laminate as described above a method of making a stencil for abrading or etching using a negative acting or positive acting photoresist laminate as described above, is provided comprising:

- (a) Exposing the laminate and a pattern to radiation to cause hardening of some portions to define the pattern as a latent image in the photoresist first film layer by providing some portions that are soluble or dispersible in water, and other portions that are substantially insoluble or non-dispersible
- (b) Processing the laminate from (a) by spraying water on the laminate to remove the soluble or dispersible portions of the first layer, and at least those portions of the second layer covering the soluble or dispersible portions of the first layer, but not the substantially insoluble or non-dispersible patterns of the first layer to ultimately produce a stencil. And
- (c) using the stencil from (b) as a mask on the surface of an object to etch or abrade the surface of the object where the photoresist film has been removed to form a surface texture in the object that stimulates the latent image.

Where the first layer comprises first and second clearly different colored portions, one atop of the other, then (b) is practiced to first remove substantially all of the soluble or dispersible portions of the first color, and only then to carefully start to remove the soluble or dispersible portions of the second color. The invention also relates to a stencil produced by practicing (a) and (b) of the method as described above.

It is the primary object of the present invention to provide a photoresist laminate which substantially eliminates or minimizes the sticking problem present in conventional photoresist laminates, in a simple and cost effective manner, which does not require changes in the method of utilization thereof to produce a stencil for masking and ultimately producing an etched or abraded object. This and other objects of the invention will become clear from an inspection of the detailed description of the invention and from the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side enlarged cross sectional view, with the relative thicknesses of the components exaggerated for clarity of illustration, of one embodiment of a photoresist laminate according to the present invention;

FIG. 2 is a view like that of FIG. 1 for another embodiment of a laminate according to the present invention;

FIG. 3 is a schematic perspective view of the laminate of the FIGS. 1 and 2 in a roll configuration; and

FIG. 4 is a schematic side exploded view of the laminate of FIGS. 1 and 2 during stacking, wherein one sheet of laminate will be brought into contact with another in a stack.

DETAILED DESCRIPTION OF THE DRAWINGS

One embodiment of an exemplary photoresist laminate provided according to the present invention is illustrated generally at **10** in FIG. 1. It includes a substrate **11** having

a first face **12** and a second face **13**. The substrate (also often referred to as a support carrier) **11** may be of any suitable material and any suitable thickness. For example, the substrate **11** may comprise PET film of a thickness of between about 0.002–0.003 inches. Other materials that may be utilized include BOPP, and Mylar® polyester film (such as type S-200 gauge available from du Pont) with either a clear unmatted surface or a matte surface, etc.

The laminate **10** further comprises a first film layer **14**. The layer **14** may comprise a plurality of layers made by coating first one layer and then another, or may comprise a single layer. Regardless of how the film layer **14** is constructed, it preferably typically has a thickness of between about 0.002–0.009 inches, and is a photoresist material, that is, it is a radiation sensitive (either positive or negative acting) material which is soluble or dispersible in water but will harden upon sufficient exposure to radiation (e.g. UV) so as to become substantially insoluble or non-dispersible. The first film layer **14** is provided so that it is operatively disposed on the first face **12** of the substrate **11**. By “operatively disposed” is meant that either the first film layer **14** actually contacts and is adhered to the first face **12**, or there are one or more intermediate layers which provide effective attachment of the first film layer **14** to the first face **12**. The radiation sensitive material forming the first film layer **14** may comprise any suitable conventional material which performs a function such as disclosed in U.S. application Ser. No. 09/137,702, U.S. Pat. No. 4,674,449, or U.S. Pat. No. 5,427,890.

According to the invention, the laminate **10** also comprises a second layer **15** of a material and thickness so that it substantially prevents sticking of the first film layer **14** while not significantly interfering with the radiation sensitivity thereof. The second layer **15** is adhered to the first film layer **14** during use. If a water soluble formula is used, the second layer **15** is adhered to the first film layer **14** until the washout process that occurs after radiation exposure. During washout, layer **15** is dissolved away. If a water insoluble formula is used then layer **15** prematurely remains in contact to layer **14**. Since layer **15** is the layer that will be glued to the article being blasted, it never is contacted with the etching abrasive and therefore will not disintegrate during use.

Typically the second layer **15** has a maximum thickness of about 0.0003 inches, depending upon the material of which it is made. While any material may be utilized for the second layer **15** that substantially prevents or minimizes sticking of the first film layer **14** to any other object or material (such as to the second face **13** of the substrate **11** of another laminate **10**, or another portion of the laminate **10**) while not significantly interfering with the radiation sensitivity of the first film layer **14**, one particularly suitable material that may be utilized as the second layer **15** is a mixture of polyvinyl alcohol solution and polyvinyl acetate emulsion. The range may be 2–98% by weight of one and 98–2% of the other. If a water soluble formula is desired so as to facilitate washaway of the second layer during processing, preferably about 80%–98% by weight polyvinyl alcohol solution with the remainder polyvinyl acetate solution (and perhaps some inert materials is provided). If a substantially water insoluble formulation is desired it comprises about 80–98% by weight polyvinyl acetate solution with the remainder polyvinyl alcohol solution (and perhaps inert ingredients). One particular polyvinyl alcohol solution that may be utilized is AIRVOL 540, and one particular polyvinyl acetate emulsion is VINAC XX-240, both available from Air Products and Chemicals, Inc.

The second layer **15** is typically applied with a thickness of between about 0.0001–0.0002 inches, and may be applied by any conventional technique such as utilizing conventional direct roll coating processes, spraying, or the like. Because the second layer **15** is so thin, and is substantially radiation transparent, it cost effectively substantially eliminates or minimizes the sticking problem while not introducing another step for the utilization of the laminate **10**, and while allowing normal utilization thereof to etch or abrade an object.

The laminate **10** may consist essentially of the substrate **11**, first film layer **14**, and second layer **15** or may comprise a wide variety of other layers for performing different functions. Another embodiment which includes an additional layer is illustrated schematically at **10'** in FIG. 2. In FIG. 2 components comparable to those in FIG. 1 are shown by the same reference numeral.

In FIG. 2, the laminate **10'** is shown with a membrane support layer **17**, for example having a thickness of between about 3–5 microns and of any suitable material which would adhere to both the first surface **12** of the substrate **11** and the first film layer **14**, is provided to operatively adhere the first film layer **14** to the substrate **11**. The laminate **10'** may consist essentially of the elements **1**, **17**, **14**, and **15**, or may comprise still further layers.

The laminate **10**, **10'** is illustrated schematically at **19** in FIG. 3 in roll form, with a corner of the leading edge **20** of the roll **19** curled back so as to clearly illustrate that the second layer **15** of one portion of the laminate **10**, **10'**; and the roll **19** engages the second face **13** of the substrate **11** of another portion of the roll **19**, in a substantially non-stick manner which will allow utilization of the roll **19** even if stored for a relatively long period of time, and even in humid conditions.

FIG. 4 schematically illustrates a stack **22** of laminates **10**, **10'** in the form of sheets **23**. While FIG. 4 shows the sheets **23** separated from each other, that is simply for clarity of illustration; in use the sheets **23** will engage each other stacked one above the other with the second layer **15** of one sheet engaging a second face **13** of the substrate **11** of an overlying or underlying sheet **23**.

As described in copending application Ser. No. 09/137,702, the first film layer **14** may comprise two different clearly colored portions one atop of the other which may be removed (after exposure to UV radiation or the like) in the manner described in said copending application Ser. No. 09/137,702, or the laminates **10**, **10'** may be otherwise utilized in a method for making a stencil for abrading or etching using a negative acting or positive acting photoresist laminate **10**, **10'**. Typically the laminate **10**, **10'** is utilized by exposing the laminate **10**, **10'** in a conventional pattern to radiation (e.g. UV radiation) to cause hardening of some portions to define the pattern as a latent image in the photoresist film layer **14** by providing some portions that are soluble or dispersible in water, and other portions that are substantially insoluble or non-dispersible. The second layer **15** is of a thickness and material so that it does not significantly interfere with the passage of the effective radiation (e.g. UV) into contact with the first film layer **14**, nor interfere with the formation of the latent image therein.

The method is continued by processing the laminate after exposure to radiation, as described above, by spraying water

on the laminate to remove the soluble or dispersible portions of the first layer **14** and at least those portions of the second layer **15** covering the soluble or dispersible portions of the first layer **14**, but not the substantially insoluble or non-dispersible portions of the first layer **14**, to ultimately produce a stencil. Typically because of the thinness of the material of which the second layer **15** is formed, it will be completely removed during the spraying process, particularly if of a water soluble composition.

It will thus be seen that according to the present invention a photoresist laminate is provided, as well as a method of utilization thereof, and a stencil formed therefrom, which substantially eliminates or minimizes the sticking problem of the photoresist material that is inherent in conventional laminates. It does so in a manner that does not require a separate removable sheet, and does not complicate the method of utilization of the laminate, and in a cost effective manner.

While the invention has been herein shown and described in what is presently conceived to be the most practical and preferred embodiment thereof it will be apparent to those of ordinary skill in the art that modifications may be made thereof within the scope of the invention, which scope is to be accorded the broadest interpretation of the appended claims so as to encompass all equivalent products and procedures.

What is claimed is:

1. A photoresist laminate comprising:

a substrate having first and second faces;

a first film layer of radiation sensitive material which is soluble or dispersible in water but will harden upon sufficient exposure to radiation so as to become substantially insoluble or non-dispersible, and operatively disposed on said substrate first face;

a second layer of a material and thickness so that it substantially prevents or minimizes sticking of said first film layer to other photoresist laminates while not significantly interfering with the radiation sensitivity thereof;

said second layer on the opposite side of said first film layer from said substrate;

a membrane support layer between and adhering to said substrate and said first film layer and engaging both said substrate and said first film layer; and

wherein said first film layer has a thickness of about 0.002–0.009 inches, said substrate has a thickness of about 0.002–0.003 inches, and said second layer has a thickness of about 0.0001–[0.0002] 0.0005 inches.

2. A photoresist laminate as recited in claim 1 wherein said second layer comprises a mixture of about 80–98% by weight polyvinyl alcohol solution and about 20–2% by weight polyvinyl acetate emulsion.

3. A photoresist laminate as recited in claim 1 wherein said laminate is in sheet form, and stacked with other substantially identical laminates so that said second layer of one sheet engages said second face of said substrate of another sheet.

4. A photoresist laminate as recited in claim 1 wherein said first film layer comprises two clearly different color portions one atop the other.

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