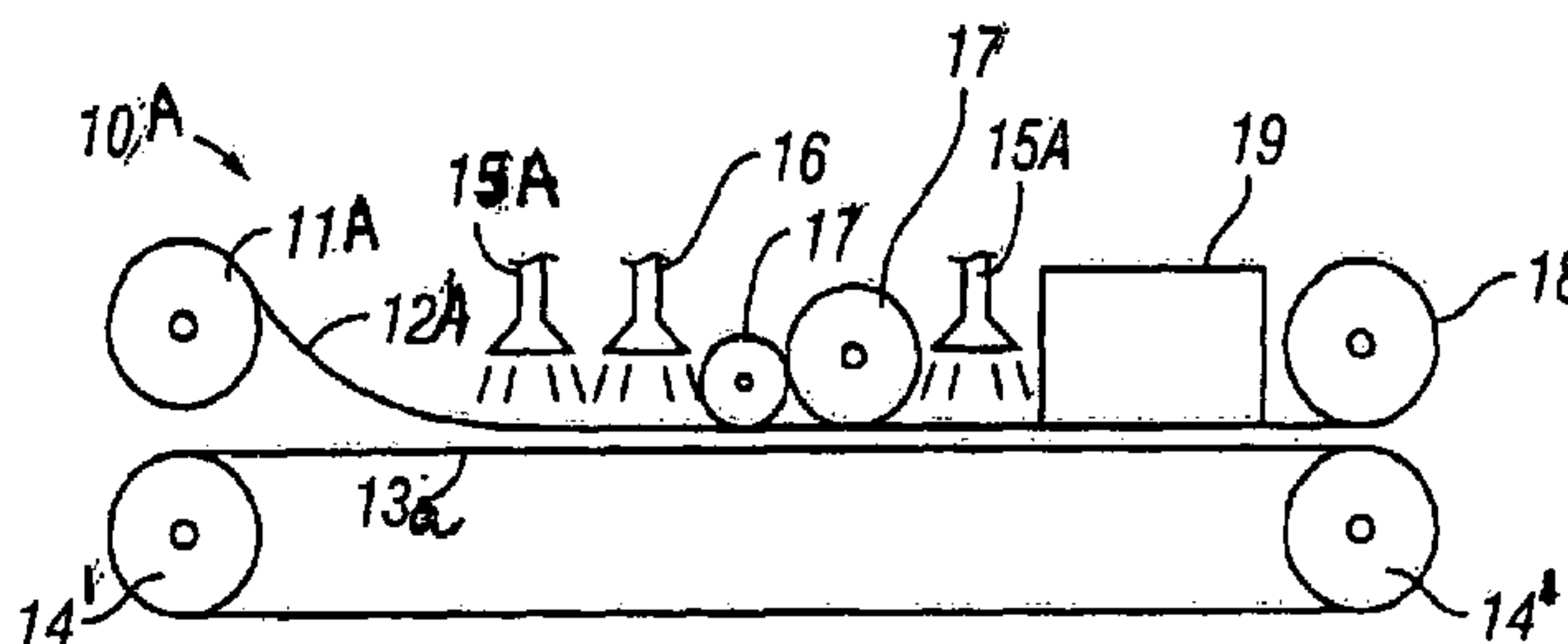




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 (54) Title: NOVEL POLYVINYL ALCOHOL ARTICLES



(57) Abrégé/Abstract:

The present invention relates to novel polyvinyl alcohol non- woven films and fabrics which have been modified so as to have a breathable coalesced lower porosity surface polyvinyl alcohol layer attached to a fibrous polyvinyl alcohol layer by a transition layer and to a process for their preparation.

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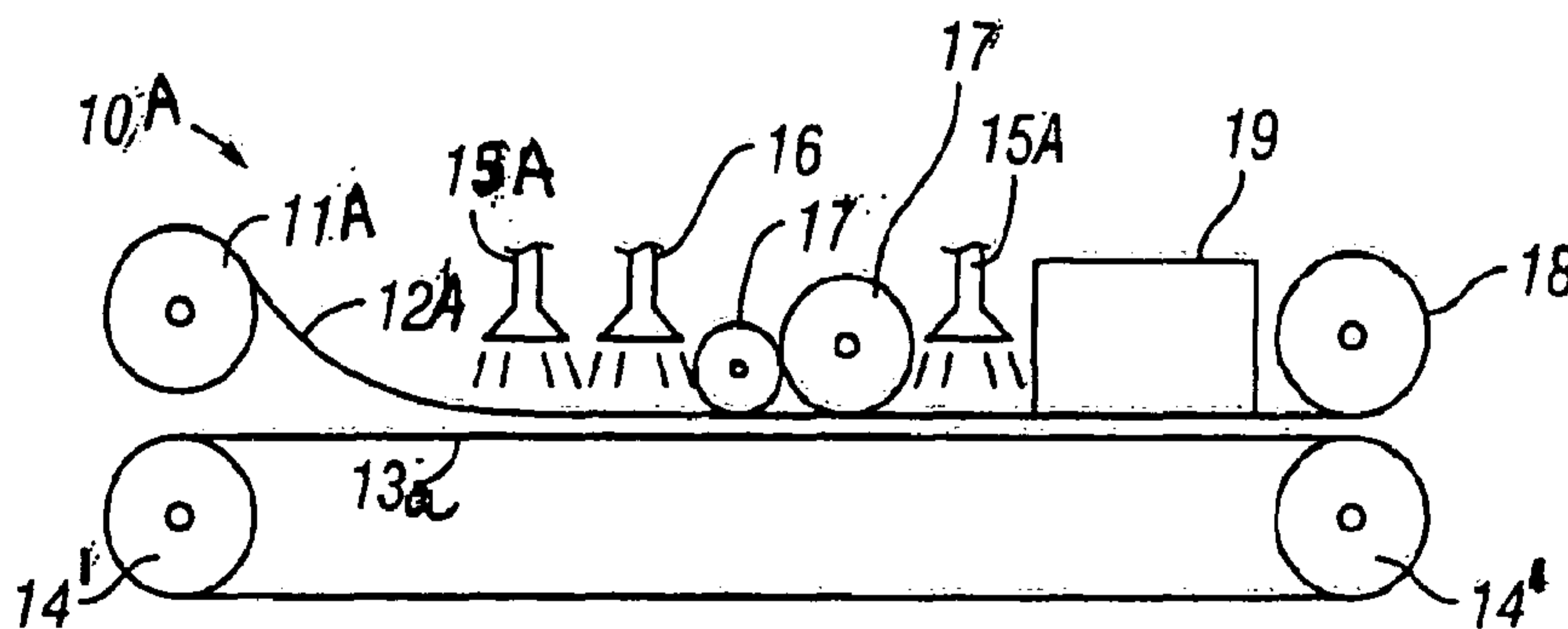


FIG. 6

(57) Abstract: The present invention relates to novel polyvinyl alcohol non- woven films and fabrics which have been modified so as to have a breathable coalesced lower porosity surface polyvinyl alcohol layer attached to a fibrous polyvinyl alcohol layer by a transition layer and to a process for their preparation.

WO 2013/012854 A1

Novel Polyvinyl Alcohol Articles

Field of the Invention

The present invention relates to articles and garments with a modified polyvinyl alcohol film fabric having the utility of a material sold by DuPont de Nemours and Company under the trademark TYVEK® which is a non-woven spunbonded polyolefin. More particularly there is provided a modified polyvinyl alcohol fibrous film having the combination of a lower porosity film like surface layer of coalesced or fused fibers with a core fibrous layer attached thereto and a process for their production.

Background of the Invention

The prior art has recognizes uses for polyvinyl alcohol compositions in the manufacture of water soluble useful articles. For example, Patent No. 3,413,229 teaches the production of water soluble bags or pouches for which packets or the like are produced containing such materials as detergents, bleaches, insecticides, medicinals, chemicals, dyes, pigments, industrial additives and other materials. It is taught that the contents of the packets are dispersed merely by dropping the packets into water whereupon the bags dissolve and release their contents into aqueous dispersions. However, the referenced patent teaches the production of such films which are both hot and cold water soluble.

U.S. Patent No. 3,859,125, teaches the production of layered articles which include coatings of polyvinyl alcohol. The subject reference teaches coating polyvinyl alcohol on a paper membrane whereby it is taught that the coated paper is soluble in either high or low temperature water. Similarly, U.S. Patent No. 4,343,133 teaches the coating of polyvinyl alcohol onto a non-woven fiber sheet impregnated with latices of polyvinyl acetate in the manufacture of a pre-moistened towelette which can be disposed of by flushing in plain water without danger of clogging a plumbing system.

Both U.K. Patent No. 1,187,690 and Japanese Patent No. 72041741, teach the production of stand alone polyvinyl alcohol films which are water soluble. The U.K. patent teaches the production of hospital bags and packaging material for such products as detergents and agricultural chemicals while the Japanese patent teaches the use of polyvinyl alcohol films to make laundry bags which dissolve releasing soiled garments contained therein. However, neither reference teaches the unique films of the present invention which can be configured into useful garments and like materials.

U.S. Patent No. 4,272,851 to Goldstein discloses a protective garment of non-woven, spun bonded polyolefin manufactured by DuPont de Nemours & Co. which is coated on one side by a polyethylene film. The film provides tear resistance, and the film prevents chemical penetration. One of the problems is the cost of manufacture and the problem of scorching during manufacture of the film.

None of the prior patents relate to modifying a polyvinyl alcohol breathable non-woven fabric to form a top surface of infinitely controllable porosity and susceptible to thermal transfer in combination with a fibrous polyvinyl alcohol layer.

Summary of the Invention

According to one embodiment, the present invention provides a modified a non-woven, fabric or laminate of polyvinyl alcohol (PVOH) to use alone or in a laminate to provide a film or fabric which can be formed into useful breathable films, non-woven fabrics and articles.

More particularly, there is provided a polyvinyl alcohol film wherein at least one surface has been selectively modified to provide a fused substantially lower porous layer that is susceptible to thermal transfer and is attached to a flexible soft fibrous polyvinyl alcohol layer by a transition layer.

The variable or low porosity layer is attached to the fibrous polyvinyl alcohol layer by a transition layer. The transition layer is the combination of coalesced film or fused layer which is formed during processing and the fibrous layer which is composed of the original nonwoven fabric which remains during formation.

Advantageously, at least one of the surfaces of the polyvinyl alcohol film has lower porosity and breathability.

The variably porous surface layers can be provided during manufacture with a water repellent layer or an anti-microbial coating.

“Variable” means that the amount of pores produced by controlling the moisture conditions of the polyvinyl alcohol at the time of manufacture of the fabric.

Preferably, the amount of pores formed in the surface layer is from the surface treatment of the nonwoven fabric by steam impinging the surface or occurring by water held by the film or fabric combined with momentary pressure and direct heat application.

The surface layer or layers can vary in porosity depending upon the amount of water held by the initial fiber or fabric or the humidity at the time of manufacture so as to be at least slightly porous and breathable.

In accordance with another embodiment of the invention, the modified polyvinyl alcohol is manufactured into films, garments, wraps, fabrics, including pillow covers, linens, etc. where TYVEK® has been found to be useful.

According to a further embodiment, the present invention provides a process for modifying a film, fabric or laminate of polyvinyl alcohol (PVOH) to use alone or in a laminate to provide a film or fabric which can be formed into useful films, non-woven fabrics and articles.

More particularly, a process comprises impinging steam on a surface of a film of polyvinyl alcohol to raise the temperature of the polyvinyl alcohol surface to about its glass transition temperature to soften the surface and cause it to become coalesced or melted.

It is therefore a general object of the invention to provide at least one surface of a woven or non-woven polyvinyl alcohol film or fabric with a lower porosity surface by raising its temperature to its glass transition temperature at a controlled depth.

It is therefore a general object of the invention to provide a polyvinyl alcohol film with at least one surface with a breathable selected porous surface bonded to a fibrous polyvinyl alcohol layer.

It is another object of the invention to prepare and to provide a laminate with a polyvinyl alcohol film having a coalesced surface layer with a porosity that is regulated by preconditioning the amount of water held by the polyvinyl alcohol prior to formation of the laminate.

It is a further object of the invention to provide wraps, garments and other useful articles with a film having similar characteristics of TYVEK®.

It is a still further object of the invention to provide protective garments and medical garments which are readily disposable after use.

One embodiment of the invention is a non-woven breathable polyvinyl alcohol article comprising three polyvinyl alcohol layers each formed from a common fibrous polyvinyl alcohol material, the article comprising: a first layer consisting of the fibrous polyvinyl alcohol material as coalesced to have a reduced porosity relative to the fibrous polyvinyl alcohol material, and that is more susceptible to thermal transfer than the fibrous polyvinyl alcohol material; a second layer comprising the fibrous polyvinyl alcohol material in an unmodified state and having a higher porosity than the first layer; and a transition layer interposed between the second layer of fibrous polyvinyl alcohol and the first layer and formed during modification of the fibrous polyvinyl alcohol to make the first layer, wherein the transition layer comprises a mixture of the fibrous polyvinyl alcohol and coalesced polyvinyl alcohol; wherein the article comprises polyvinyl alcohol from the fibrous polyvinyl alcohol material extending throughout the first layer and transition layer.

Another embodiment of the invention is a method for producing a breathable, reduced porosity, polyvinyl alcohol article comprising three polyvinyl alcohol layers each formed from a common fibrous polyvinyl alcohol material, the method comprising the steps of; controlling the amount of water in an initial film or fabric; controlling the temperature of

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and fusing a surface layer of the article so as to form a first layer consisting of the fibrous polyvinyl alcohol material along a surface of the article as coalesced to have a reduced porosity relative to the fibrous polyvinyl alcohol material, and that is more susceptible to thermal transfer than the fibrous polyvinyl alcohol material, wherein during the step of forming a first layer, a transition layer adjacent the first layer is formed and comprises a mixture of the fibrous polyvinyl alcohol and coalesced polyvinyl alcohol, and wherein the article comprises a second layer consisting of the fibrous polyvinyl alcohol material in an unmodified state adjacent the transition layer and having a higher porosity than the first layer, wherein the transition layer is interposed between the first and second layers, and wherein the article comprises polyvinyl alcohol from the fibrous polyvinyl alcohol material extending throughout the first layer, transition layer and second layer.

These and other objects and advantages will become more apparent for the Description of Preferred Embodiment and the following drawings.

Brief Description of the Drawings

Fig. 1A is a microscopic photograph of a cross-sectional view of the end of the film or fabric of the invention.

Fig. 1B is a microscopic photograph of a cross-sectional view of the side of the film or fabric of Fig. 1A.

Fig. 2 is a schematic view of the fabric of Fig. 1.

Fig. 3 is a cross sectional view of the fabric of the invention having two modified surfaces.

Fig. 4 is a cross-sectional view of the fabric of Fig. 2 with a bottom thermoplastic layer.

Fig. 5 is a cross-sectional view of the fabric of Fig. 4 with a water repellent coating on the surface layer.

Fig. 6 is a schematic illustration of an apparatus which can be used in forming the modified polyvinyl alcohol of the invention.

Fig. 7 is a modification of the apparatus of Fig. 6.

Description of the Preferred Embodiments:

According to one embodiment of the present invention there is provided a film, fabric, garment or article comprising a breathable polyvinyl alcohol film in which at least one surface layer has been modified so as to possess a tightly controlled porosity.

Fig. 1A and 1B are microscopic photograph of the modified polyvinyl alcohol film (10) of the invention.

Fig. 2 is a schematic illustration of the film (10) of **Fig. 1A**. The film (10) comprises a surface layer (11) in which the polyvinyl alcohol fiber has been modified so as to regulate control and reduce its porosity. The low porous porous surface (11) is attached to a fibrous portion (13) through a transition layer (12) which is a mixture of a coalesced polyvinyl alcohol film and a fibrous polyvinyl alcohol which has been formed during the modification of the surface layer (11).

As shown in **Fig. 3**, there is provided a film (**20**) wherein the upper surface comprises a coalesced lower porosity polyvinyl alcohol layer (**11**) and the bottom layer (**11**¹) also comprises a coalesced low porosity polyvinyl alcohol layer of the same porosity or different porosity (**12**¹) that is adhered to the fibrous polyvinyl alcohol layer (**13**) through a transition layer (**12**¹).

As shown in **Fig. 4**, the film or fabric (**30**) comprises a top surface (**11**) of a coalesced polyvinyl alcohol which is bound to a fibrous layer (**13**) of polyvinyl alcohol by means of a transition layer (**12**). On the bottom a thermoplastic layer (**14**) is adhered to the fibrous polyvinyl alcohol layer by compression or use of an adhesive or otherwise.

As shown in **Fig. 5**, a film or fabric (**40**) similar to the non-woven film or fabric (**30**) in **Fig. 4** is provided with a topically applied water repellent coating (**15**). The film or fabric (**40**) has similar properties to TYVEK® and also some additional advantages.

The non-woven films or fabrics of the invention have a surface layer which is more susceptible to thermal transfer than the interior fiber layer (**13**). In this way they can be bonded into a near film-like exterior while leaving the inner fibers unbonded. In so doing, one would effectively alter the monolithic fiber structure of a spunlaced PVOH fabric into a fabric with three distinct layers. The two outside layers would be highly compacted and bonded to improve fabric strength and abrasion resistance, while the inner core of the fabric would be highly compacted but would not be bonded together and resulting in a soft flexible fabric.

The film or fabric of the invention can be only polyvinyl alcohol with or without acetyl groups and cross-linked or uncross-linked.

The film or fabric can comprise a laminate formed with polyvinyl alcohol and another thermoplastic, preferably, a polyolefin, i.e. polyethylene to provide added tear strength.

Precursor polymer or sheet materials useful in practicing the present method comprise polyvinyl alcohol with or without acetyl groups, cross-linked or uncross-linked. The garments of the invention are comprised of a polyvinyl alcohol homopolymer that has been highly oriented by post drawing or heat annealing. Ideal for use in the present invention would be a highly crystallized, at least approximately 98% saponified or hydrolyzed polyvinyl acetate. Commercially, polyvinyl alcohol which is sold under the trademark Vinex 1003.TM. and 1002.TM. by Air Products could be used herein. Useful PVOH fibers are typically 0.5 denier to 5.0 denier and are preferably from 1.0-2.0 denier and most preferably sized at 1.2-1.5 denier.

The precursor fabric useful in practicing the present invention can be constructed by any well known technique for making woven, non-woven, knitted or otherwise formed fabric. Such non-woven techniques useful in practicing the present invention include spun bonding, melt blowing or wet laying, hydro entangling with cold water and/or thermally bonding with 30-70% of the surface melted to form essentially a non porous surface. When products are configured of sheets of suitable thermoplastic material, the sheets are approximately 3 to 20 mils in thickness and more preferably 8 to 12 mils in

thickness and most preferably approximately 8 mils in thickness. Suitable non-woven fabric or sheets are approximately from 15 g/yd² to 200 g/yd² in weight and more preferably from 20 g/yd² to 70 g/yd² and most preferably from 25 g/yd² to 80 g/yd².

As noted previously, polymer or sheet material useful in practicing the present invention is comprised of polyvinyl alcohol with or without acetyl groups, cross-linked or uncross-linked. It is proposed that the polyvinyl alcohol be substantially fully hydrolyzed, that is, having 98% or greater hydrolyzed acetyl groups.

For the sake of adequate mechanical strength, in some cases the polyvinyl alcohol-based non-woven fabric or sheet material should have a degree of polymerization of at least 700 and no greater than approximately 1500. Ideally, such materials should have a degree of polymerization of approximately 900 and be substantially crystallized.

To enhance the manufacture of suitable polyvinyl alcohol resin-based materials, suitable quantities of a plasticizer may be necessary. It is contemplated that up to 15% (wt.) of a suitable plasticizer such as glycerine or polyethylene glycol may be employed to assist in providing a smooth melt extrusion from the polyvinyl alcohol-based pellets.

It was found that the manufactured fabric for use as disposable medical garments displayed nearly identical physical properties similar to fabric manufactured from polyester and polypropylene. However, the fabric manufactured was unaffected by cool or warm water (23°-37°C) but when exposed to hot water (80°-90°C), immediately dissolved.

The incorporation of a water repellent to the surface of the modified polyvinyl alcohol film or fabric is quite a useful adjunct to minimize surface attack by liquid

moisture at a temperature lower than that at which solubility occurs. It has been found that even with polyvinyl alcohol films and fabrics which become water soluble only at elevated temperatures, when exposed to water, the surface of such material tends to take on a slick "feel" and the use of water repellents tends to minimize this effect. Suitable repellents include fluorocarbons offered by the 3M Co. sold under its trademarks FC 824 and 808. Oleic acid and fatty acids are also useful repellants. These materials are useful in the range of between 0.1 to 2.0% (wt.) based upon the weight of the polyvinyl alcohol polymer.

Antimicrobial agents can be added to the surface particularly for medical applications such as gowns, drapes, etc. Antimicrobials include GERM PATROL® sold by Germ Patrol, LLC, silanes, silver or copper antimicrobials, and the like.

The surface can also be modified by utilizing the water retention held by the precursor film or fabric. In this regard the film or fabric can be preconditioned by subjecting the film or fabric to a fixed humidity and temperature for time sufficient for equilibrium between fiber and the atmosphere to occur, 24 to 96 hours, 72 hours beginning preferred and then utilizing heated rollers and pressure rollers to create the steam to melt and compact the surface and form a layer of reduced porosity while leaving the adjoining fibers in tact. The films or fabrics of the present invention are useful in making medical clothing, gowns, drapes, etc. The films or fabrics can be formed into envelopes, building wraps for inert articles.

According to another embodiment of the invention, the process for preparing the modified polyvinyl alcohol film, fabric or laminate can be accomplished using an apparatus illustrated in **Fig. 6**.

As shown in **Fig. 6**, a film, fabric or laminate (**12A**) on a roller (**11A**) is processed on an apparatus (**10A**). The film comprises polyvinyl alcohol film, fabric or a laminate (**12A**) placed on a conveyor (**13A**) which is moved by rollers (**14A**, **14B**) under a steam jet (**15A**) wherein steam at a temperature of about 100-120°C impinges on the polyvinyl alcohol film so as to raise the temperature of the surface to about the glass transition T_g so as to melt the surface and form a coalesced layer.

The treated film passes under a delivery means (**16**) which can deliver an additive such as a colorant or an anti-blocking agent such as silicon dioxide polymer, talc, fumed silica, etc in an amount between 0.1 to 5%(wt), preferably between 2 to 3%(wt) or a water repellent. The film (**12A**) then proceed under at least one heated calendar (**17**) to press the additives into the softened portion and/or to stretch the film.

After passing the calendar (**17**) having one or more rollers, a further delivery means (**15A**) can deliver a water repellent.

The treated film can be conveyed through a drying oven (**19**) and then onto a take-up roller (**18**). Both sides of the film (**12A**) can be treated by further passing the film on roller (**19**) through the apparatus (**10A**) to treat the other surface of the processed film (**12A**).

The film (**12A**) can be only polyvinyl alcohol with or without acetyl groups, and cross-linked or uncross-linked.

The film (12A) may comprise a laminate formed with polyvinyl alcohol and another thermoplastic, preferably, polyethylene to provide added tear strength similar to TYVEK®.

As shown in Fig. 7, the apparatus can have a steam jet (18A) on the underside of the film or fabric (12A) so that both surfaces can be modified. Also tension rollers (17A) may be provided to stretch the film or fiber (12A) depending upon its utility.

As noted previously, polymer or sheet material useful in practicing the present invention is comprised of polyvinyl alcohol with or without acetyl groups, cross-linked or uncross-linked. It is proposed that the polyvinyl alcohol be substantially fully hydrolyzed, that is, having 98% or greater hydrolyzed acetyl groups.

To enhance the manufacture of suitable polyvinyl alcohol resin-based materials, suitable quantities of a plasticizer may be necessary. It is contemplated that up to 15% (wt.) of a suitable plasticizer such as glycerin or polyethylene glycol may be employed to assist in providing a smooth melt extrusion from the polyvinyl alcohol-based pellets.

It was found that the manufactured fabric for use as disposable medical garments displayed nearly identical physical properties similar to fabric manufactured from polyester and polypropylene. However, the fabric manufactured was unaffected by cool or warm water (23°-37°C) but when exposed to hot water (80°-90°C), immediately dissolved.

The incorporation of a water repellent within the polyvinyl alcohol film or fabric is quite a useful adjunct to minimize surface attack by liquid moisture at a temperature lower than that at which solubility occurs.

The following Examples are merely illustrative of the process of the invention and modifications are within those skilled in the art.

Example 1

A non-woven polyvinyl alcohol fabric (20 mil thickness) was passed through a calender as shown in **Fig. 6** with the gap between the rolls set at 16 mils. The rolls were heated at 100°C and a narrow slot of steam was directed at the fabric just before the fabric passed through the rolls. The treated fabric was reduced in thickness to 16 mil and the fabric surface transformed from a porous fibrous nature to almost continuous film surface on one side with substantially less porosity suitable for a use in disposable protective clothing or disposable medical articles.

Example 2

A non-woven polyvinyl alcohol fabric (20 mil thickness) was passed through a calender as shown in **Fig. 6** with the gap between the rolls set at 14 mils. The rolls were heated at 90°C and a narrow slot of steam was directed at the top surface of the fabric just before the fabric passed through the rolls. A fine mist of water repellent coating was sprayed on

the fabric after the fabric emerged from the calender. The treated fabric was then passed through a drying oven to fix the water repellent coating on the surface of the fabric. The treated fabric was reduced in thickness to 14 mil and the fabric surface transformed from a porous fibrous nature to a continuous film surface with substantially less porosity suitable for a use in disposable protective clothing. Drops of water beaded and rolled off the surface of the fabric.

Example 3

A laminate of polyvinyl alcohol and polyethylene (20 mil thickness) was passed under a steam jet with steam of 100-120°C impinging on the polyvinyl surface onto a conveyor as shown in **Fig. 6**. The conveyor transported the laminate through heated calender rolls (100°C) which was then sprayed with fluorocarbon water repellent agent and then passed through a drying oven. The laminate could be used in replacement of TYVEK®.

While the foregoing is illustrative of a preferred and a modified embodiment of the invention, other embodiments may be had within the scope hereof.

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CLAIMS:

1. A non-woven breathable polyvinyl alcohol article comprising three polyvinyl alcohol layers each formed from a common fibrous polyvinyl alcohol material, the article comprising:
 - 5 a first layer consisting of the fibrous polyvinyl alcohol material as coalesced to have a reduced porosity relative to the fibrous polyvinyl alcohol material, and that is more susceptible to thermal transfer than the fibrous polyvinyl alcohol material;
 - a second layer comprising the fibrous polyvinyl alcohol material in an unmodified state and having a higher porosity than the first layer; and
 - 10 a transition layer interposed between the second layer of fibrous polyvinyl alcohol and the first layer and formed during modification of the fibrous polyvinyl alcohol to make the first layer, wherein the transition layer comprises a mixture of the fibrous polyvinyl alcohol and coalesced polyvinyl alcohol;
 - wherein the article comprises polyvinyl alcohol from the fibrous polyvinyl
 - 15 alcohol material extending throughout the first layer and transition layer.
 2. The article of claim 1 comprising a further polyvinyl alcohol surface layer formed by modifying an outermost portion of the second layer of the fibrous polyvinyl alcohol opposite the first layer, wherein the further surface layer is coalesced and has a reduced porosity relative to the second layer of the fibrous polyvinyl alcohol.
 - 20 3. The article of claim 1 or 2 wherein the first layer is formed with steam.
 4. The article of any one of claims 1 to 3 further comprising a thermoplastic polymer layer attached to the second fibrous polyvinyl alcohol layer, wherein the thermoplastic polymer layer is formed from a material different from that of the fibrous polyvinyl alcohol.
 - 25 5. The article of claim 4 wherein the thermoplastic polymer layer is a polyolefin.

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6. The article of any one of claims 1 to 5 having a degree of polymerization of 700 to 1500.
7. The article of any one of claims 1 to 6 further comprising a water repelling composition disposed on the first surface layer.
- 5 8. The article of any one of claims 1 to 7 further comprising an antimicrobial composition disposed on the first surface layer.
9. The article of any one of claims 1 to 8 wherein the polyvinyl alcohol is cross-linked.
10. The article of any one of claims 1 to 9 wherein the first layer is substantially
10 non porous.
11. The article of any one of claims 1 to 10 wherein the polyvinyl alcohol has acetyl groups.
12. Clothing comprising the article as defined in any one of claims 1 to 11.
13. The clothing of claim 12 wherein the article contains a plasticizer.
- 15 14. The clothing of claim 12 or 13 including an antimicrobial coating.
15. The clothing of claim 14 which comprises medical clothing.
16. The clothing of any one of claims 12 to 15 wherein the polyvinyl alcohol is spun laced.
17. The article of any one of claims 1 to 11 which is a film or fabric.
- 20 18. A method for producing a breathable, reduced porosity, polyvinyl alcohol article comprising three polyvinyl alcohol layers each formed from a common fibrous polyvinyl alcohol material, the method comprising the steps of;

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controlling the amount of water in an initial film or fabric;

controlling the temperature of and fusing a surface layer of the article so as to form a first layer consisting of the fibrous polyvinyl alcohol material along a surface of the article as coalesced to have a reduced porosity relative to the fibrous polyvinyl alcohol material, and that is more susceptible to thermal transfer than the fibrous polyvinyl alcohol material, wherein during the step of forming a first layer, a transition layer adjacent the first layer is formed and comprises a mixture of the fibrous polyvinyl alcohol and coalesced polyvinyl alcohol, and wherein the article comprises a second layer consisting of the fibrous polyvinyl alcohol material in an unmodified state adjacent the transition layer and having a higher porosity than the first layer, wherein the transition layer is interposed between the first and second layers, and wherein the article comprises polyvinyl alcohol from the fibrous polyvinyl alcohol material extending throughout the first layer, transition layer and second layer.

19. The method as recited in claim 18 wherein the article is a film or a fabric.

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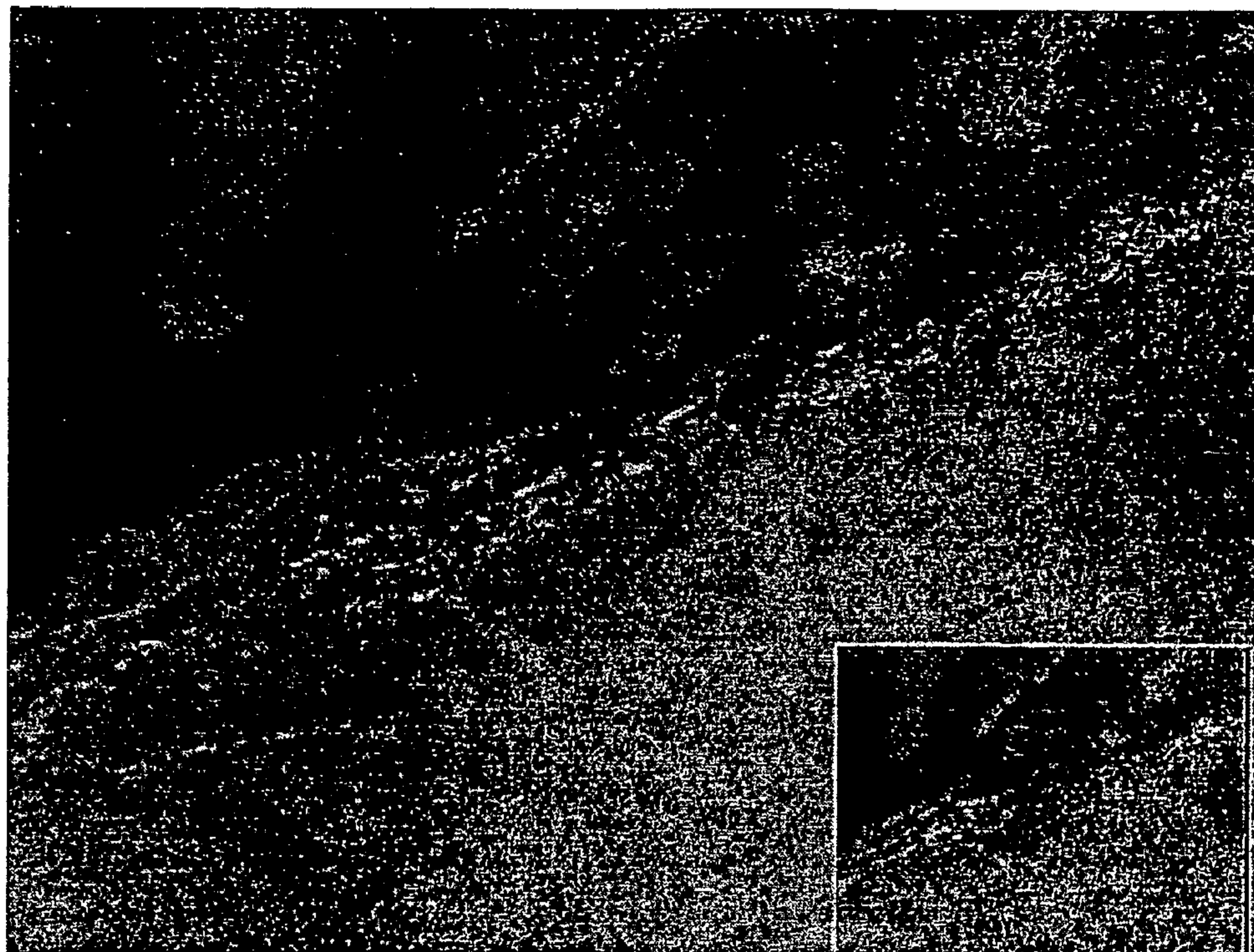


FIG. 1A

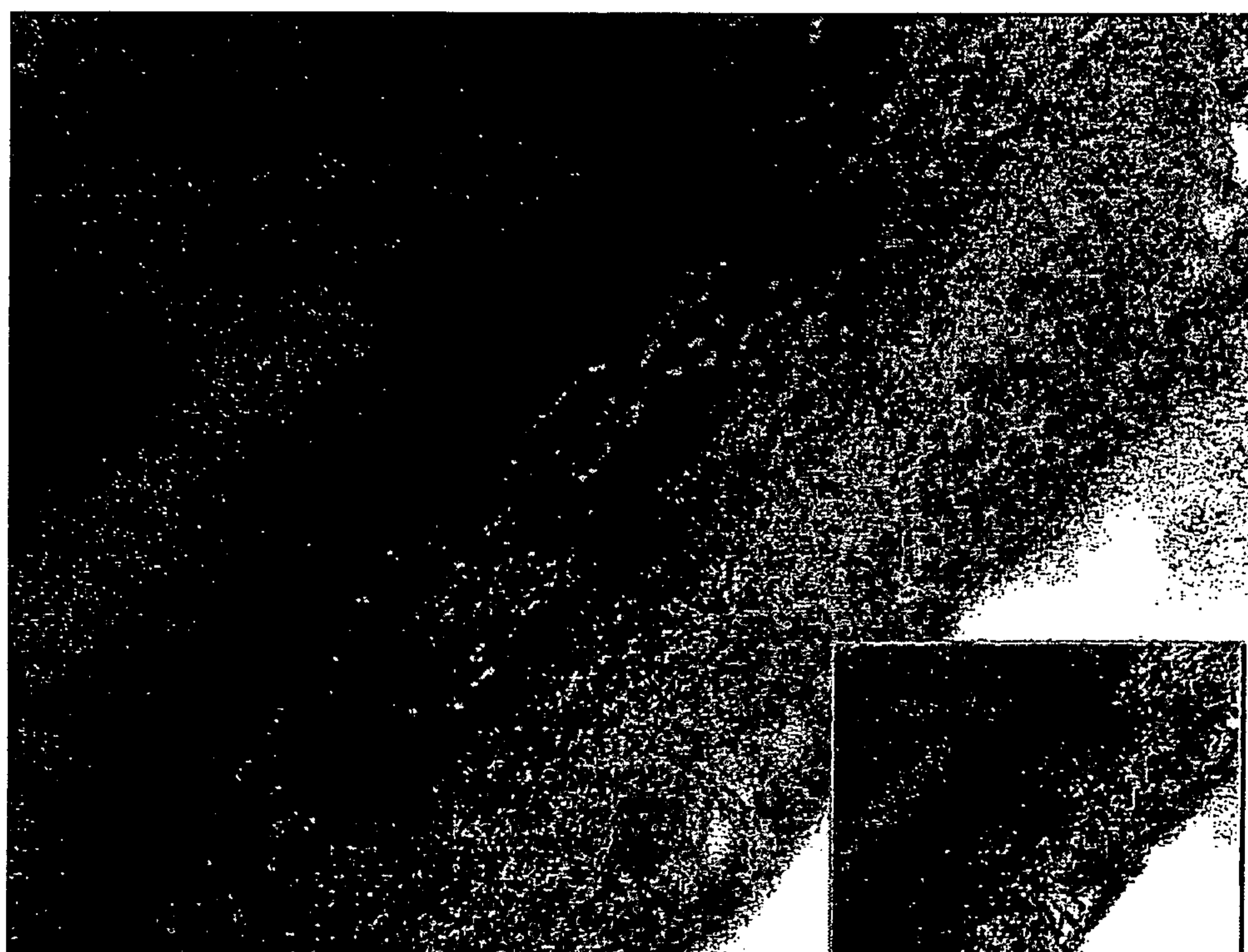


FIG. 1B

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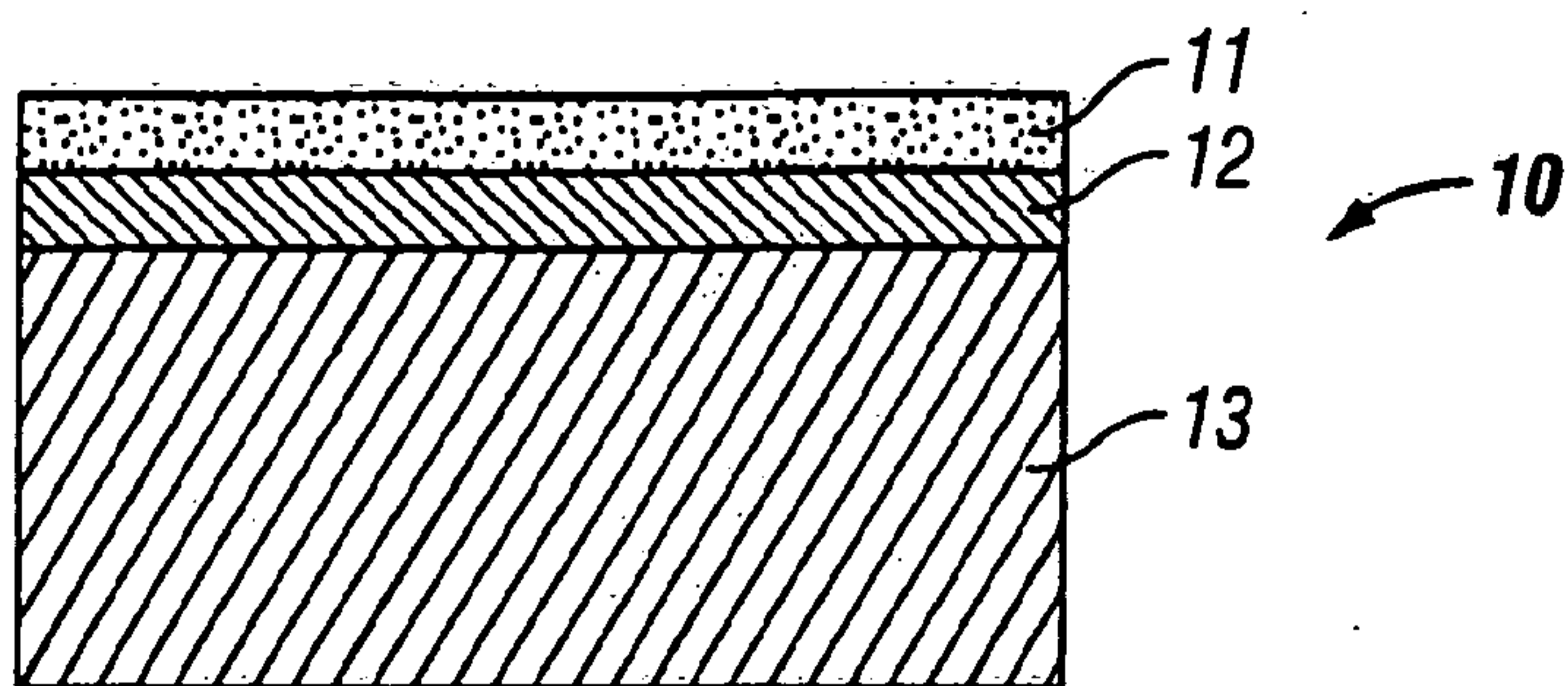


FIG. 2

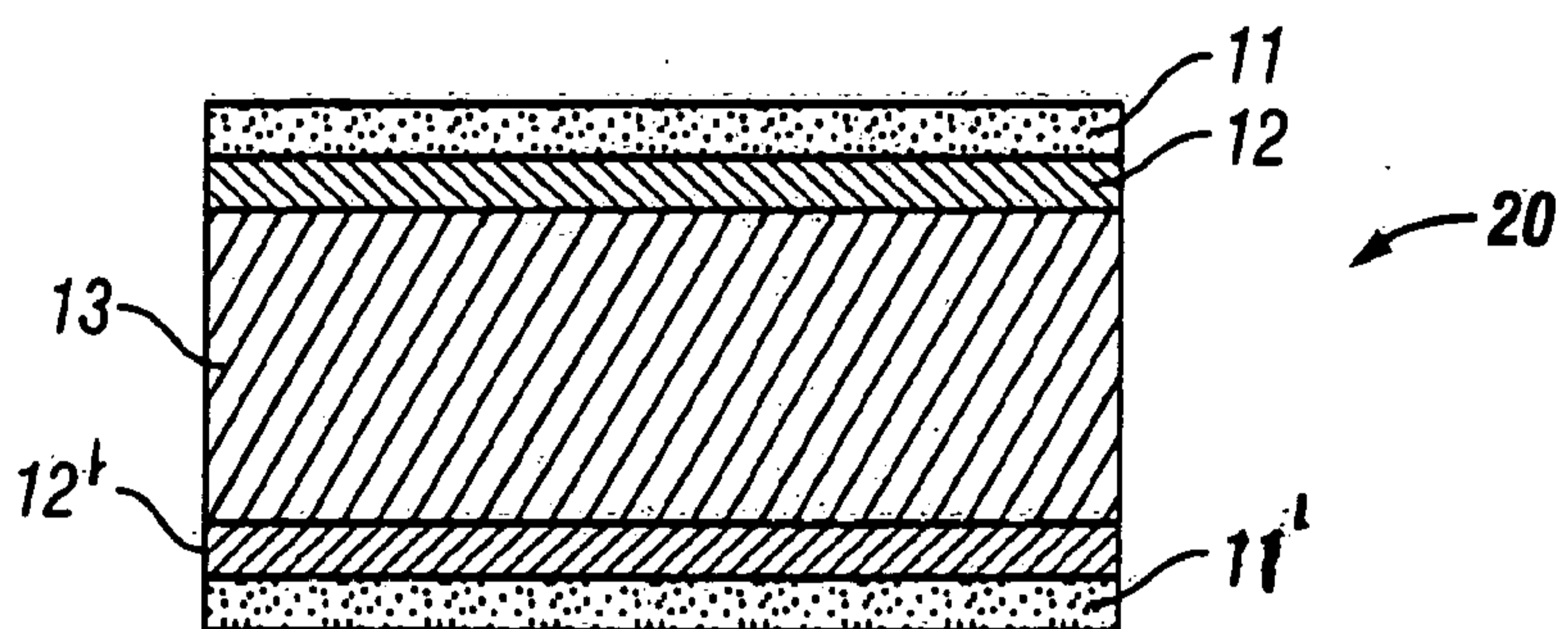


FIG. 3

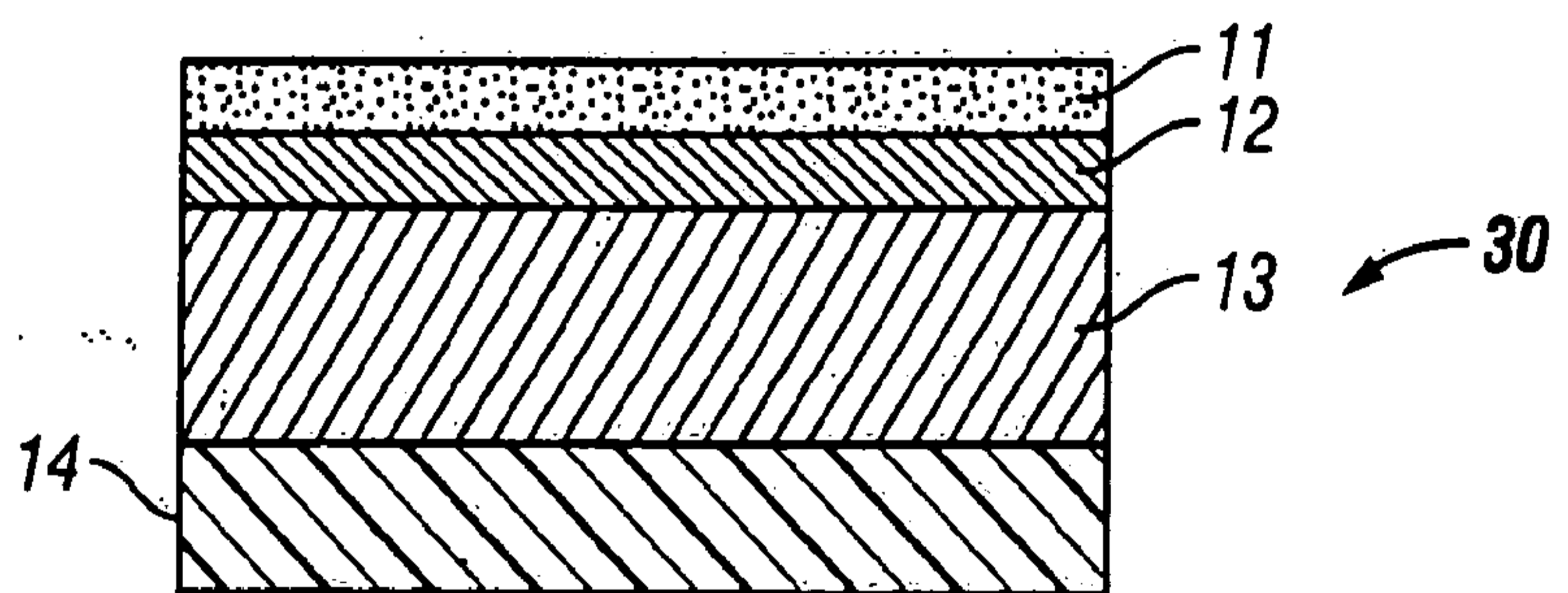


FIG. 4

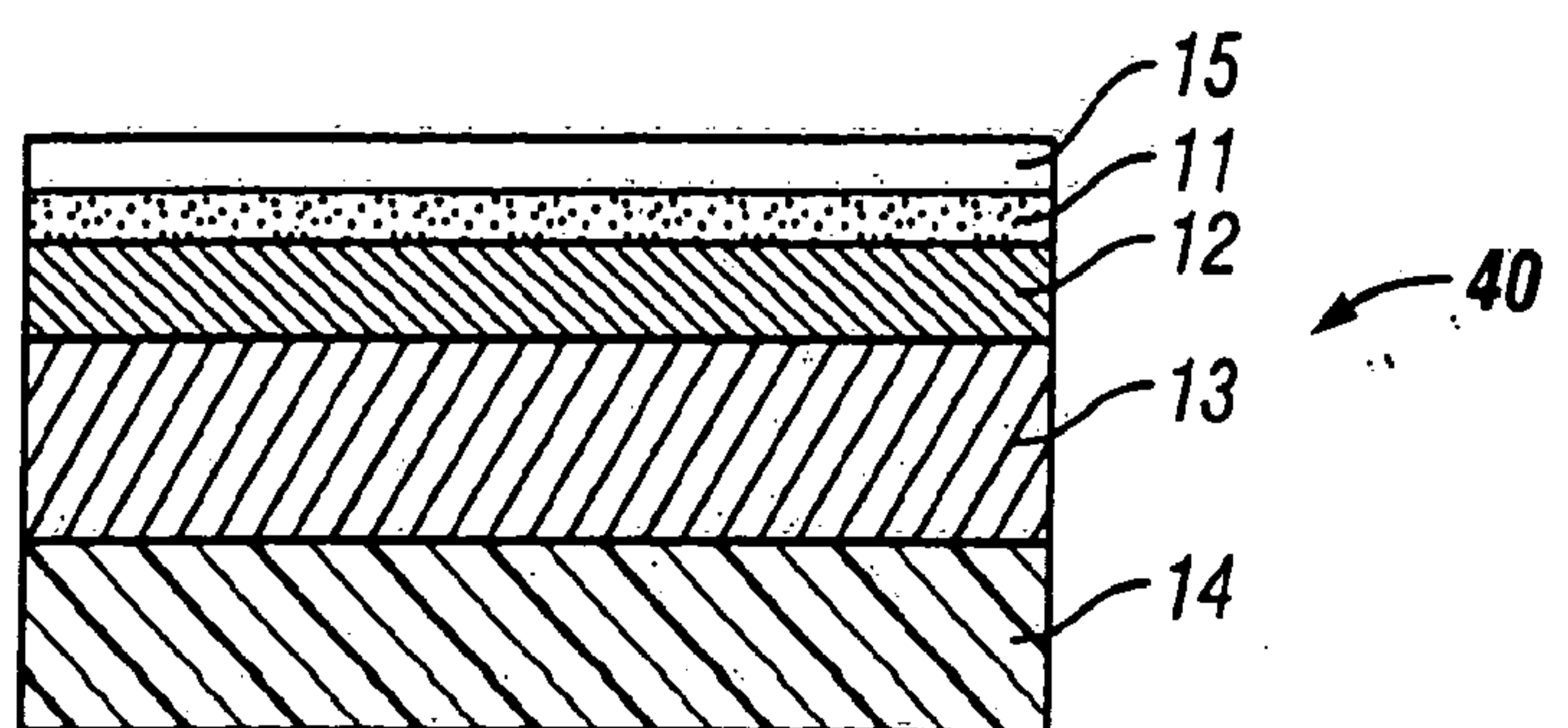


FIG. 5

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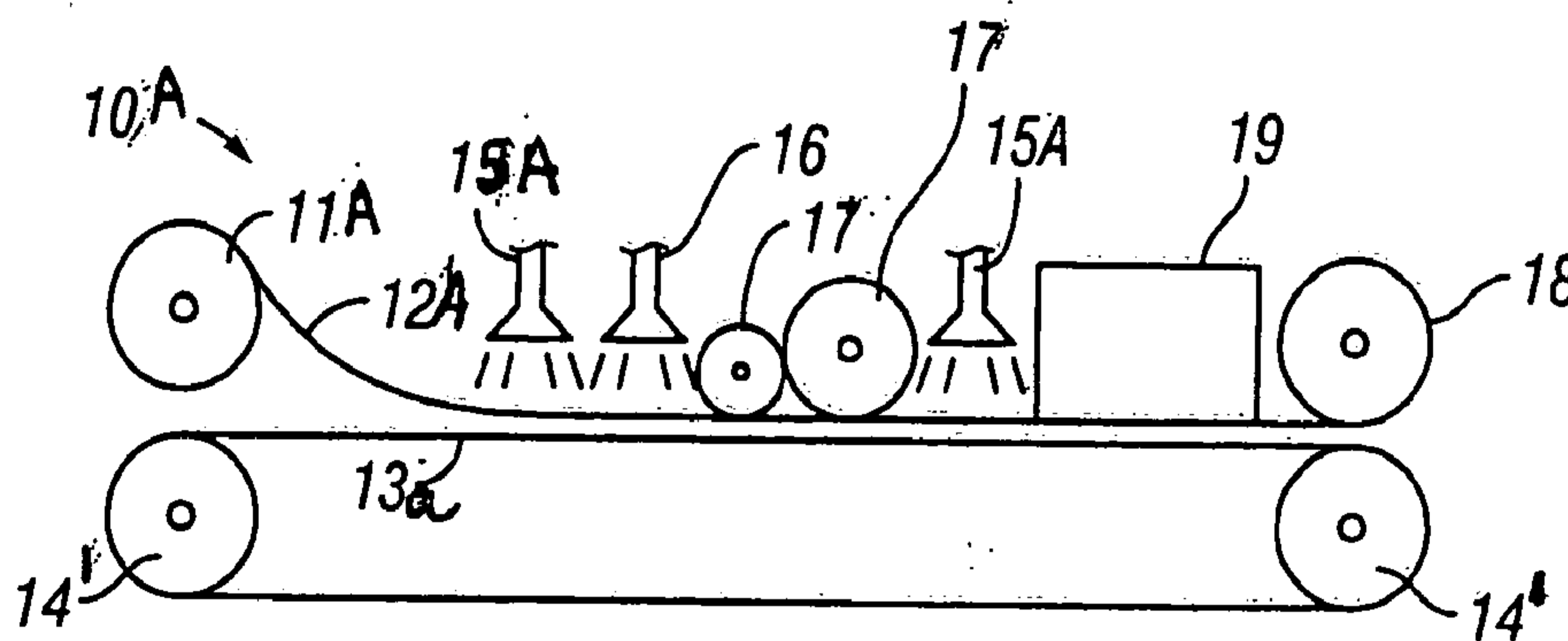


FIG. 6

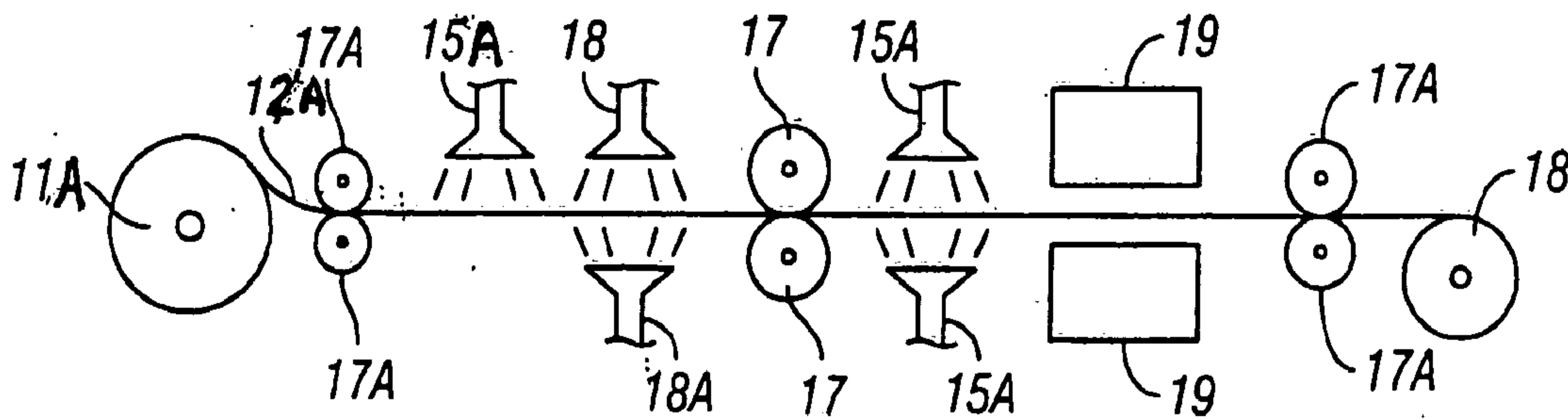


FIG. 7

