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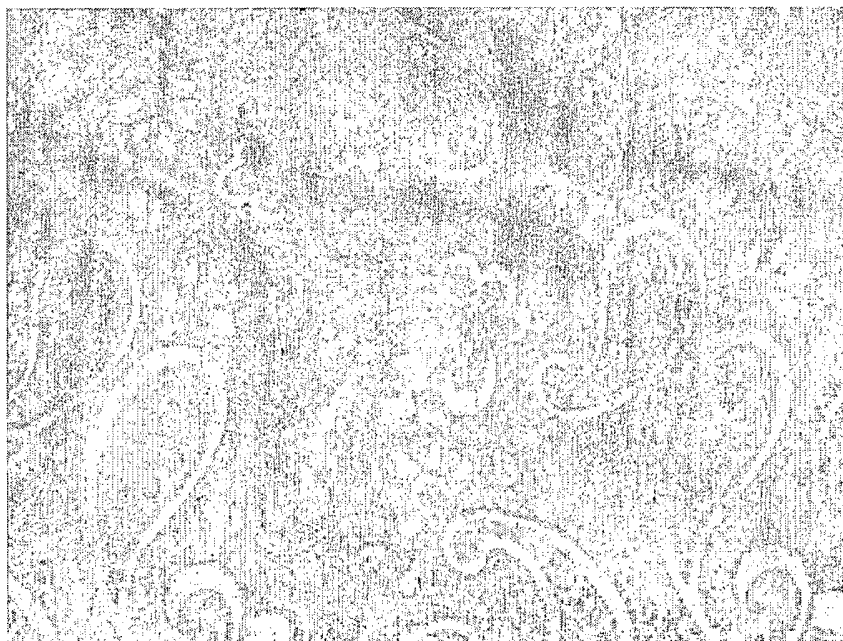
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(54) Title: NOVEL POLYMER FILMS AND TEXTILE LAMINATES CONTAINING SUCH POLYMER FILMS



(57) Abstract: Polymer film having at least two regions of differing translucency. The at least two regions of differing translucency can be obtained by selectively compressing regions of the polymer film. Laminate comprising textile material and such a polymer film. The laminates can be breathable and/or waterproof. Suitable uses for the laminate include, for example, garments, tents, and sleeping bags.

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**TITLE OF THE INVENTION**

Novel Polymer Films and Textile Laminates Containing Such Polymer Films

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**RELATED APPLICATION**

This application is a continuation-in-part of commonly owned and copending U. S. Patent Application S.N. 10/738,353, filed December 3, 2003.

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**FIELD OF THE INVENTION**

This invention relates to polymer films and laminates comprising such films and at least one textile material that provide, among other things, improved aesthetics and methods for making such films and laminates.

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**BACKGROUND OF THE INVENTION**

Porous, expanded polytetrafluoroethylene (hereinafter ePTFE), made by expansion by stretching at a temperature below the crystalline melt temperature of PTFE, has been known for some time. These porous, fibrillated materials and their manufacture were originally described by Gore in U.S. Pat. Nos. 3,953,566 and 4,187,390. They possess the known attributes of PTFE while adding additional benefits resulting from their porous microstructure. They are typically hydrophobic, inert, water resistant, strong, and can be made to be thin and flexible. Applications for these materials include, for example, wire insulation, gaskets, and waterproof and breathable rainwear.

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The mechanical properties of these materials have been the focus of much research and many inventions. The use of elongation at high rates and elevated temperatures to increase the tensile strength of PTFE was first taught by Gore in U.S. Pat. No. 3,953,566.

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The creep resistance of ePTFE has been shown to increase by densification at high temperatures under vacuum by Knox, et al. in U.S. Patent No. 5,374,473. Densification of at least two layers of ePTFE was performed under vacuum at temperatures from 330°C to 390°C and under pressures from 150 psi to 350 psi.

35

Likewise, creep resistant articles of ePTFE such as gaskets, O-rings, and valve seats have been produced under similar extreme process conditions. Fuhr, et.al., in U.S. Patent No. 5,792,525, teach that densification of ePTFE in an autoclave at temperatures over 300°C for an hour or more will significantly reduce the creep of the resultant ePTFE articles. In addition, Fuhr et al. teaches

that partial densification results in an ePTFE structure that has a dense surface skin and a non-densified core.

The cut resistance of ePTFE articles has also been improved by densification at high temperatures. U.S. Patent No. 4,732,629 teaches that  
5 densification and heating ePTFE wire-wrapping tapes to over 345°C for a period of time increases the cut resistance of the resultant cable shield by more than 50%.

Complimentary layers have been combined with ePTFE films to enhance specific performance attributes. The addition of a layer of hydrophilic polymer  
10 to the ePTFE film was first taught by Gore in U.S. Patent No. 4,194,041. This patent showed that the contamination resistance of waterproof, breathable articles, such as garments, could be enhanced by the addition of a layer of breathable polymer to an ePTFE film. It is also known to sandwich such a complimentary layer between two or more layers of ePTFE film, or to provide a  
15 complimentary layer to both sides of the ePTFE film.

It is further known to form ePTFE containing laminates, which include at least one layer of ePTFE film adhered directly to at least one textile material. Moreover, the ePTFE film can contain the above mentioned layer of hydrophilic polymer, if desired. In such an embodiment, the hydrophilic polymer layer can  
20 serve to adhere together the ePTFE film and the textile material, or a suitable adhesive material can be supplied to adhere the hydrophilic polymer and ePTFE combination to the textile material. Moreover, in the case where a hydrophilic polymer layer is not provided, an adhesive material can be supplied to adhere the ePTFE film to the textile material. Any suitable adhesive can be used. The  
25 adhesive can be supplied in a discontinuous pattern (e.g., as a discreet dot pattern, as lines of adhesive, etc.), as a substantially continuous layer (e.g., substantially covering the surface of the ePTFE), in which case the adhesive should be capable of allowing water vapor to pass through (i.e. be breathable, such as the hydrophilic polymers mentioned above, and particularly hydrophilic  
30 layers of polyurethane), or the adhesive can be supplied as a continuous pattern, such as the grid pattern disclosed in US Patent No. 5,660,918, to Dutta.

All of the above teachings have lead to the development of ePTFE films and laminates which are ideally suited for protective clothing articles used for wear in wet conditions (such as rain, snow, etc.); in outdoor activities (such as  
35 skiing, biking, hiking, etc.); in handling hazardous chemicals, in preventing contamination, in avoiding infection, articles should in each instance protect the wearer by preventing leakage of water or other fluids and microorganisms into the article while keeping the wearer comfortable by allowing perspiration to



polymer film. The two surfaces are brought together with sufficient pressure to effectively compress only the portions of the polymer film where the pattern is raised while concurrently retaining non-compressed portions where the pattern is not raised. Heat can optionally be applied to effect the contrast between the compressed and non-compressed portions of the desired pattern. Patterns can be created by using at least one hardened surface comprising multiple levels to which the raised surface is raised. Each different raised level can create a correspondingly different amount of compression (and, thus, degree of translucency) of the polymer film. As the polymer film is compressed, it becomes more translucent, as compared to the non-compressed (or less compressed) portion of the film. The degree of translucency increases with increasing level of compression. Therefore, selective compression accomplished through the use of patterned raised surfaces can create aesthetically enhanced polymer films and polymer film/textile laminates. Due to the optical change (i.e., increased translucency) of the polymer film upon compression, the image of the patterned surface can be transferred to the polymer film or polymer film/textile laminate.

### **BRIEF DESCRIPTION OF THE FIGURES**

Figure 1 is a schematic drawing of a process according to the invention;  
Figure 2 is a schematic drawing of a process according to the invention;  
Figure 3 is a schematic drawing of a process according to the invention;  
Figure 4 is an optical micrograph of a laminate according to the invention;  
Figure 5 is an optical micrograph of a laminate according to the invention;  
Figure 6 is an optical micrograph of a laminate according to the invention;  
Figure 7 is a combination of an optical micrograph and a corresponding grey-scale spectra showing the range of shades of grey in a laminate according to the invention;  
Figure 8 is an optical micrograph of a laminate according to the invention;  
Figure 9 is a combination of an optical micrograph and a corresponding grey-scale spectra showing the range of shades of grey in a laminate according to the invention;  
Figure 10 is an SEM of a laminate according to the invention;

Figure 11 is a three-dimensional surface map depicting the various depths of a laminate according to the invention;

Figure 12 is a Zygo profilometer scan of the surface of a laminate according to the invention;

5 Figure 13 is an optical micrograph of a section of a prior art laminate that has been subjected to abrasion testing;

Figure 14 is an optical micrograph of a section of a laminate according to the invention that has been subjected to abrasion testing.

Figure 15 is an SEM of a laminate formed in Example 19.

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### **DETAILED DESCRIPTION OF THE INVENTION**

Polymer film having at least two regions of differing translucency is provided.

15 Laminate comprising at least one layer of textile material having a first side and a second side and polymer film, having a first side and a second side, adhered to at least one of the first and second sides of the textile material, wherein the polymer film has at least two regions of differing translucency is also provided. In an aspect of the invention the polymer film comprises a  
20 multitude of regions differing in translucency. In a further aspect of the invention the regions of differing translucency comprise a substantially repeating pattern. In a further aspect of the invention, at least about 10% of the surface area of the polymer film is more translucent than the remaining surface area of the polymer film. In a still further aspect of the invention, at least about  
25 25% of the surface area of the polymer film is more translucent than the remaining surface area of the polymer film. In yet a further aspect of the invention, at least about 50% of the surface area of the polymer film is more translucent than the remaining surface area of the polymer film.

30 As used herein "polymer film" includes any polymer structure whose optical properties (i.e. translucency) change upon compression. In an aspect of the invention "polymer film" can be a polymer film having at least some interconnected porosity. Examples of suitable polymer films include porous polytetrafluoroethylene films (and particularly porous, expanded polytetrafluoroethylene films ("ePTFE")), porous polyurethane films, porous  
35 polyolefin films, porous polyester films, and multi-colored polyurethane films. Although polymer films can be any polymer structure, as discussed above, for simplicity the remainder of the disclosure will exemplify an embodiment

wherein the polymer film comprises porous, expanded polytetrafluoroethylene film.

Suitable textile materials may be woven or non-woven, employing synthetic fibers, natural fibers, or blends of synthetic and natural fibers. Textiles  
5 may also be knits, interlocks and brushed knits.

Laminate can be formed by the selective compression of an ePTFE film or of an ePTFE film/textile laminate which will result in, among other things, improved aesthetics while other attractive properties (such as breathability) are not significantly affected. A selectively compressed ePTFE film and/or ePTFE  
10 film/textile laminate can be produced by a number of suitable methods. ePTFE film/textile laminates provide a useful material for many applications where water vapor permeability (i.e., breathability) is required while providing some degree of water resistance or even water proofness.

Laminates comprising ePTFE film and textile can be produced by any  
15 suitable method. Such methods are known in the art and include those as described in, for example, U.S. Patent No. 5,289,644 to Driskill et al. For example such laminates can be produced by printing an adhesive onto one layer in a discontinuous pattern, in an intersecting grid pattern, in the form of continuous lines of adhesive, as a thin continuous layer, etc., and then  
20 introducing the second layer in a way that the adhesive effectively joins and adheres together the two adjacent surfaces of the ePTFE film and the textile material. A 3 layer laminate can similarly be produced by printing adhesive onto both sides of an ePTFE film and then introducing both a first and second textile to opposing surface of the ePTFE film onto which the adhesive has been  
25 printed. Alternately, a 2 layer laminate can be produced first and then an adhesive printed or otherwise provided onto the ePTFE side of the 2 layer laminate prior to the introduction of a second textile layer onto said second ePTFE surface.

The at least two regions of differing translucency can be obtained by a  
30 process where regions of the polymer film are selectively compressed, and other regions are not compressed. Such a process can comprise compressing a polymer film or a polymer film/textile laminate between two hardened surfaces, at least one of which may contain a pattern that is to be imparted into the polymer film. The two surfaces are brought together with sufficient pressure to  
35 effectively compress only the portions of the polymer film where the pattern is raised while concurrently retaining non-compressed portions where the pattern is not raised. Heat can optionally be applied to effect the contrast between the compressed and non-compressed portions of the desired pattern. Patterns can be



created by using at least one hardened surface comprising multiple levels to which the raised surface is raised. Each different raised level can create a correspondingly different amount of compression of the polymer film. As the polymer film is compressed, it becomes more translucent, as compared to the non-compressed (or less compressed) portion of the film. The degree of translucency increases with increasing level of compression. Therefore, selective compression accomplished through the use of patterned raised surfaces can create aesthetically enhanced polymer films and polymer film/textile laminates. Due to the optical change (i.e., increased translucency) of the polymer film upon compression, the image of the patterned surface can be transferred to the polymer film or polymer film/textile laminate.

Turning to the Figures, Figure 1 is a schematic of a process by which selective compression of an ePTFE film/textile laminate can be accomplished. As shown in Figure 1, an ePTFE film 2 has been laminated to textile material 3. The laminate can be calendered between two smooth hard rolls 1 and 4 under pressures, temperatures, and speeds so that the raised yarns of the textile are sufficient to locally compress the ePTFE microstructure; thereby creating a selectively compressed ePTFE film/textile laminate. In both woven and knitted textiles, the plies of the yarns can be alternated one over the other. One yarn can be raised and then descend under the other yarn as the textile is intertwined together which creates surface topography. As the ePTFE laminate is subjected to pressure (and heat when used), such as when compressed between the two smooth rolls, the raised cross-overs of the yarns create high pressure spots that result in selective compression of the ePTFE microstructure, which results in the compressed regions of the film being more translucent than the non-compressed regions of the film. Furthermore, the pattern of selective compression in this case will match that of the textile used to create the high pressure points.

A 3 roll lab calendering system, from B.F Perkins of Rochester, N.Y. is an example of a suitable calendering system which can be used for such a method. The machine has a 22" wide face and can be run at between about 10 feet per minute and about 15 feet per minute in most cases. However, the speed with which ePTFE film/textile laminate can be passed through the nip of the smooth rolls can be altered greatly, depending on desired results. For example, higher line speeds will reduce the residence time under the pressure of the nip and accordingly will, generally, tend to produce less selective compression. Moreover, the temperature of the rolls can be adjusted to affect the degree of selective compression. Particularly suitable roll temperatures may be between about 80°C and about 160°C. However, a selective compression image can be

created at both lower and higher temperatures. The nip pressure between the two smooth rolls can be varied, with pressures between about 250 pounds per linear inch and about 6,000 pounds per linear inch being particularly suitable. At low pressures, the intensity of the selectively compressed image may be  
5 lower. As the nip pressure is increased, the resultant selectively compressed image may become sharper up to a point, beyond which, the image may become more diffuse.

A second method for the selective compression of ePTFE film or ePTFE film/textile laminates is through the use of a pattern roll. A schematic of this  
10 process configuration is depicted in Figure 2. In such a method, a pattern of high and low areas is created on an otherwise smooth roll. Typically, a hardened metal roll is engraved with the desired pattern 1'. This patterned roll 1' can then be matched with smooth, hard roll 4. The smooth roll 4 is typically comprised of hard rubber, plastic, or a filled fiber such as a filled cotton. A  
15 filled cotton roll is comprised of cotton fibers with an optional binder which are compressed to form a hard, packed solid material. This material can then be machined smooth to produce a suitable surface for smooth calendering. This pair of rolls can then be mounted in a machine so that a nip is formed between the rolls as depicted by the gap between 1' and 4 in Figure 2. The desired ePTFE  
20 film (or ePTFE film 2/textile 3 laminate) can then be fed through the nip that is formed between the patterned roll 1' and the smooth roll 4. As the ePTFE film (or ePTFE film 2/textile 3 laminate) passes through the closed nip, the pattern can selectively compress the ePTFE microstructure where the pattern surfaces are raised. This results in the compressed regions being more translucent than  
25 the non-compressed regions.

Suitable process roll temperatures can be between about 300°F and about 400°F, although both higher and lower temperatures can also produce selectively compressed ePTFE microstructures. The nip pressure can be varied depending on the desired degree of compression. Nip pressures of between  
30 about 10 and about 2000 pounds per linear inch ("pli") are believed to be particularly acceptable. In an aspect of the invention nip pressures of between about 100 pli and about 1000 pli may be acceptable. In a further aspect of the invention nip pressures of between about 200 pli and about 800 pli may be acceptable. The gap between the two compression rolls should be set to impart  
35 the desired nip pressure. Likewise, the line speed controls the residence time in the nip. Thus, slower line speeds will enable the ePTFE article to be subjected to the nip environment for a longer time as compared to when higher line speeds are used. In an aspect of the invention a line speed of between 1 yard per minute

("ypm") and 50 ypm can be used. In a further aspect of the invention, a line speed of between 5 ypm and 30 ypm can be used. In a still further aspect of the invention a line speed of between 10 ypm and 20 ypm can be used.

A third process for the selective compression of ePTFE film or ePTFE  
5 film/textile laminate is through the use of two pattern rolls as depicted in Figure 3. In this process, the high and low portions of each pattern roll 1' and 1'' are synchronized so that the two rolls effectively mate with each revolution. This male/female set creates an enhanced, selective compression pattern. The  
10 intensity of the pattern can be adjusted based on the tolerances between the two mating parts. The extent of selective compression imparted to the ePTFE film or ePTFE film/textile laminate depends in part on the gap between the two mating rolls, the temperature and pressure of the rolls, as well as the speed with which the article passes through the nip. As shown in Figure 3, while this  
15 process can be used on ePTFE film alone or on a 2 layer ePTFE film 2/textile 3 laminate, the process can also be used on 3 layer laminate of textile 3 /ePTFE film 2/textile 5, as shown in the Figure.

A fourth process for the creation of selectively compressed ePTFE film or ePTFE film/textile laminates is through the selective compression of an  
20 ePTFE film followed by lamination of the selectively compressed ePTFE to at least one textile material. In this process, an ePTFE film can be compressed between either a patterned surface and a smooth surface or between two patterned surfaces, as described above. If two patterned surfaces are used, these two surfaces do not need to be the same. In practice, this compression can be produced by passing the ePTFE film between the nip which is formed between  
25 either one patterned roll and one smooth roll or comprised of two pattern rolls.

Irrespective of the process used, it is also possible to add further materials to the selectively compressed polymer film or polymer film/textile laminate. For example, it may be desirable to provide various colors to a surface of the film or laminate. This can be achieved by, for example, providing colored  
30 materials (such as colored polymers or pigments, colored polymer films, etc.) in contact with a surface of the film or laminate prior to selective compression. Upon completion of selective compression, the desired colored material can be selectively visible through the compressed film regions.

Other suitable processes for selectively compressing polymer film or  
35 polymer film/textile laminates will now be readily apparent to the skilled artisan. The resultant material is not only aesthetically pleasing, but has other surprising, improved properties, as compared to a non-compressed polymer film or polymer film/textile laminate. For example, selectively compressed ePTFE film/textile

lamine will remain breathable and will also compact better than a similar, but non-compressed lamine. Furthermore, selectively compressed ePTFE film/textile lamine will result in an ePTFE film layer that resists scratching, as compared to a similar, but non-compressed lamine. Moreover, selectively  
5 compressed ePTFE film/textile lamine has better (i.e. softer) "hand" (as described herein), than a similar, but non-compressed lamine.

The selectively compressed polymer film/textile laminates will have many useful applications as the skilled artisan will now understand. Exemplary articles that can be produced using the laminates include, for example, garments  
10 such as shirts, pants, gloves, shoes, jackets, vests, hats, etc. Further articles include, for example, tents, sleeping bags, etc. Such articles can be produced so that the polymer film faces outward and is the outer surface of the article. Moreover, such articles can be produced so that the polymer film faces inward (such as the inside surface of a garment) and is the inner surface of the article,  
15 thus obviating the need for an inner textile layer. Moreover, garments can be engineered to be fully reversible, so that the polymer film can face either outward or inward.

### **DEFINITIONS**

20 "Breathable" refers to polymer film/textile laminates that have a Moisture Vapor Transmission Rate (MVTR) of at least about 1,000 (grams/(m<sup>2</sup>)(24 hours)).

"Selective compression" refers to any process by which a region of the polymer film is compressed relative to a second region within the same  
25 specimen, resulting in the compressed region being more translucent than the non-compressed region. Thus, a selectively compressed polymer film will have at least two regions of differing translucency.

"Lamine" refers to any layered composite that comprises at least one polymer layer and at least one textile layer, the layers of which are, typically,  
30 adhered together.

By "Adhered" or "Adhered together" it is meant that the polymer material (e.g., ePTFE film) and textile material are joined together by suitable bonding media. The bonding media can be adhesive dots, adhesive applied as a continuous grid pattern, adhesive applied as continuous lines, a continuous,  
35 breathable adhesive layer, a fusion bonded interface, or any other material which provides for adhesion between the textile layer and the polymer layer. In an aspect of the invention at least one layer of material (typically hydrophilic polymer) can be provided between the polymer film and the textile material.

For example, a thin layer of hydrophilic polyurethane can be provided to the surface of an ePTFE film before the film is adhered to a textile material. Suitable adhesive can then be applied to the breathable polyurethane layer and then joined to the textile material. According to the invention the ePTFE film and the textile are considered adhered together even though at least one layer of material (such as hydrophilic polymer) is provided between them, in addition to the adhesive. In a further aspect of the invention the at least one layer of material can act as both a hydrophilic layer and as the adhesive material, thus obviating the need for applying another layer of adhesive material. Further variations will be apparent to the skilled artisan.

“Waterproof” is determined by conducting waterproof testing as follows: Laminates are tested for waterproofness by using a modified Suter test apparatus, which is a low water entry pressure challenge. Water is forced against a sample area of about 4 ¼ inch diameter sealed by two rubber gaskets in a clamped arrangement. The sample is open to atmospheric conditions and is visible to the operator. The water pressure on the sample is increased to about 1 psi by a pump connected to a water reservoir, as indicated by an appropriate gauge and regulated by an in-line valve. The test sample is at an angle and the water is recirculated to assure water contact and not air against the sample’s lower surface. The upper surface of the sample is visually observed for a period of 3 minutes for the appearance of any water which would be forced through the sample. Liquid water seen on the surface is interpreted as a leak. A passing (waterproof) grade is given for no liquid water visible within 3 minutes. Passing this test is the definition of “waterproof” as used herein.

25

## **TEST METHODS**

### **COMPACTION**

Compaction volume of a pattern selectively compressed ePTFE laminate and non-selectively compressed samples are tested using ASTM Designation F 1853-98, Standard Test Method for Measuring Sleeping Bag Packing volume. The method quantifies and compares the packing volume of sleeping bags and like textile constructions under a standardized load. The standard cylinder used to test sleeping bags measures about 18 inches in diameter by about 32 inches high. However, for smaller test specimens, an about 5.5 inch diameter by about 31 inch high cylinder is used. The weight used to compress garment and laminate samples is about 25 pounds. The test sequence requires placing the test specimen within the circular round cylinder, and allowing it to settle, and when stable a plate that is slightly undersized, but closely matches the inside diameter

of the measuring cylinder is placed on top of the garment, and the 25 pound weight load is lowered into place on top of the plate. The material is compressed by the weight. The height of the compacted material within the cylinder is measured by a scale affixed to the measuring cylinder.

5 Measurements are taken of the compressed material at two location opposite to one another to the nearest 1/16 inch. The material is then removed, the laminate shaken out and allowed to relax. After several minutes it is replaced within the cylinder, and the test repeated. The four resulting height measurements are then averaged to yield the garment compaction height.

10

### **WEIGHT**

Weight of samples are measured on a Mettler-Toledo Scale, Model 1060. The scale is recalibrated prior to weighing specimens. All weights are recorded in ounces to the nearest half ounce.

15

### **HAND**

AATCC (American Association of Textile Chemists and Colorist) Evaluation Procedure 5 is used to measure the effect of selective compression on the hand of ePTFE laminates by using a bending test. The equipment used is a Handle-O-Meter, Model 211-5-10 manufactured by Thwing/Albert Instrument Co. Philadelphia, PA. Ten test specimens of the desired material are cut to about 4 inch x about 4" squares. Five are cut in the fill direction. Five are cut in the warp direction. All specimens are then conditioned at  $70 \pm 2$  °F,  $65 \pm 2\%$  Relative Humidity (hereinafter "RH") for about 4 hours prior to testing. An about 1000 gram beam is used to push the test specimens through an about 1/4" slot. The resistance force, related to the bending stiffness of the fabric, is measured and displayed digitally. The peak force is recorded and used to compare samples. The samples are then averaged tested for hand using the Handle- O-Meter.

30

### **MOISTURE VAPOR TRANSMISSION RATE TEST-- (MVTR)**

Samples are die-cut circles of 7.4 cm diameter. The samples are conditioned in a 23°C, 50%  $\pm 2\%$  RH test room for 4 hours prior to testing. Test cups are prepared by placing 15 ml of distilled water and 35 g of sodium chloride salt into a 4.5 ounce polypropylene cup, having an inside diameter of 6.5 cm at the mouth. An expanded PTFE membrane (ePTFE), available from W. L. Gore and Associates, Incorporated, Elkton, Maryland, is heat sealed to the lip of the cup to create a taut, leakproof microporous barrier holding the salt

35

solution in the cup. A similar ePTFE membrane is mounted taut within a 5 inch embroidery hoop and floated upon the surface of a water bath in the test room. Both the water bath and the test room are temperature controlled at 23°C.

5 The sample is laid upon the floating membrane, a salt cup is weighed, inverted and placed upon the sample. After one hour, the salt cup is removed, weighed, and the moisture vapor transmission rate is calculated from the weight pickup of the cup as follows:

$$10 \quad \text{MVTR (grams/(m}^2\text{)(24 hours)) = Weight (g) water pickup in cup/ [Area (m}^2\text{) of cup mouth multiplied by the Time (days) of test].}$$

A combined moisture permeability is determined by one of two ways. The preferred way is to place the two adherends physically in contact, without adhesive, between the two ePTFE membranes of the test, as taught above. In this  
15 manner the adherends are positioned such that the measurement is a direct determination of the moisture vapor transmission rate of the adherends in series. There are certain situations where this configuration is not practical and as such the combined moisture permeability (used interchangeably with moisture vapor transmission rate herein, MVTR) can be mathematically determined from the  
20 previously independently determined moisture transmission rate of the two adherends. This is accomplished by equating the sum of the reciprocals of the adherend MVTRs to the reciprocal of the combined MVTR and solving for the combined MVTR.

### 25 ABRASION

The test used for abrasion is the Abrasion Resistance of Textile Fabrics Abrasion standard test method D. 4966-98 (Martindale Tester Method), by  
subjecting specimens to a rubbing motion against a piece of felt for 3,000 movements. The abraded samples are visually inspected for any change in  
30 aesthetics. Samples are preconditioned, then placed in a conditioned room at 70 °F ± 2° F and 65 ± 2% RH for at least four hours prior to testing. A piece of felt measuring about 5.5 inches square followed by a piece of the standard laminate of the same size is placed on the testing table. The machine mounting weight is placed on the table to flatten the felt/laminate samples. The felt/laminate is  
35 secured to the table with the mounting weight in place, then the weight is removed to inspect for tucks or ridges. The specimen is then placed face down into the specimen holder. The assembled holder is placed on the machine with a foam and wool abradent and the required weight is added to give pressure on

each specimen. The amount of pressure is  $1.31 \pm 0.03$  psi. The counter is set to record the desired movements, and the machine started. After 3,000 movements, visual examination is done.

### 5 CURL

Curl of desired fabric laminates is measured using Gore Test Method Fabla 00179. Test specimens are cut into about 5 inch by 5 inch squares. Three specimens are tested in the fill direction, and three in the warp direction. After cutting, specimens are taken into a conditioned lab, maintained at  $70 \pm 2^\circ\text{F}$ , and  
10  $65 \pm 2\%$  RH for about four hours. The specimens are observed to detect any curl. If some curl is present, each specimen is placed with the curled side up on a flat surface away from drafts or air from fans. If no curl is obvious, each specimen with the film side up is placed onto a flat surface away from drafts or air from fans. If no curl is obvious on the fabric side, the sample is placed fabric  
15 side up on a flat surface away from drafts or air from fans. Specimens are allowed to lay undisturbed for about four hours.

After the about four hour equilibration period, each specimen is visually inspected and given a score of from 0 to 5. The direction of curl, if present, is also recorded for both fill and warp specimens. A lower curl score indicates a  
20 sample that lies more flat. A curl score of 5 indicates a sample that will spontaneously roll up into a rod-like shape. A curl score of 0 indicates a sample that lies flat.

### GREY-SCALE

25 The grey-scale of the micrographs of selectively compressed and of non-compressed control samples were analyzed via the following method. Depending on the magnification required, the micrograph image was captured from either an optical microscope or a scanning electron microscope. The captured digital image was then converted to pixels. Image analysis software by  
30 EDAX was then used to create a frequency distribution of the grey-scale pixels.

### 3-DIMENSIONAL SURFACE MAP

A 3-dimensional surface map of selectively compressed laminate samples was created using a Zygo Optical Surface Profilometer. A ten times  
35 objective lens was used and unless otherwise stated, a 100 micro bipolar distance was scanned. The resulting 3-dimensional surface map was then saved as a bit map for subsequent inclusion in other files.



The following non-limiting examples are provided to further exemplify aspects of the invention.

## EXAMPLES

### 5 Example 1

A 2 layer laminate comprised of a brushed knit and an ePTFE film from W.L. Gore & Associates, Inc., of Elkton, MD, part number KAEX001000D was selectively compressed using the following process. A 3 roll lab calendering system, from B.F Perkins of Rochester, N.Y. was used. The  
10 machine, having an about 22" face, was run at a speed of about 10 to about 15 feet per minute, with floor mounted unwind and rewind, and a 2 zone fluid heating system. The rollers were heated to a temperature of about 240°F. A hardened metal leather patterned roll and a smooth, filled cotton mating roll were used. One sample of the laminate was run through with the ePTFE surface  
15 facing the patterned roll. A second sample of the laminate was run through with the fabric surface facing the patterned roll. In both cases, the image of the pattern was transferred onto the ePTFE film side of the 2 layer laminate. Both appearance and texture had been changed. The ePTFE surface had the appearance of the leather pattern of the roll.

20 Figure 4 is an optical micrograph of the ePTFE side of the laminate, after selective compression. The selectively compressed regions of the ePTFE appear to be darker in color, but in fact are more translucent and show the color of the textile on the opposite side of the ePTFE. The non-compressed regions are clearly shown to be the known "white" color of non-compressed ePTFE.

25

### Example 2

A 2 layer laminate comprised of a brushed knit and an ePTFE film from W.L. Gore & Associates, Inc., of Elkton, MD, part number KAEX00100D was selectively compressed using the following process. A 2 roll production  
30 calendering system at Lee Fashion Fabrics, Inc. of Johnstown, N.Y. was used. The machine, having an about 56 inch face, was run at a speed of about 30 feet per minute. The rolls were heated to about 350°F. A hardened metal paisley patterned roll and a smooth, hard rubber roll were used. One sample of the laminate was run with the ePTFE surface facing the patterned roll. A second  
35 sample of the laminate was run with the fabric surface facing the patterned roll. In both cases, the image of the pattern was transferred onto the ePTFE film side of the laminate. Figure 5 is an optical micrograph of the ePTFE film side of the laminate. Both appearance and texture had been changed. The ePTFE surface

had the appearance of the paisley pattern of the roll. As in Example 1, the selectively compressed regions of the ePTFE film appear to be darker, but in fact are more translucent and show the color of the textile material on the opposite side of the ePTFE. The non-compressed regions are clearly seen to be  
5 the known "white" color of ePTFE.

### **Example 3**

A 2 layer laminate comprised of a brushed knit and an ePTFE film from W.L. Gore & Associates, Inc., of Elkton, MD, part number KKRX620000 was  
10 selectively compressed using the following process. A 2 roll production calendering system at Lee Fashion Fabrics, Inc. of Johnstown, N.Y. was used. The machine, having an about 56 inch face, was run at a speed of about 30 feet per minute. The rolls were heated to about 350°F. A hardened metal leather patterned roll and a smooth, hard rubber roll were used. One sample of the  
15 laminate was fed through with the ePTFE surface facing the patterned roll. A second sample of the laminate was fed through with the fabric surface facing the patterned roll. In both cases, the image of the pattern was transferred onto the ePTFE film side of the laminate, as depicted in the optical micrograph shown in Figure 6. Both appearance and texture had been changed. The ePTFE surface  
20 had the appearance of the leather pattern of the roll.

The various depths of the image on the patterned roll produced a surface image and pattern of varying degrees of translucency. Figure 7 is a grey-scale spectra that depicts the range of shades that were effectively imparted to the formerly white ePTFE film-side of the laminate.  
25

### **Example 4**

A 2 layer laminate comprised of a knit and an ePTFE film from W.L. Gore & Associates, Inc., of Elkton, MD, part number KKRX620000 was selectively compressed using the process and machine described in Example 2.  
30 The roller temperature was about 350°F. The machine was run at a speed of about 30 feet per minute. A hardened metal, stripe-patterned roll and a smooth, hard rubber roll were used for this example. A sample of the laminate was fed with the ePTFE surface facing the patterned roll. A second sample of the laminate was fed with the fabric surface facing the patterned roll. The image of  
35 the stripe pattern was transferred onto the laminate. When the white ePTFE film side was facing the patterned roll, the image transferred to the film appeared crisp and sharp. When the knit faced the patterned roll, the image transferred to the ePTFE film and while still very clear, was slightly more diffuse and subtle.

Figure 8 is an optical micrograph that shows the surface image created by the stripe pattern selective compression. Figure 9 shows the corresponding grey-scale frequency distribution highlighting the fact that the translucency varies with the degree of selective compression. Figure 10 shows an SEM cross-section micrograph of the transition between the compressed and non-compressed areas. Figure 11 shows a 3-dimensional surface map depicting the various depths of selective compression that resulted. Figure 12 shows a Zygo profilometer scan of the surface of a single stripe of this stripe patterned selectively compressed laminate sample.

10

### **Example 5**

A 2 layer laminate comprised of a knit and an ePTFE film from W.L. Gore & Associates, Inc., of Elkton, MD, part number KKRX62000 was selectively compressed using the process and machine described in Example 2. The roller temperature was about 350°F. The machine was run at a speed of about 30 feet per minute. A hardened metal, snake skin-patterned roll and a smooth, hard rubber roll were used. One sample of the laminate was fed with the ePTFE surface facing the patterned roll. A second sample of the laminate was fed with the fabric surface facing the patterned roll. The image of the linen pattern was transferred onto the laminate. When the white ePTFE film side was facing the patterned roll, the image transferred to the film appeared crisp and sharp. When the knit faced the patterned roll, the image transferred to the ePTFE film and while still very clear, was slightly more diffuse and subtle.

### **Example 6**

A 2 layer laminate comprised of a knit and an ePTFE film which was coated with a breathable polyurethane layer from W.L. Gore and Associates, part number WNAX467000 was selectively compressed using the process described in Example 1, using the same roller temperature and line speed. A hardened metal, linen-patterned roll and a smooth, hard rubber roll were used. One sample of the laminate was fed with the ePTFE surface facing the patterned roll. A second sample of the laminate was fed with the fabric surface facing the patterned roll. The image of the linen pattern was transferred onto the laminate. When the white ePTFE film side was facing the patterned roll, the image transferred to the film appeared crisp and sharp. When the knit faced the patterned roll, the image transferred to the ePTFE film and while still very clear, was slightly more diffuse and subtle.

**Example 7**

A 2 layer laminate comprised of a brushed knit and an ePTFE film from W.L. Gore & Associates, Inc., of Elkton, MD, part number KAEX00100D was selectively compressed using the following process. A 3 roll lab calendering system, from B.F Perkins of Rochester, N.Y. was used. The machine, having a 22" face, was run at a speed of about 10 to about 15 feet per minute, with floor mounted unwind and rewind, and a 2 zone fluid heating system. A smooth, hardened metal roll and a smooth, filled cotton counter roll were used. One sample of the laminate was fed with the ePTFE surface facing the metal roll. A second sample of the laminate was fed with the fabric surface facing the metal roll. In both cases, the yarns of the knit material caused the ePTFE film to be selectively compressed so that the knit pattern was effectively transferred onto the ePTFE film of the laminate.

**Example 8**

A 3 layer laminate comprised of a knit material on each side of a two layer ePTFE film construction, between which was sandwiched a breathable polyurethane layer, was selectively compressed. One side of the 3 layer laminate had a lighter weight knit than the opposite side (W.L. Gore and Associates, part number KPBX602607). The 3 layer laminate was selectively compressed using the process described in Example 2, using the same roller temperature and same line speed. A hardened metal, snake skin-patterned roll and a smooth, hard rubber roll were used. The laminate was fed through the rollers with the lighter-weight knit surface facing the patterned roll. The image of the snake-skin pattern was transferred onto the 3 layer laminate.

**Example 9: Compaction tests**

Three selectively compressed laminate samples and their respective controls were tested for compaction using the test method described above. Sample 1 was a three layer ePTFE containing laminate (Gore Part #WNAX002604A). The control for Sample 1 was a non-compressed laminate of this material. Sample 1 was produced by taking a sample of this laminate and selectively compressing the laminate as described in Example 2, using a snake skin patterned roll. Sample 2 was a two layer ePTFE containing laminate (Gore Part #WKPX003000). The control for Sample 2 was a non-compressed laminate of this material. Sample 2 was produced by taking a sample of this laminate and selectively compressing the laminate as described in Example 2. Sample 3 was a three layer ePTFE containing laminate (Gore Part #

KPBX602607). The control for Sample 3 was a non-compressed laminate of this material. Sample 3 was produced by taking a sample of this laminate and selectively compressing the laminate as described in Example 2.

Each laminate was then cut to a size of about 72 inches by about 52 inches to produce samples for compaction testing. Each laminate sample was lowered into the test cylinder, allowed to settle for about 1 minute. When stable, weights measuring about 25 pounds were lowered on top of the plate. The test specimen was compressed by the weight. The height of the compacted test specimen within the cylinder was measured by a scale affixed to the measuring cylinder. Measurements of the height of the compressed test were taken at two locations opposite to one another, with height measurements being to the nearest 1/16 inch. As discussed above, the test was repeated for each sample and the measurements averaged to yield the reported Compacted Height.

Table 1

Sample	Selective Compression Process	Control Sample Compacted Height (inches)	Selectively Compressed Sample Compacted Height (inches)
Sample 1	Compressed as described in Example 2	2.75	2.50
Sample 2	Compressed as described in Example 2	3.00	2.63
Sample 3	Compressed as described in Example 2	3.13	2.75

**Example 10 – Hand**

Following the procedure described in Example 2 above, a 3 layer ePTFE laminate (Gore Part #WNAX002604A) was selectively compressed. The hand of this test specimen was compared to the control laminate (non-compressed Gore Part # WNAX002604A). A lower hand score indicates a softer sample. The control laminate registered a hand of 194 and the selectively compressed laminate registered a hand of 134.

**Example 11 – Curl**

Following the procedure described in Example 2 above, a lightweight 2 layer ePTFE laminate (Gore Part # ASND 152000P3) was selectively compressed. The curl of this test specimen was compared to the control (non-compressed Gore Part #ASND 152000P3) laminate. The control laminate was

judged to have a curl value of 0 and the selectively compressed laminate was judged to have a curl value of 4.

**Example 12 – Breathability and waterproofness results**

- 5 Six laminate materials were selectively compressed as described in Example 2. The selectively compressed laminates and control laminates (the same laminate, but not selectively compressed) were tested for Water Vapor Transmission Rate (i.e. breathability) using the test method described above. Each laminate sample was tested before and after selective densification.
- 10 Moreover, each selectively compressed laminate was tested for waterproofness. The results are shown in Table 2.

Table 2

Sample	Pattern used to impart selective compression	Control MVTR (g/(m <sup>2</sup> )(24 hours))	Selectively Compressed MVTR (g/(m <sup>2</sup> )(24 hours))	Waterproof Testing Results
2 Layer ePTFE laminate Gore part # KKRX620000	Leather	13,859	12,029	Pass
2 Layer ePTFE laminate Gore part # KKRX620000	Stripe	13,859	12,533	Pass
2 Layer ePTFE laminate. Gore part # WNOX117000	Snake-skin	14,604	12,278	Pass
3 Layer ePTFE laminate. Gore part # KPBX602607	Snake-skin	8,303	7,840	Pass
3 Layer ePTFE laminate. Gore part # WANX002604A	Snake-skin	7,406	6,058	Pass
WINDSTOPPER® brushed knit laminate. Gore part # KAEX00100D	Paisley	19,241	16,178	Pass

15

**Example 13 – Abrasion results**

A first sample of a two layer ePTFE containing laminate (Gore Part #KAEX00100D) was selectively compressed as described in Example 2, using a

paisley patterned roll. A second sample of the same laminate was not selectively compressed. Each sample was then subjected to the Abrasion test described above (i.e. Abrasion Resistance of Textile Fabrics Abrasion standard test method D. 4966-98 (Martindale Tester Method)), with the ePTFE side of each sample being subjected to abrasion.

Optical micrographs of a section of each sample were then taken. Figure 13 is an optical micrograph of a section of the sample that was not selectively compressed. The Figure clearly shows the stark contrast between a portion of the sample that was subjected to the abrasion testing (i.e. the darker portion of the sample) and a portion of the sample that was not subjected to abrasion testing (i.e. the lighter portion of the sample). Figure 14 is an optical micrograph of a section of the sample that was selectively compressed. As can be seen, the paisley pattern of the sample is still present. Although there is still a contrast between the portion of the sample that was subjected to the abrasion testing and the portion of the sample that was not subjected to the abrasion testing, the contrast is not as stark as in the non-selectively compressed sample.

#### **Example 14**

A three layer composite was produced from two ePTFE films and a colored polyurethane film as follows. The colored, 1 mil monolithic polyurethane film was from Deerfield urethanes, Deerfield, MA. In this example, the layers were stacked such that one ePTFE layer was on the bottom, the colored polyurethane film in the center, and the other ePTFE membrane on the top. This stack of films was fusion bonded together using a standard carver press-type apparatus for one minute at 150°C. A silicone foam pad was used on the lower platen to accommodate any pressure variance due to misalignment of the platens. Next, a pattern was created on this three layer composite film using a flat metal die in the shape of a butterfly. The flat metal die was placed beneath the composite three layer film and then the heat press closed for one minute at 150°C. The result was that the image of the metal tool was embossed into the three layer composite. The resulting film exhibited the patterned image of the butterfly-shaped embossing tool in the densified areas of both ePTFE surfaces. As shown in Figure 15, selectively densified ePTFE areas were created where the embossing tool exerted higher pressure on the film. The color of the underlying colored polyurethane film was visible in these selectively densified areas. Conversely, the relatively undensified areas did not allow the color of the colored film to show through the otherwise white surface of the undensified ePTFE film. By varying the number and colors of films used in

conjunction with the ePTFe membrane or membrane, a broad range of performance and aesthetic effects can be provided by this invention. Moreover, it is possible to laminate the film according to this example to textiles to form a laminate material.



## CLAIMS

What is claimed:

1. Laminate comprising:  
5 at least one layer of textile material having a first side and a second side;  
polymer film, having a first side and a second side, adhered to at least  
one of the first and second sides of the textile material, wherein the  
polymer film has at least two regions of differing translucency formed by  
selectively compressing the polymer film.  
10
2. The laminate of claim 1, wherein the polymer film comprises at least  
some interconnected porosity.
3. The laminate of claim 1, wherein the polymer film is directly adhered to  
15 the at least one layer of textile material.
4. The laminate of claim 3, wherein the polymer film is directly adhered to  
the at least one layer of textile material by an adhesive material.
- 20 5. The laminate of claim 3, wherein the polymer film is directly adhered to  
the at least one layer of textile material by fusion bonding.
6. The laminate of claim 2, wherein the polymer film comprises a material  
selected from polytetrafluoroethylene, polyester, polyurethane, and  
25 polyolefin.
7. The laminate of claim 1, wherein the at least one layer of textile material  
is adhered to the polymer film with a discontinuously applied adhesive  
material.  
30
8. The laminate of claim 6, wherein the laminate is breathable.
9. The laminate of claim 1, wherein the polymer film is  
polytetrafluoroethylene.  
35
10. The laminate of claim 9, wherein the polytetrafluoroethylene film further  
includes polyurethane applied to at least one of the first side and the  
second side of the polytetrafluoroethylene film.

11. The laminate of claim 10, wherein the polyurethane is applied as a continuous, breathable layer of polyurethane.
12. The laminate of claim 11, wherein the laminate is waterproof.
- 5 13. The laminate of claim 1, wherein the first side of the polymer film is adhered to the at least one layer of textile material and the second side of the polymer film is adhered to a second textile material.
- 10 14. The laminate of claim 1, wherein the laminate is waterproof.
15. The laminate of claim 14, wherein the laminate is breathable.
16. A garment comprising the laminate of claim 1.
- 15 17. The garment of claim 16, wherein the garment is selected from the group consisting of shirts, pants, gloves, shoes, hats, and jackets.
18. The garment of claim 17, wherein the polymer film is provided as an outer layer of the garment.
- 20 19. The garment of claim 17, wherein the polymer film is provided as an inner layer of the garment.
- 25 20. A sleeping bag comprising the laminate of claim 1.
21. A tent comprising the laminate of claim 1.
22. Laminate comprising:
- 30 at least one layer of textile material having a first side and a second side; porous, expanded polytetrafluoroethylene film, having a first side and a second sides, adhered to at least one of the first and second sides of the textile material, wherein the porous polytetrafluoroethylene film has at least two regions of differing translucency formed by selectively
- 35 compressing the polymer film.

23. The laminate of claim 22, wherein the porous, expanded polytetrafluoroethylene is directly adhered to the at least one layer of textile material.
- 5 24. The laminate of claim 23, wherein the porous, expanded polytetrafluoroethylene is directly adhered to the at least one layer of textile material by an adhesive material.
- 10 25. The laminate of claim 23, wherein the porous, expanded polytetrafluoroethylene is directly adhered to the at least one layer of textile material by fusion bonding.
- 15 26. The laminate of claim 22, wherein the at least one layer of textile material is adhered to the porous, expanded polytetrafluoroethylene with a discontinuously applied adhesive material.
- 20 27. The laminate of claim 22, wherein the porous, expanded polytetrafluoroethylene further includes a layer of hydrophilic polymer applied to at least one of the first side and second side of the porous, expanded polytetrafluoroethylene.
- 25 28. The laminate of claim 27, wherein the hydrophilic polymer comprises at least polyurethane.
- 30 29. The laminate of claim 28, wherein the polyurethane is applied as a continuous, breathable layer.
- 30 30. The laminate of claim 22, wherein the first side of the porous, expanded polytetrafluoroethylene is adhered to the at least one layer of textile material and the second side of the porous, expanded polytetrafluoroethylene is adhered to a second textile material.
- 35 31. The laminate of claim 22, wherein the laminate is waterproof.
32. The laminate of claim 22, wherein the laminate is breathable.
33. The laminate of claim 31, wherein the laminate is breathable.
- 40 34. A garment comprising the laminate of claim 22.

35. The garment of claim 34, wherein the garment is selected from the group consisting of shirts, pants, gloves, shoes, hats, and jackets.
36. A sleeping bag comprising the laminate of claim 22.
- 5 37. A tent comprising the laminate of claim 22.
38. The garment of claim 34, wherein the porous, expanded polytetrafluoroethylene is provided as an outer layer of the garment.
- 10 39. The garment of claim 34, wherein the porous, expanded polytetrafluoroethylene is provided as an inner layer of the garment.
40. Polymer film having at least two regions of differing translucency formed by selectively compressing the polymer film.
- 15 41. The polymer film of claim 40, wherein the polymer film comprises at least some interconnected porosity.
42. The polymer film of claim 40, wherein the polymer film comprises a material selected from the group consisting of polytetrafluoroethylene, polyester, polyurethane, and polyolefin.
- 20 43. The polymer film of claim 42, wherein the polymer film comprises porous, expanded polytetrafluoroethylene.

25

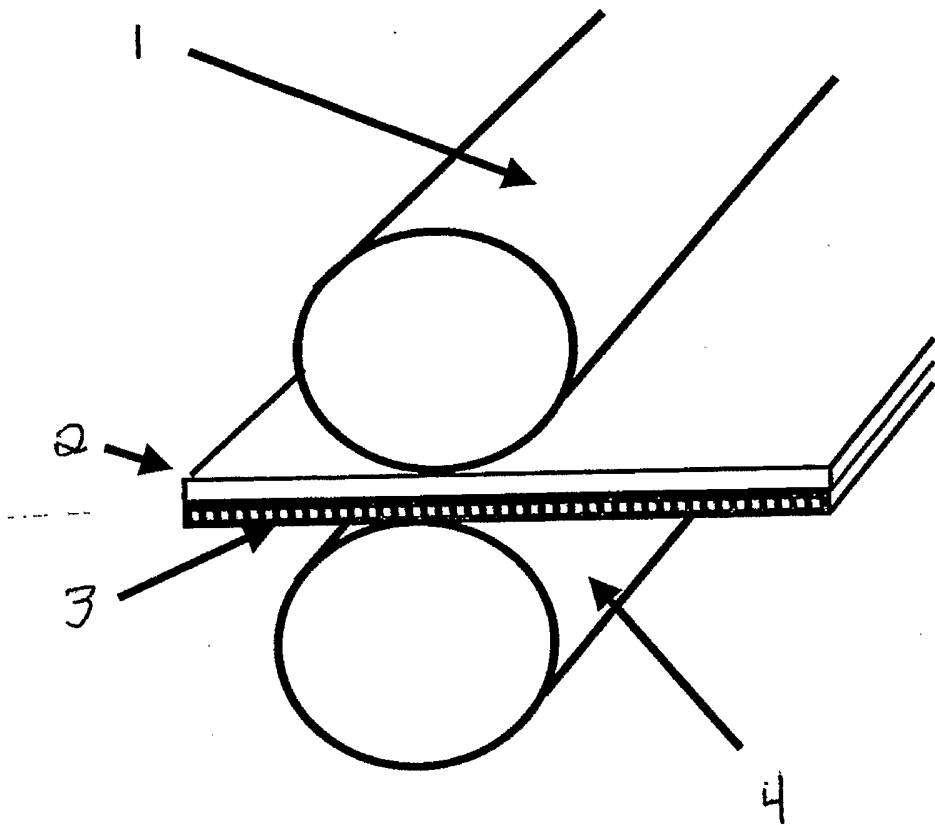


FIGURE 1

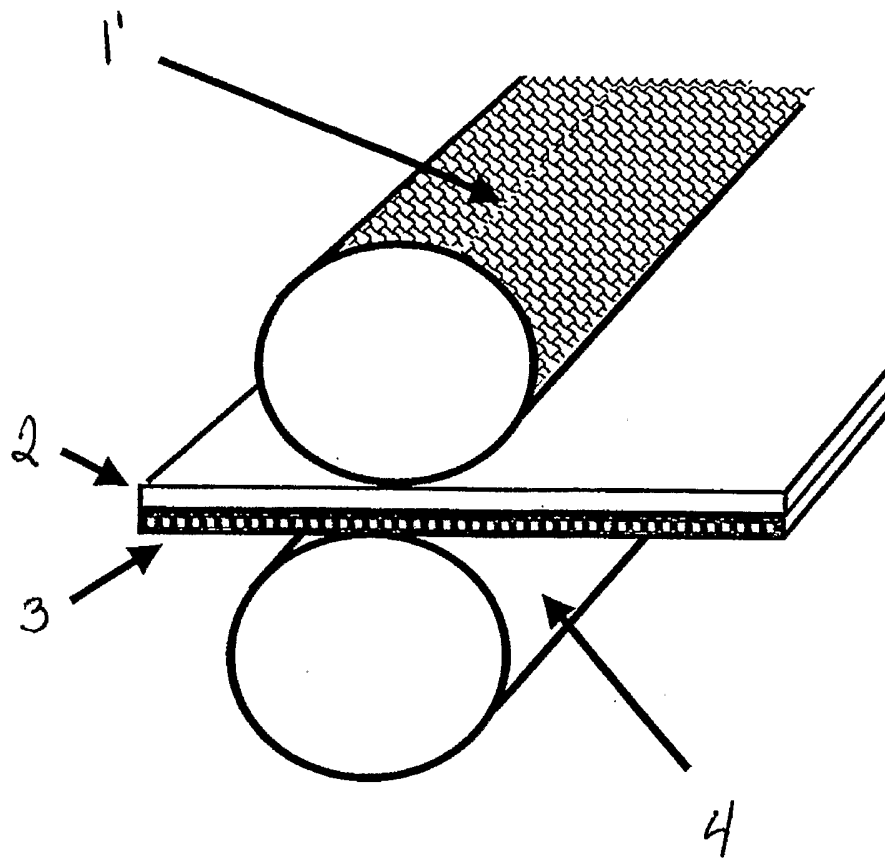


FIGURE 2

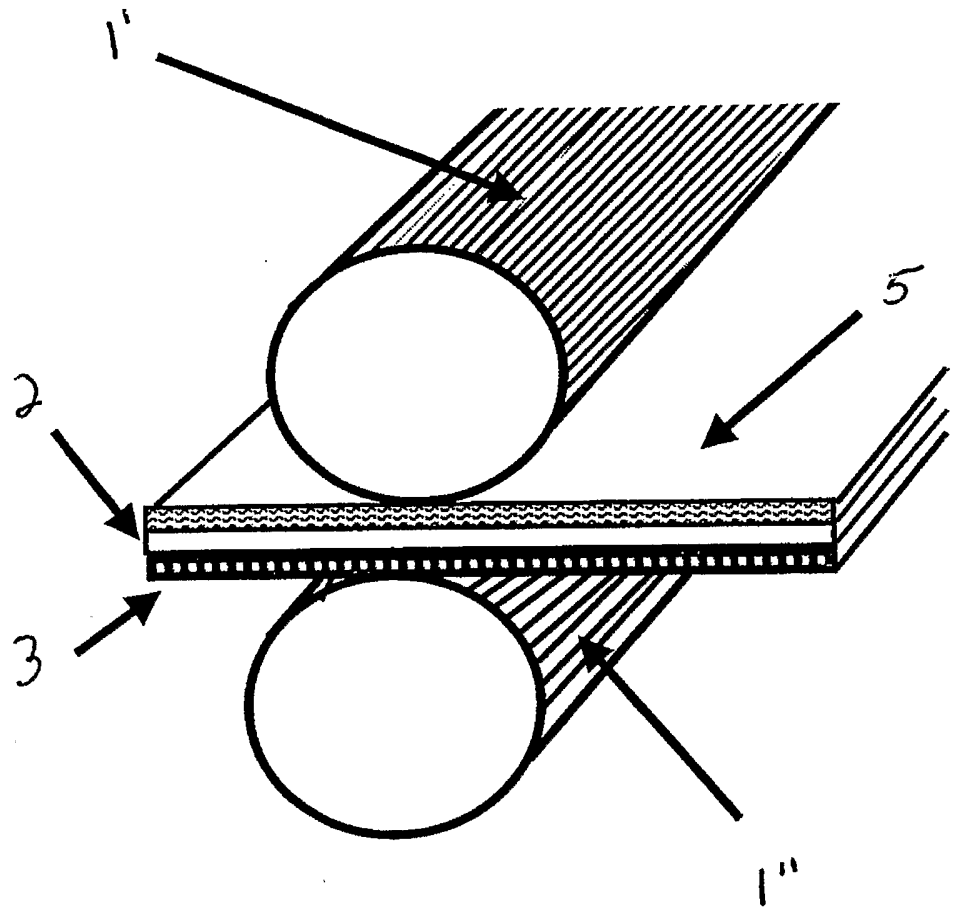


FIGURE 3

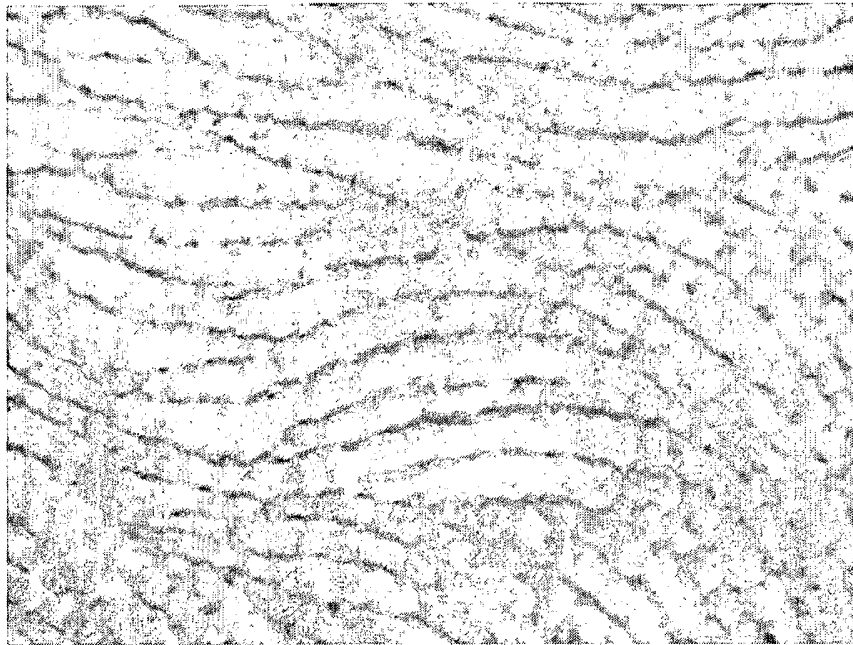


FIGURE 4

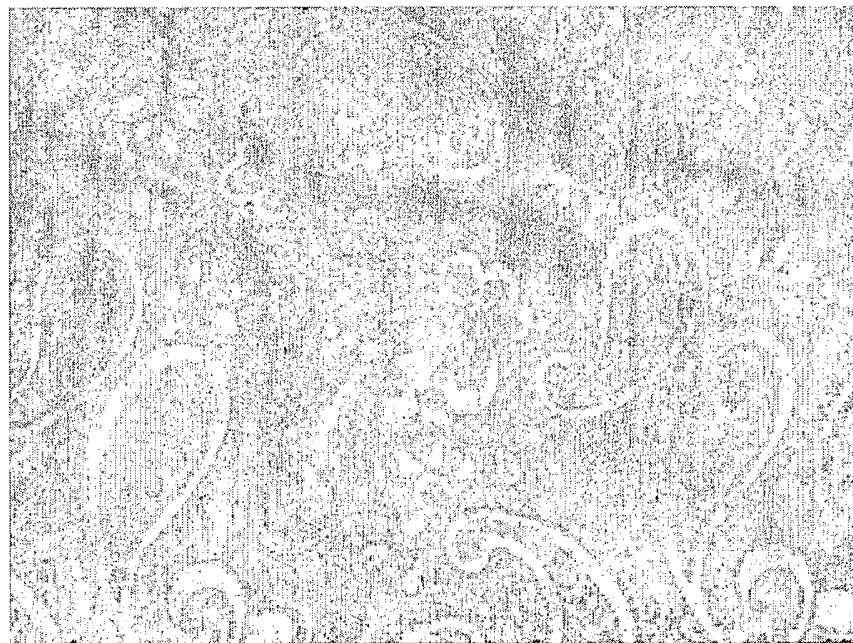


FIGURE 5



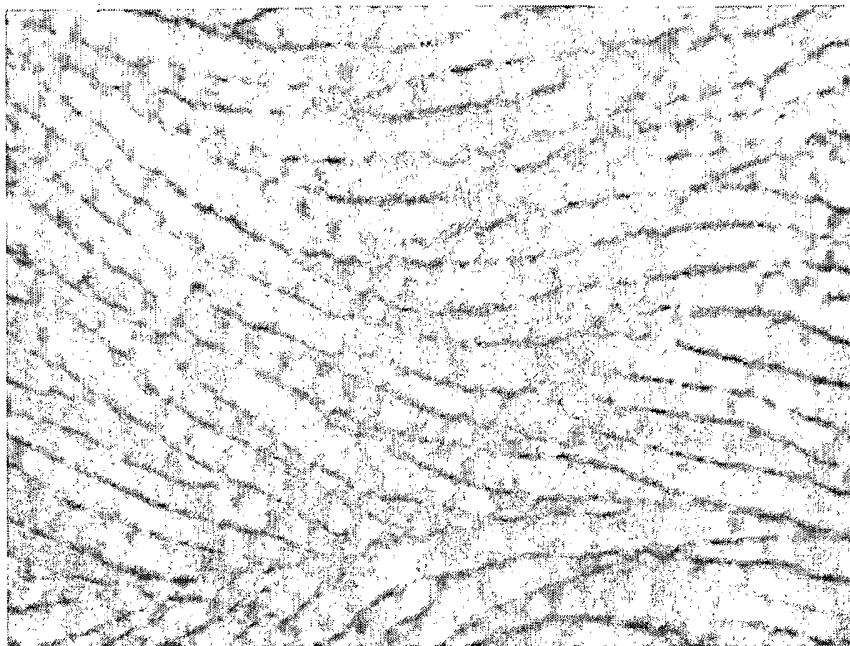


FIGURE 6

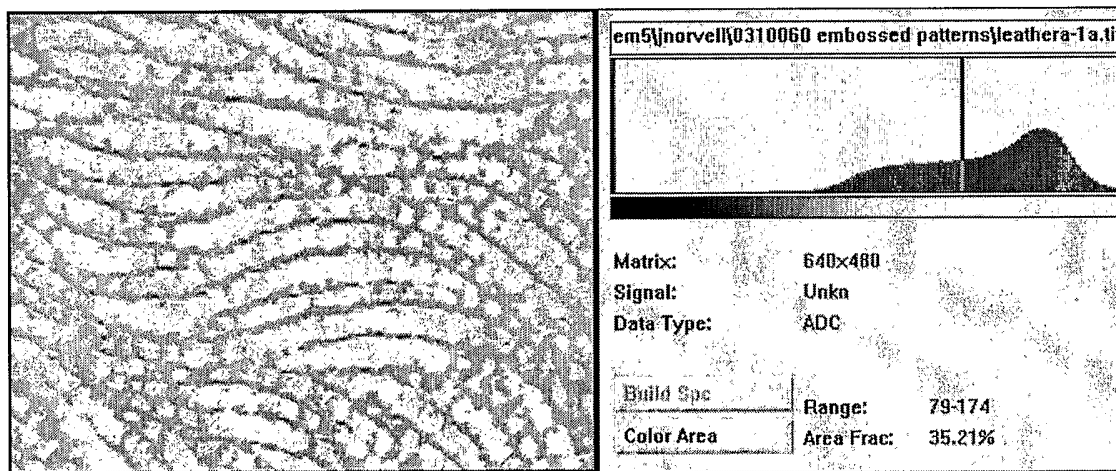


FIGURE 7

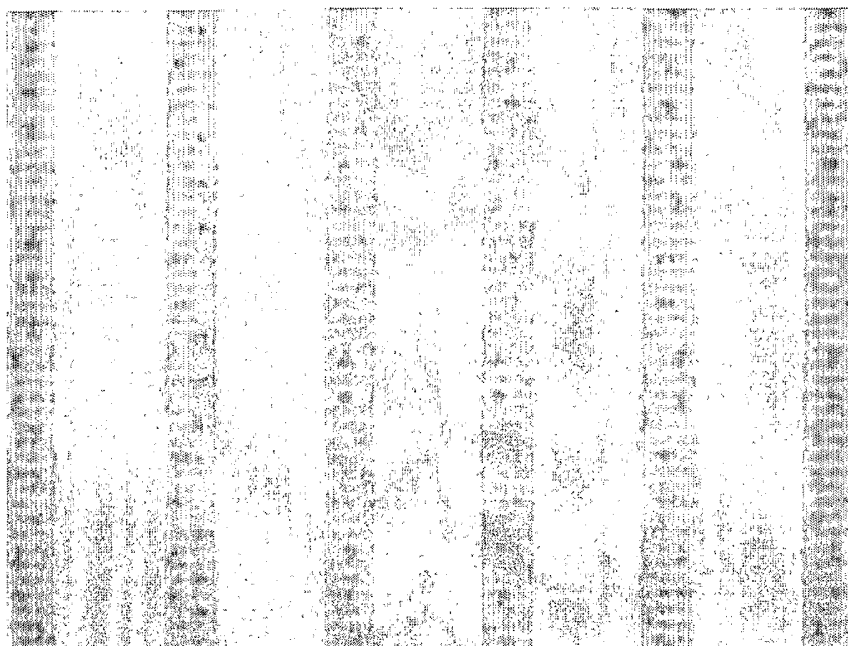


FIGURE 8

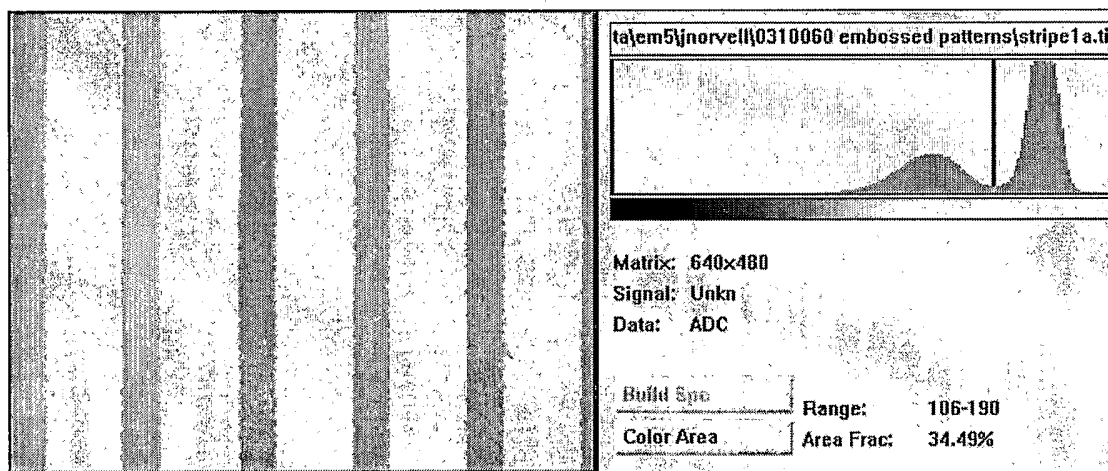


FIGURE 9

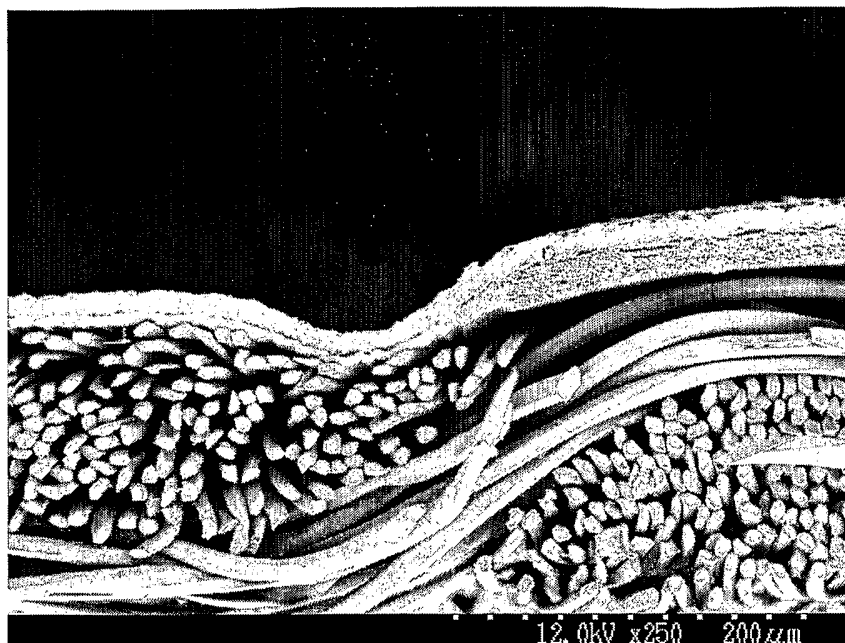


FIGURE 10

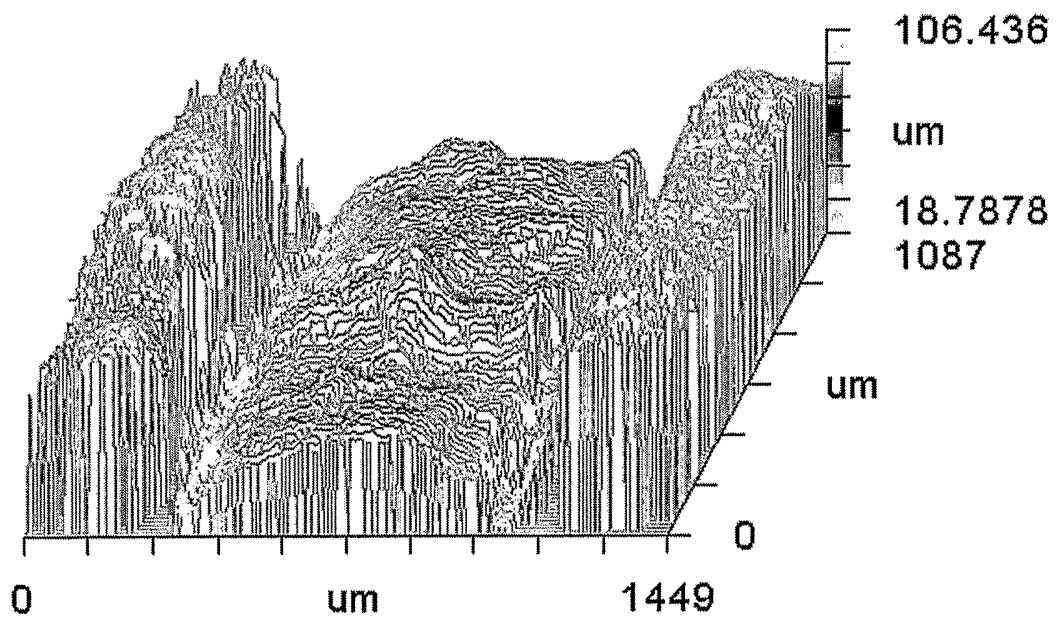


FIGURE 11

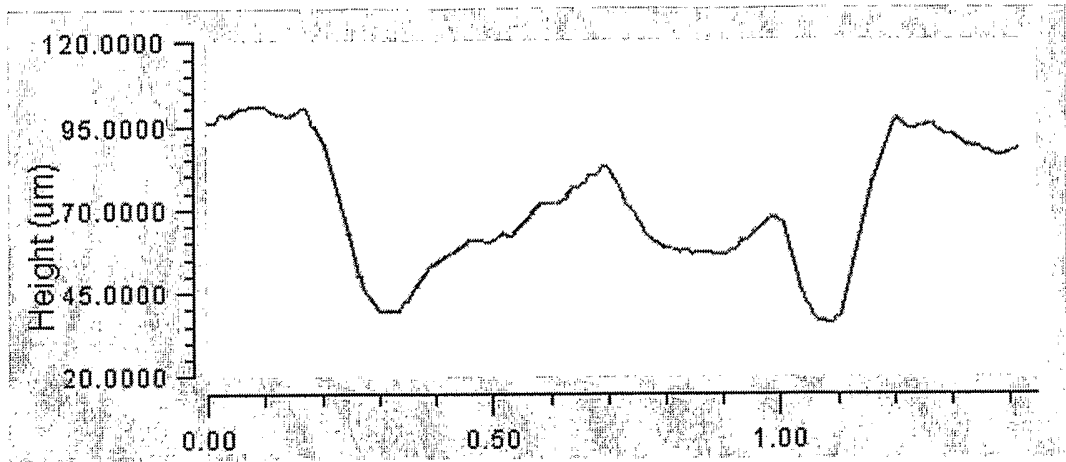


FIGURE 12

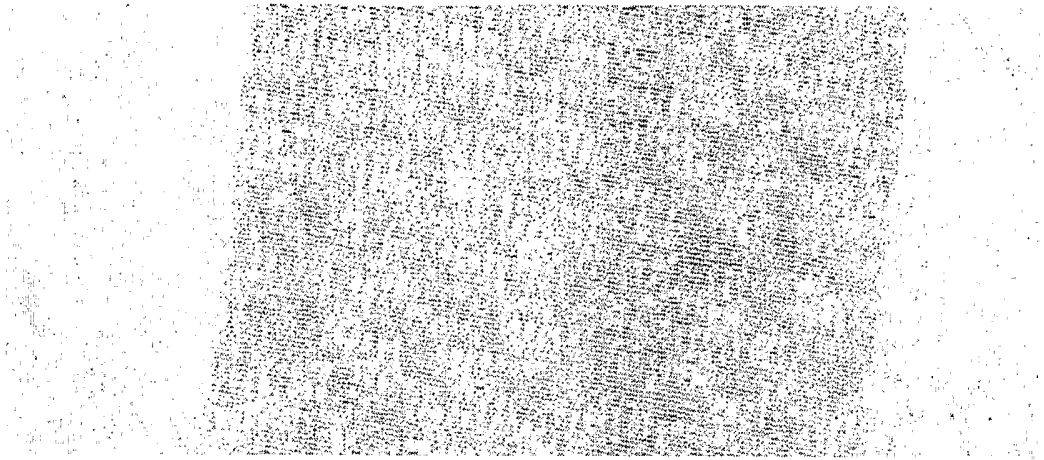


FIGURE 13

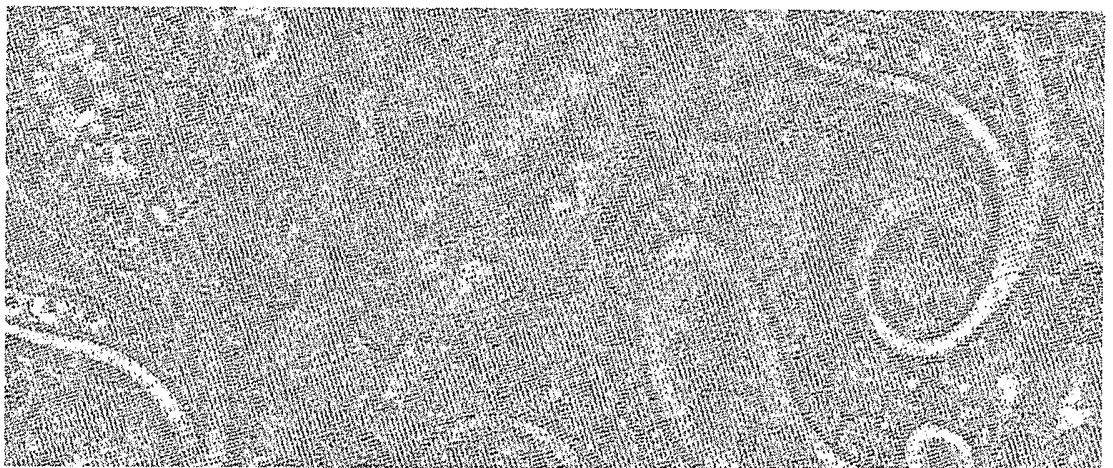


FIGURE 14

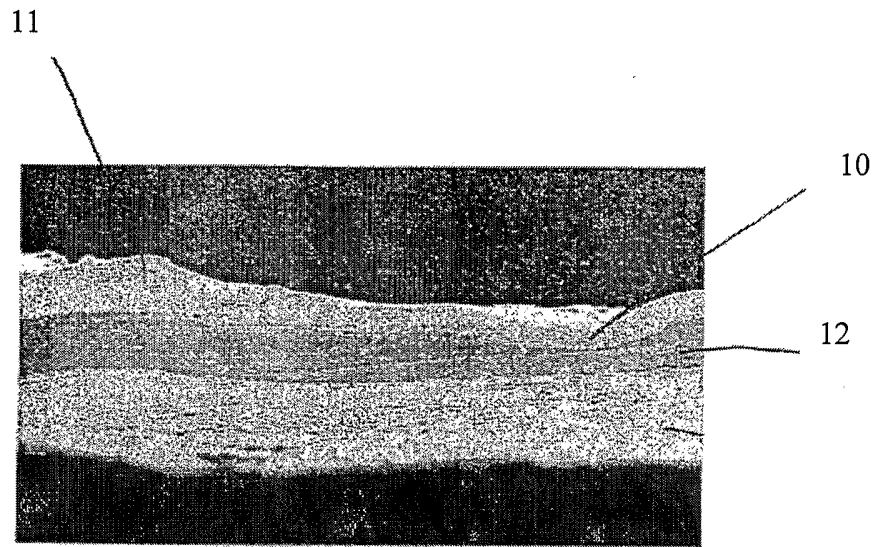


FIGURE 15

INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/040748

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/30 B32B27/36 B32B27/40 B32B5/18 C08J5/18  
B32B27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B32B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 897 541 A (UITENBROEK ET AL) 27 April 1999 (1999-04-27)  abstract column 2, line 18 - column 6, line 60; figures 1,2 column 6, lines 10-41; claims; examples	1-3, 5, 6, 8, 14-18, 40-42
X	EP 0 319 222 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 7 June 1989 (1989-06-07) page 4, line 5 - page 6, line 32; examples examples 7,8	40-42
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search

7 March 2005

Date of mailing of the international search report

21/03/2005

Name and mailing address of the ISA

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Authorized officer

Hutton, D

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/040748

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 277 479 B1 (CAMPBELL STEPHEN MICHAEL ET AL) 21 August 2001 (2001-08-21)  abstract; figures column 2, line 14 - column 17, line 30; examples column 15, line 58 - column 16, line 27 column 11, lines 1-6; claims	1-6, 8, 14-16, 18, 40-42
X	WO 00/38915 A (KIMBERLY-CLARK WORLDWIDE, INC) 6 July 2000 (2000-07-06) page 8, line 22 - page 9, line 13; figures; examples	40-42
X	US 4 609 584 A (CUTLER ET AL) 2 September 1986 (1986-09-02) column 1, line 57 - column 3, line 40 column 3, lines 34-40 column 4, line 4 - column 5, line 59 column 5, lines 43-59; claim 1; examples	1-5, 40-42
X	DE 34 36 065 A1 (HOECHST AG) 17 April 1986 (1986-04-17) page 6, line 10 - page 13, line 2; claims; examples	40, 42
X	US 4 598 003 A (RENHOLTS ET AL) 1 July 1986 (1986-07-01) the whole document	40-43
X	DATABASE WPI Section Ch, Week 197822 Derwent Publications Ltd., London, GB; Class A35, AN 1978-39376A XP002320200 & JP 53 044214 A (TOPPAN PRINTING CO LTD) 20 April 1978 (1978-04-20) abstract	40, 42
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 03, 30 March 2000 (2000-03-30) & JP 11 349702 A (KAO CORP), 21 December 1999 (1999-12-21) abstract	40-42



INTERNATIONAL SEARCH REPORT  
Information on patent family members

International Application No  
PCT/US2004/040748

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5897541	A	27-04-1999	AU 702372 B2	18-02-1999
			AU 3214095 A	26-04-1996
			CA 2152407 A1	31-03-1996
			DE 69515891 D1	27-04-2000
			DE 69515891 T2	07-12-2000
			EP 0785762 A2	30-07-1997
			ES 2143063 T3	01-05-2000
			FR 2725155 A1	05-04-1996
			GB 2293573 A ,B	03-04-1996
			JP 3485325 B2	13-01-2004
			JP 10506586 T	30-06-1998
WO 9610380 A2	11-04-1996			
ZA 9507567 A	17-04-1996			
EP 0319222	A	07-06-1989	US 4824718 A	25-04-1989
			AR 240241 A1	30-03-1990
			AU 2588888 A	15-06-1989
			BR 8806398 A	22-08-1989
			EP 0319222 A2	07-06-1989
			JP 2000504 A	05-01-1990
			JP 7010580 B	08-02-1995
			US 4902553 A	20-02-1990
			ZA 8808910 A	25-07-1990
US 6277479	B1	21-08-2001	AU 739163 B2	04-10-2001
			AU 1923499 A	12-07-1999
			BR 9813648 A	18-06-2002
			CN 1282289 A	31-01-2001
			DE 69815891 D1	31-07-2003
			DE 69815891 T2	18-12-2003
			EP 1042114 A1	11-10-2000
			JP 2001526127 T	18-12-2001
			RU 2218276 C2	10-12-2003
			WO 9932272 A1	01-07-1999
WO 0038915	A	06-07-2000	AU 2222200 A	31-07-2000
			BR 9916639 A	15-06-2004
			DE 19983893 T0	29-11-2001
			GB 2364512 A ,B	30-01-2002
			WO 0038915 A1	06-07-2000
			US 6719742 B1	13-04-2004
US 4609584	A	02-09-1986	BR 8604353 A	12-05-1987
			CA 1280879 C	05-03-1991
			EP 0219978 A2	29-04-1987
			JP 62068459 A	28-03-1987
DE 3436065	A1	17-04-1986	NONE	
US 4598003	A	01-07-1986	NONE	
JP 53044214	A	20-04-1978	JP 1398421 C	07-09-1987
			JP 62002998 B	22-01-1987
JP 11349702	A	21-12-1999	NONE	