3,594,213
PROCESS FOR CONTROLLING POROSITY IN FIBROUS WEBS
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12 Claims

ABSTRACT OF THE DISCLOSURE
A process for controlling porosity in fibrous webs, The process includes a combination of steps comprising imparting movement to a fibrous web so as to present a moving surface, depositing a substantially liquid material on the moving surface, embedding the liquefied material into continuous portions of the moving surface, and applying a force equally on each continuous portion simultaneously and continuously with the embedding step so as to cause attachment of additional liquefied material with the embedded material. This process is particularly adapted for manufacture of products which are useful in filtering gases, chemicals, and liquids. Waterproof fabrics having air and water-vapor permeability may also be produced according to the process.

DESCRIPTION OF PRIOR ART
It is generally known that conventional mechanical devices and methods used in coating and impregnating webs such as paper, fabric, and the like, with liquid materials of various viscosities, are not adaptable for obtaining uniform or controlled porosities in the webs. This is particularly true, for example, of devices and methods employing rotating rollers but it is also the case with conventional doctor blade applicators. When rotating rollers are used, extreme accuracy of porosity control in the web becomes almost an impossibility because of the eccentricity of the periphery of the roller surface, which usually cannot be held to less than .001 inch. Virtually all of the conventional doctor blades are designed with an angle cut out of the bottom of the blade so that it terminates in a smooth and somewhat rounded edge over which the freshly coated web is made to drag. The sliding action of web against the smooth edge seems to flatten down the coating and, in some cases, to cause somewhat of a penetration of the web, but these devices are incapable of controlling the amount or distribution of the coating over the entire web or selected portions thereof. Also, because of the extremely short time in which the edge of such doctor blades is in contact with the web in those cases where impregnation is important, it is extremely difficult to get a sufficiently deep penetration of the web structure. This is particularly true when the web in those cases where impregnation is important, it impregnant.

SUMMARY OF THE DISCLOSURE
It is therefore an object of this invention to provide an improved process for impregnating and/or coating fibrous webs in which means are provided for controlling the porosity of the webs.
It is a further object of this invention to provide an improved apparatus which is instrumental in obtaining said controlled porosity.
Another object of this invention is to provide a fabric which is waterproof but also gas and water-vapor permeable.
Generally speaking, these and other objects of the present invention are realized in a process for applying a liquefied material to a fibrous web, the combination which comprises, imparting movement to a fibrous web so as to present a moving surface, depositing a substantially liquid material on the moving surface, embedding the deposited material into continuous portions of the moving surface and, applying a force equally on each continuous portion simultaneously and continuously with the embedding step so as to cause attachment of additional liquefied material with said embedded material.

BRIEF DESCRIPTION OF THE DRAWING
Further illustration of the present invention can be had by reference to the accompanying drawing.
FIG. 1 is a side elevational view of the coating and impregnating apparatus of this invention.
FIG. 2 is a side cross-sectional view of the apparatus shown in FIG. 1.
FIG. 3 is an enlarged fragmentary cross-sectional view of a metering blade, such as used in the invention, showing its contact with the moving web.
FIG. 4 shows an enlarged plan view of a blade means used in another embodiment of the invention.
In FIG. 1, a fabric web 1 is moved in a lateral direction by rotating rollers 2. A frame 3 supports a metering blade 4 which is effective in impregnating and/or coating the web with a coating material 5. Infrared lamps 6 serve to dry the fabric after it has been impregnated with the coating solution.
FIG. 2 substantially shows a cross-sectional view of the apparatus shown in FIG. 1. The rollers 2 move the fabric 1 in a horizontal plane. A coating solution 5 is permitted to drop from a reservoir 7 onto the fabric which then passes under the metering blade 4 to effect impregnation. Generally, in order to effect an impregnation which is not visible on the fabric, a metering blade having a contact width of between 5 and 150 mils will be necessary.
FIG. 3 shows an enlarged cross-sectional view of the metering blade 4. The leading edge 8 of the blade embeds the coating solution 6 in the fabric. The leading or upstream edge of the blade will have a keen configuration. The front side of the blade will be at a substantially right angle to the upstream edge. As used herein a substantially right angle includes both acute and obtuse angles. The contact width 9 of the blade forces a controlled amount of additional coating material into the interstices of the fabric in addition to the initially embedded solution. The contact width of the blade determines the amount of additional material forced into the fabric.
FIG. 4 shows metering blade 10 having a gradient contact width 11. Such a blade is effective in depositing controlled but varied amounts of coating material across the width of a fabric. For example, that portion of the blade having a narrow contact width will deposit less coating material than the broader contact width portion.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS
As previously mentioned the present invention relates to an improved process for coating and impregnating fibrous webs.
In general, any substantially liquefied coating material may be used in the invention.
Illustrative examples of polymeric materials which can be used as the coating material are butadiene polymers including copolymers of butadiene with acryonitrile, styrene, acid esters of acrylic acid, and diisocyanate linked condensation elastomers such as urethanes, polyurethanes, for example those resulting from the reaction of toluene diisocyanate with relatively short linear polyest molecules, and modified polyurethanes.
Organosilicon compositions which may also be used as the coating material include, for example, monomeric sil-
anes such as dimethyl dichlorosilane, octadecyltriacetoxy silane, trimethylchlorosilane, vinylidisopropoxysilane, and phenylmethylmethoxysilane; polymeric silanes such as methylsiloxanes, poly(methylsiloxanes containing Si-Si linkages such as dimethyl tetramethyldisiloxane and siloxanes such as Me₃Si(CHOH)₄Si(CH₃)₂Me₂ and siloxanes such as methylhydrogensiloxane, dimethylsiloxane, mono-
methylsiloxane, octadecyl methyl siloxane, octadecyl hydro-
gensiloxane, phenylhydrogensiloxane and mixtures and copolymers of dimethylsiloxane and methylhydrogen-
siloxane, ethylhydrogensiloxane and trimethylsiloxanes; and alkali metal salts of organosilanes such as MeSi(ONa)₃, EtSiO₂(OK)₂, C₆H₅SiOOLi, and mixtures thereof.

In several cases an oil or stain-repellant compound may be employed either alone or along with another coating such as for example a water-repellent coating. Illustrative examples of such repellent substances include fluorochemical compounds such as those defined in U.S. Pats. 2,642,416; 2,826,564; 2,839,513; and 2,803,615. Other fluorochemical compounds which can be employed include the chromium coordination complexes of saturated perfluorocarboxylic acids and perfluorooctanoic acid. Fluorochemical compounds suitable for use herein are available commercially, for example, those marketed under the trade name “Scotchgard” such as Scotchgard FC205 and FC208 products, which are available in emulsion form, may be described according to U.S. Pat. 2,803,615 by the following general formula:

\[
\text{FC}-(\text{CF}_2)-\text{SO}_{3}^{-}-\text{N-R-O-C}=\text{O}-\text{Si}=\text{O}
\]

\[\text{R}\]

in which \(x\) is a value between 3 and 13 inclusive, \(R^1\) is a lower alkyl, such as methyl, ethyl, propyl, and the like, having 1-6 carbon atoms. \(R^2\) is an alkylene consisting of 1-12 carbon atoms and \(R^3\) is H, methyl or ethyl.

The product “Zepel” is also available in emulsion form and while it is chemically different from the Scotchgard products, it is a fluorochemical oil repellent containing fluorocarbon tails composed of CF₄ groups which may end in a terminal CF₃ group.

Generally speaking, fluorochemical compounds of the type indicated (e.g. Scotchgard) are known to demonstrate a water repellent effect but they are not considered to be waterproofing materials. Nevertheless when employed in the treatment of fabrics as described in the process of the present invention superior waterproofing results are achieved.

Compounds imparting crease resistant properties to treated fabrics may also be used in this invention. Compounds of this type are described in U.S. Pats. 2,517,750; 2,825,732; 2,974,432; and 3,049,446.

Water-swellable hydrophilic elastomers such as for example those described in U.S. 3,265,529 may also be used in the invention. Other compounds such as plasticizers, pigments, curing agents, soil release agents, etc. may also be added to the coating mixture or solution.

It will be recognized that the invention is applicable broadly and all webs or fabrics comprising natural and/or synthetic fibers, e.g. cotton, rayon, glass, nylon, polyester (polyethylene terephthalate), acrylics, viscos, cellulose esters (e.g. cellulose acetate) cellulose ethers, asbestos, flax, hemp, wool paper and so on.

The conditions used for drying and/or curing the web after application of the coating material will vary depending on the structure of the fabric and the nature of the material used. Usually, however, the temperature of drying is in the range about between 200-300 degrees F. for 1-10 minutes. When curing is required, exposure to temperatures between about 250-375 degrees for an additional 1-10 minutes will be necessary. The temperature of the cure is determined by the properties of the fabric in the web and/or the nature of the applied coating material.

The coating material will generally be applied to the web from a solution, dispersion, or emulsion in which the liquid medium may be water or an organic liquid may be used. Since the organic solvent is not critical, it may be chosen from any number of organic solvents which are commercially available and economically feasible for use in the process. However, it should be emphasized that the organic liquid must be inert in relation to the web and the coating material itself. A preferred solvent is Varsol although other vehicles which may be used include xylene, toluene, benzene, heptane, butylacetate, trichloroethylene, Cellosolve, perchlorelthylene, methyl
ehtylketone or any other solvent which is compatible with the coating material. Cellosolve is the trade designation for 2-ethoxyethanol and is commercially available from Union Carbide Corporation. Varsol is the trade designation for a straight petroleum aliphatic solvent and is commercially available from the Standard Oil Co. of New Jersey.

The process of the present invention is particularly adapted for the manufacture of products which are useful in filtering gases, solids, chemicals, and/or liquids.

In one particular embodiment of the invention, cigarette filters may be produced. Generally the porosity of such filters will be controlled to provide a range of porosity and/or rate of filtration desired. For example, the amount of nicotine and tar which may be removed from the cigarette smoke can be regulated to a substantial degree by controlling the porosity of the filter. This may be accomplished by means of a plurality of filters or a single filter. According to the process of this invention such filters may be produced, for example, from paper or fabric and will generally be cut to the desired size and supported by a round frame which is fitted in the cylindrical body of the cigarette.

Another product having controlled air porosity produced according to this invention is parachute fabric. The porosity of such fabric generally is a factor in determining the parachute's rate of descent. Air porosity in such a fabric may be controlled to as low a degree as desired but is limited, of course, in its maximum degree by the type of weave employed in the fabric.

When polyester/cotton, polyester/rayon and 100% polyester fabrics are intended for a particular application, a problem of major concern is the difficulty of removing oily stains, food stains and soil therefrom. The oil staining problem of polyester is due in part to the smooth surface of the fiber. Because of its smoothness the oil can act as a wick for oils. Added to this is the oleophilic nature of the polyester fiber itself. According to the process of this invention, any of the conventional soil release materials such as polyurethane or acrylic emulsions may be applied to an underlying fabric and will retain its soil releasing properties even after multiple home launderings and dry cleanings. The soil release finish may be applied in conjunction with wrinkle free materials or waterproofing compounds.

One of the more important products produced according to this invention is an impregnated fabric suitably for use as rainwear, which is breathable and waterproof and also demonstrates a highly desirable fabric hand and appearance. This may be achieved by treating a basic fabric with a waterproof material, either hydrophobic or hydrophilic, according to the process of this invention such as previously described. The basic fabric which is to be made waterproof may have been treated previous to the process of this invention such as previously described. The basic fabric which is to be made waterproof may have been treated previous to the process of this invention with a thermosetting resin such as used in the wrinkle free fabrics. Such fabrics are commercially sold under the trade names Perma-Press, and Koraltron. "Perma-Press" is a trade designation for a coated fabric having permanent press properties, said coating being...
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"Permafresh 183" which is a trade designation for a carbamate chemical and which is commercially available from Sun Chemical Corporation. "Perma-Press" is commercially available from Sears Roebuck and Co. "Koratron" is a trade designation for a coated fabric having permanent press properties, said coating being "Permafresh 183." The fabric may also have been previously treated with an oil or stain repellant compound such as previously described herein.

It should be emphasized that the order in which the underlying web is impregnated is not particularly important to obtain the results intended. For example, a fluorocarbon impregnant can be applied under a polyurethane impregnant and still render the fabric resistant to stains. It should also be emphasized that the impregnants applied to the underlying webs according to this invention remain fast in the web even after repeated washings or dry cleanings.

Rainwear fabric made according to this invention can be laundered repeatedly in conventional washing machines without damage to its resistance to water. It can also be dry cleaned with the usual dry cleaning fluids such as perchlorethylene, and remains supple and water-vapor permeable even during extended use.

With the present method the natural voids formed by the interstices of the web or fabric are filled so that microscopic voids are achieved. However, perhaps the most important fact of this method is that control of such voids is achieved. In the absence of indication to the contrary all proportions are expressed on weight basis.

The following examples will further illustrate the invention.

EXAMPLE 1

A test fabric composed of 75% Dacron, 25% Avril fibers was tested at 3 locations for air porosity along its width. Dacron is the trade designation for the condensation product of terephthalic acid and ethylene glycol, which is subsequently polymerized, and is commercially available from E. I. du Pont de Nemours & Co., Inc. Avril is the trade designation for a modified viscose rayon fiber having a high strength and is commercially available from American Viscose Co. Air porosity was tested on a Frazier apparatus. The same fabric was treated according to the process of this invention with a modified polyurethane manufactured and sold by Hooker Chemical Corp. under the trade name Rucothane Co.-75. The polyurethane was dissolved in a methyl ethyl ketone-tolnol (50/50) solvent resulting in a solution having a viscosity of 20,000 cp. and air porosity results of the same three locations along the width of the fabric were noted. The variation in porosity in the control specimens as opposed to that in the treated fabric is shown in Table 1.

TABLE 1—AIR POROSITY, CU. FT./MIN.

<table>
<thead>
<tr>
<th>Location 1</th>
<th>Location 2</th>
<th>Location 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>12</td>
<td>15.8</td>
</tr>
<tr>
<td>Treated</td>
<td>0.09</td>
<td>0.10</td>
</tr>
</tbody>
</table>

EXAMPLE 2

As previously mentioned, the solids content of the impregnating solution and the contact width of the metering blade will determine the air porosity of the treated fabric. This example illustrates the different porosities which may be obtained by a variance in the contact width of the metering blade.

A 65/35 Dacron/cotton fabric was treated according to the process of this invention, with the modified polyurethane solution used in Example 1 except in this case the solution had a viscosity of 10,000 cps. A different metering blade was used to treat the test specimens. Specimen 1 was treated with a blade having a contact width of 19 mils, specimen 2 with a blade having a contact width of 11 mils, and specimen 3 with another blade having a contact width of 40 mils. The varying air porosity achieved by the use of these different metering blades are noted below in Table 2.

TABLE 2

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Air porosity, cu. ft./min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>1.7</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

EXAMPLE 3

A 65% Dacron polyester 35% cotton rainwear fabric previously treated with Scotchgard 205 resin and a urea was placed in an apparatus similar to the illustration in FIG. 1. The urea previously treated to the fabric was an organic compound having more than one —NH₂ group per molecule and aided in waterproofing the fabric. This treated fabric (specimen 1 below) was coated with a 40% solids solution. The metering blade used in the process had a contact width of 11 mils but no open angle. At the same time a control sample (specimen 2) of the same fabric was coated with the same modified polyurethane solution. The control sample was coated on the sample apparatus; however, a 1/4 inch knife having an 8 degree open angle was substituted for the 11 mil blade of specimen 1. After coating, the specimens were tested for air porosity, cured in an oven at a temperature of 300 degrees F. for 3 minutes and tested for water resistance. The results are indicated below in Table 3.

TABLE 3

<table>
<thead>
<tr>
<th>Appearance after coating</th>
<th>Air porosity</th>
<th>Weight, g.</th>
<th>Rain test (in. water penetration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen 1.</td>
<td>Invisible</td>
<td>8.0</td>
<td>6.7</td>
</tr>
<tr>
<td>Specimen 2.</td>
<td>Slightly visible</td>
<td>6.9</td>
<td>6.9</td>
</tr>
</tbody>
</table>

1 Slowinski Rain Test: 6 feet head for 10 minutes.

The beneficial effect resulting from the use of the present invention is readily apparent from the above example. Thus specimen 2 failed the waterproof test at 3 min. Specimen 1 was more successful in passing the waterproof test yet it maintained good air porosity. It was found that the fabric treated as specimen 1 is durable to laundering and dry cleaning and maintains a relatively soft hand.

EXAMPLE 4

A 65/35% Dacron/cotton fabric (specimen 1) was treated with a Zepol coating by conventional means using the 3/4 inch, 8 degree open angle blade described in Example 3. A second specimen (specimen 2 below) of the same fabric was treated according to the process of this invention with a metering blade having a contact width of 25 mils and no open angle using the same Zepol coating. The results obtained are indicated below in Table 4.

TABLE 4

<table>
<thead>
<tr>
<th>Spec. 1</th>
<th>Spec. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil repellency</td>
<td>5</td>
</tr>
<tr>
<td>Oil repellency after three dry cleanings</td>
<td>0.2</td>
</tr>
<tr>
<td>Gms. water absorbed (10 ft. head/10 min.)</td>
<td>14.7</td>
</tr>
<tr>
<td>After 3 dry cleanings (0 ft. head/10 min.)</td>
<td>1</td>
</tr>
<tr>
<td>Moisture transmission (gms./hr.)</td>
<td>1.75</td>
</tr>
<tr>
<td>After 3 dry cleanings</td>
<td>1.75</td>
</tr>
</tbody>
</table>

1 Saturated.
This example amply illustrates the superior results achieved by using the blade described in the present invention. Particularly astounding are the results noted in the Slowinski Rain Test before and after successive launderings. The moisture transmission results indicated that the improved impregnation obtained with the process of this invention stabilizes the fabric and minimizes residual shrinkage after laundering and dry-cleaning.

EXAMPLE 5

This example illustrates the vastly superior water-proofing properties which are realized in using the present invention even when the test specimens ultimately have the same air porosity.

Two specimens were prepared from the same fabric comprising a 65/35 blend of Dacron and cotton. Both specimens were coated with a modified polyurethane methylethylketone solution having a 20% solids content. Specimen 1 was impregnated with a 1/4 inch blade having an 8 degree open angle. Specimen 2 was impregnated with an 11 mil blade with no open angle. The specimens were cured in an oven at 300 degrees F. and subjected to the Slowinski Rain Test. The results are indicated below in Table 5.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Air absorbed (6 ft. porosity head/90 min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen 1</td>
<td>2.5</td>
</tr>
<tr>
<td>Specimen 2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Thus ten times more water penetrated specimen 1 than did specimen 2. This illustrates the startling results achieved by the present invention.

EXAMPLE 6

This example shows the results achieved when a fabric is treated according to this invention with a soil release agent as well as a waterproofing agent. A Dacron polyester 2-ply warp fabric having a single fill was treated with a modified polyurethane methylethylketone solution such as utilized in Example 1 having a viscosity of 20,000 centipoises. The treated fabric contained 1 oz./sq. yd. of the modified polyurethane after drying at 180 degrees F. for one minute. A second impregnation was made of a silicone material sold by the Dow Corning Corp. under its trade name FC-227. The silicone material had a viscosity of 25,000 centipoises. The silicone impregnation was made on the same surface of the fabric and in the same manner as was the modified polyurethane solution. The treated fabric was then cured at a temperature of 300 degrees F., for one minute. The resulting fabric contained 3/4 oz./sq. yd. of the silicone material. The fabric was divided into test specimens and was spotted with various soiling substances such as mustard, oil, ink, etc. In all cases the fabric specimens were machine washed using Tide detergent. The test specimens were then dried and examined for soil retention. In all cases minimal traces of soil remained.

The following standard test methods are referred to in the foregoing description:

Air permeability—Frazier method ASTM D-737-46

Moisture transmission

Test specimen is sealed to top of metal container measuring 2 1/2 inches in diameter by 2 inches in depth. The lower surface of the specimen contacts an absorbent wick which is approximately .05 inches thick by 1 1/4 inches wide. The wick extends to the base of the container which contains 100 cc. of water. The container is weighed and is then suspended in an oven held at 85 degrees F. for six hours. Weight loss is recorded. Results are shown in terms of moisture transmission in grams per square foot per hour.

What is claimed is:

1. A process for applying a liquefied coating material to a fibrous web which comprises:

(a) imparting movement to a fibrous web to present a moving surface;
(b) depositing said liquefied coating material on said moving surface, a portion of said liquefied coating material being embedded in the voids of said moving fibrous web immediately upon being deposited upon said moving surface;
(c) applying by means of a metering blade a force equally on said moving surface simultaneously and continuously with said depositing step at a point on said moving surface immediately adjacent to and downstream of the point on said moving surface where said liquefied coating material is being deposited on said moving surface, said metering blade having a keen upstream edge and a downstream edge defining a continuous, essentially horizontal, flat, web-contact, metering surface therebetween, said flat metering surface being substantially parallel to and in contact with said moving fibrous web, said flat web-contact metering surface of said metering blade having a width between 5 and 150 mils, said area of said metering surface of said metering blade contacting said moving fibrous web extending unimpeded across said moving surface, and said moving fibrous web being unsupported at or near the area of contact with said metering surface of said metering blade, whereby said moving surface is depressed in the area where said force is being applied, whereby additional liquefied coating material is embedded in the voids of said moving fibrous web and whereby the total amount of liquefied coating material in the voids of the web is controlled by the width of the surface area where said force is being applied; and
(d) drying the liquefied coating material to thereby obtain a web having controlled porosity.

2. A process according to claim 1 wherein said liquefied coating material is a modified polyurethane resin.

3. A process according to claim 1 wherein said fibrous web is a fabric comprised of synthetic polymeric fibers.

4. A process according to claim 1 wherein said synthetic polymeric fibers are polyester fibers.

5. A process according to claim 1 wherein said fibrous web is a fabric which comprises a blend of synthetic polymeric fibers and natural fibers.

6. A process as described in claim 1 wherein said width of said surface area where said force is being applied is variable.

7. A process as described in claim 1 wherein said coated liquefied coating material is cured after the drying step.

8. A process as described in claim 1 wherein said liquefied coating material is a liquefied water-proofing coating material.

9. A process as defined in claim 8 wherein the waterproofing material is a hydrophobic compound.

10. A process as defined in claim 8 wherein the fabric has been previously coated with fluorochemical material.

11. A process as defined in claim 8 wherein the fabric has been previously treated with a soil release agent.
12. A process as defined in claim 8 wherein the fabric has been previously treated with a crease resistant material.

**References Cited**

<table>
<thead>
<tr>
<th>UNITED STATES PATENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>371,155 10/1887 Videto 118—415</td>
</tr>
<tr>
<td>2,271,458 1/1942 Lionne 117—111</td>
</tr>
<tr>
<td>2,423,555 7/1947 Ender 117—111</td>
</tr>
<tr>
<td>2,632,422 3/1953 Elkins 118—415</td>
</tr>
<tr>
<td>2,861,009 1/1958 Rubner 118—415X</td>
</tr>
<tr>
<td>2,989,422 6/1961 Helbing 117—111</td>
</tr>
<tr>
<td>3,000,760 9/1961 Greiller 117—111</td>
</tr>
<tr>
<td>3,222,209 12/1965 Brundige et al. 117—64</td>
</tr>
<tr>
<td>3,255,259 8/1966 Caldwell et al. 117—111X</td>
</tr>
<tr>
<td>3,302,610 2/1967 Mahoney 117—111X</td>
</tr>
</tbody>
</table>

**FOREIGN PATENTS**

456,377 11/1936 Great Britain 117—111

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U.S. Cl. X.R.