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3,427,179

METHOD OF MAKING A POROUS POLYAMIDE FABRIC

Filed Oct. 23, 1965

Sheet 1 of 2

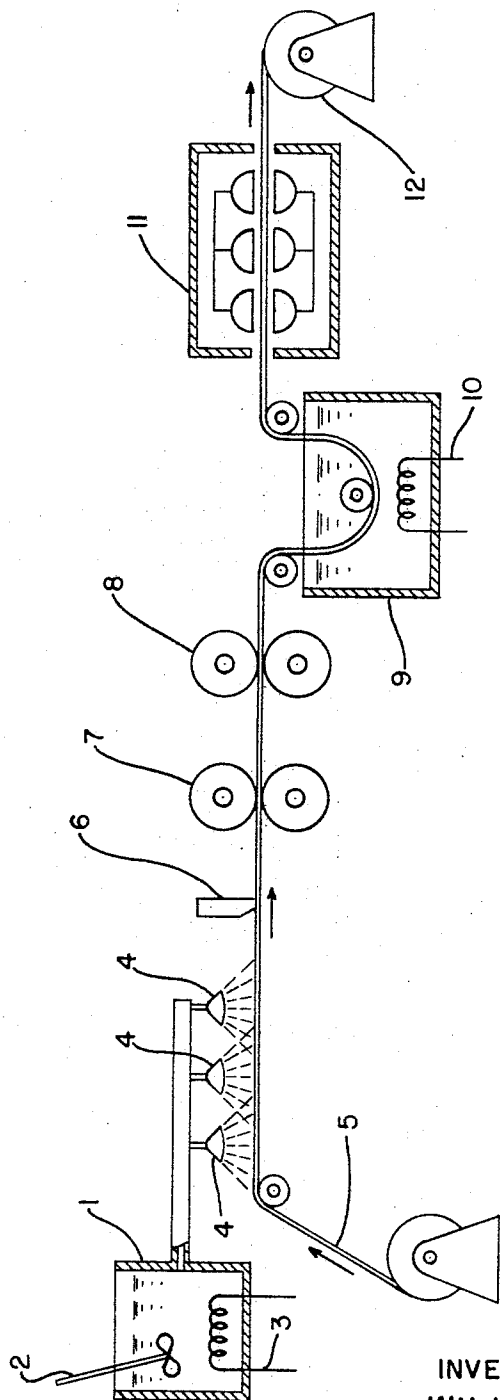


FIG. 1

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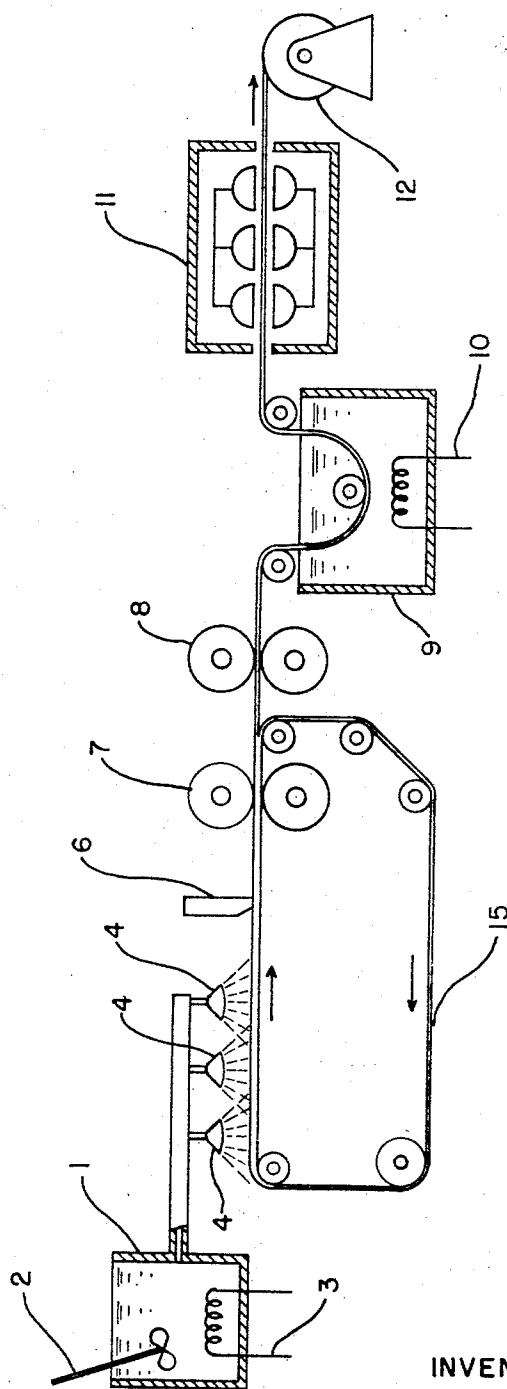


FIG. 2

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**METHOD OF MAKING A POROUS
POLYAMIDE FABRIC**

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Apr. 2, 1964. This application Oct. 23, 1965, Ser.
No. 503,730

U.S. Cl. 117-11

Int. Cl. B44f 9/12; B44d 1/44

16 Claims

ABSTRACT OF THE DISCLOSURE

Micro-porous polyamide product, e.g., leather or like fabric substitute, and method of manufacture of same. Product is formed by dissolving polyamide in liquid which is non-solvent at room temperature and solvent at elevated temperatures, applying the solution to a base, cooling the solution of polyamide and liquid solvent to a temperature below which the liquid is a solvent for the polyamide thereby forming a stable gel and liquid extraction at a temperature at which the liquid is a non-solvent.

This application is a continuation-in-part of my co-pending application Ser. No. 356,723, filed Apr. 2, 1964 and now abandoned.

This invention relates to a non-woven, vapor-pervious polyamide fabric and methods and means for its manufacture.

A number of fabrics have been commercially offered in the past few years that are comprised of non-woven, synthetic resinous materials. These have certain advantages over conventional woven fabrics, particularly with respect to their durability and ease of manufacture. Rather than being woven or knit on conventional machines, this type of fabric can be simply produced by combinations of extrusion and calendaring operations. Of particular advantage is the fact that any selected texture or surface configuration can be given to these fabrics simultaneously with the final calendaring operation.

Perhaps the biggest disadvantage to the widespread use of extruded and calendared synthetic resinous materials lies in the fact that they are impervious to gases and, as a result, will not "breathe." Because of their inability to permit the passage of body vapors, they are uncomfortable when they are worn by, or otherwise come in contact with, people. The discomfort caused by this moisture-imperviousness is well recognized and is painfully clear on a hot day to one riding in an automobile that is fitted out with extruded plastic seat covers.

In accordance with this invention, it has been discovered that by using certain novel methods, non-woven polyamide fabrics can be prepared that are pervious to gases and will permit the passage of moisture there-through. Further, it has also been found that conventional fabrics, such as may be made by weaving, knitting or felting, can be coated with polyamide resins without destroying the vapor-pervious properties of such original fabric. In this latter regard, the polyamide coating imparts hard, tough and long-wearing properties to the fabric. In either instance, textures and patterns may be imparted to the fabric by means of calendaring operations.

Accordingly, it is an object of this invention to provide methods and means for the manufacture of a vapor-pervious fabric comprised of a polyamide.

A further object of this invention is to provide a vapor-pervious fabric that can be textured and patterned by calendaring operations.

A still further object of this invention is to provide a tough, long-wearing, vapor-pervious fabric comprised of

a base fabric coated with a non-woven protective layer of polyamide.

Yet a further object of this invention is to provide a new fabric and methods for its manufacture, which fabric is comprised of a woven, knitted or felted base layer coated with a vapor-pervious protective layer comprised of a polyamide.

Briefly, these and other objects of this invention are achieved by dissolving a polyamide at elevated temperatures in a liquid that is a solvent at elevated temperatures, but a non-solvent at room temperature, forming a layer of such solution by distributing it over a surface, cooling the solution to yield a form-stable material, and removing the solvent from such material. The resulting fabric is hard, tough and wear-resistant, and is pervious to gases and water vapor. It may be used in the manufacture of wearing apparel, or in many other applications, such as set covers for automobiles, artificial leathers, or other articles in which porosity to moisture vapor is desired. Further, various textures and patterns may readily be imparted to the fabric by means of calendaring and embossing rolls.

In one variation of this invention, the surface over which the polyamide solution is distributed may be a fibrous fabric as formed by weaving, knitting or felting. In this case, the solution may be sprayed or otherwise contacted with the base fabric and uniform distribution there-over assured by devices such as doctor blades and smooth calendar rolls.

If a base fabric is not used, the solution may be distributed, for example, onto a roller and passed through a nip to obtain a uniform thickness of the resulting fabric. In this case, the rolls may be chilled in order to solidify the fabric, at least in part, prior to the time it is removed from the rolls. By another method, the solution is distributed over an endless belt or the like, and is retained thereon until the fabric is form-stable. Other methods can be used in the practice of this invention, as will occur to those skilled in the art.

The solvent may be removed from the polyamide by conventional means, and one of the simplest of these is by leaching. As most of the solvents useful in the practice of this invention are water soluble, it is often convenient to remove the solvent by contacting the fabric with a hot water bath.

Another means by which the solvent may be removed is by vaporization. However, in order to avoid excessive temperatures that would re-establish a liquid phase, the vaporization should be conducted under a vacuum and the solvent allowed to flash off.

In the drawings:

FIGURE 1 shows a diagram in schematic form illustrating a continuous process for making a fabric in accordance with this invention in which a base material is utilized.

FIGURE 2 is similar to FIGURE 1 except no base material is used.

With reference to FIGURE 1, a solution of glycol and polyamide is prepared as described in the above example by mixing them in a tank 1 that is provided with heater means 3 and a mixer 2 for gently agitating the solution. A fibrous cloth 5 is continuously fed under a spray device 4, where the solution is distributed over the cloth 5. A doctor blade 6 is provided to insure even distribution of the solution over the cloth. After the cloth has been covered by the solution, it is led between calendar rolls 7 where the temperature is reduced to solidify the coating. The pressure of the rolls also serves to insure uniform penetration of the solution throughout the cloth 5. Additionally, a set of embossing rolls 8 may be provided to impart any desired texture or pattern to the surface of the fabric.

The glycol is leached from the fabric by passing it through a leaching tank 9 that is provided with a heating element 10. Usefully, the leaching tank 9 may contain hot water.

After the glycol has been leached from the fabric, the fabric is led out of the leaching tank 10 and is passed through drying oven 11. When it is dry, it is stored on takeup roll 12.

As previously mentioned, it is not necessary to form a coating of the polyamide solution on a fabric base. In this case, the finished fabric will be comprised entirely of the moisture-pervious polyamide. One method of preparing a fabric in this manner can be understood with reference to FIGURE 2. Here, instead of spraying the solution onto a fabric, the hot glycol solution is sprayed onto an endless moving belt 15. After the solution has been solidified by passing through calendar rolls 7, the fabric is stripped from the belt 15 and then passes into embossing rolls 8. Otherwise, the operation illustrated in FIGURE 2 is identical to that in FIGURE 1.

EXAMPLE I

20% by weight of an interpolymer of type 6, type 6/6 and type 6/10 nylons were added in finely divided form to 80% by weight triethylene glycol. The mixture was heated to about 300–350° F. and gently agitated until all of the nylon was dissolved into the glycol.

Two steel platens of about the same size were sprayed with a mold release agent. A cloth fabric was stretched over one of these platens and the hot solution poured and evenly distributed over the cloth. The other platen was placed on top, and both platens were then placed in a hydraulic press where the solution-coated fabric was subjected to a pressure of about 100 p.s.i. and a temperature in the range of from about 200–250° F. After three minutes exposure to this heat and pressure, the platens were cooled by circulating water and the fabric was then removed from between them. The fabric carrying the nylon coating was immersed first in acetone and then in water to remove the glycol. After having been so leached, the sample was stretched and dried. The resulting fabric was tough, flexible, and vapor-pervious.

EXAMPLE II

30 parts by weight of a polyamide supplied by General Mills under the trade designation XX1235 was mixed with 90 parts by weight triethylene glycol and 50 parts by weight hexylene glycol. The polyamide was prepared by the amidization of a polyfunctional amine with a polyfunctional acid prepared from tall oil. (This polyamide had a ball and ring softening point of 196° C.; an inherent viscosity of 0.75 as determined with 0.5 gram per 100 milliliters of o-chlorophenol; an ultimate tensile strength of 5800 p.s.i.; and an elongation of 450%.)

The above mixture was heated under gentle agitation to 385° F., at which point the polyamide dissolved in the glycols. This solution was then poured onto a cookie sheet that had been treated with a mold release agent. Upon cooling, a gel was formed that was peeled from the sheet and then placed in a hot water bath to leach out the glycols. After drying, a tough, leather-like, moisture-pervious material suitable for use as, for example, shoe leather was obtained.

While the exact theoretical basis for this invention is not fully understood, it would seem reasonable to suggest that something approaching a true solution is formed when the polyamide and solvent are first heated, and that upon subsequent cooling, a gel-like structure results. By definition, it can be understood that some intermolecular forces between polyamide chains are overcome during solution and the chains will have relatively complete mobility with respect to each other. Upon cooling, however, the solvation power of the solvent is reduced and intermolecular forces, particularly at the amide linkages, reassert themselves and tend to cause the polymeric chains

to assume a somewhat fixed spatial relationship or orientation with respect to each other. If at this time, solvent material is included within the orienting molecules, a gel-like structure will be formed in accordance with this invention. If, on the other hand, the intermolecular forces are sufficiently great to express or occlude the solvent from between adjacent molecules, the polyamide may precipitate from solution in the form of a fine powder.

From the above, it will be appreciated that the formation of a proper gel-like structure will depend to a major extent upon the selection of a suitable polyamide. As a generalization, it may be stated that the more uniform, symmetrical, straight chained polyamides with narrow molecular weight distributions have such strong intermolecular forces that it is difficult to form the gel-like structures of this invention. On the other hand, irregular, unsymmetrical polyamides, both branched and cross-linked, that have a wide molecular weight distribution are particularly suitable for use in the formation of these gels. The latter preferred polyamides are readily identifiable since they will generally exhibit characteristics of low crystallinity and a broad softening or melting point range.

A preferred class of polyamides that may be mentioned as being particularly suitable for use in this invention are those that are prepared by the amidization of polyfunctional amines, which preferably are at least trifunctional, and may be aliphatic, alicyclic or aromatic, and a mixture of di- and trifunctional acids that have been produced from unsaturated fatty acids or their esters by reductive oligomerization. Other of the known polyamides of at least moderate molecular weight and mixtures thereof may be useful in this invention, and their initial selection may be based upon the above noted characteristics of low crystallinity and a wide softening or melting point range. The final choice of the particular polyamide used will depend upon the hardness and other properties desired in the final product.

Another group of preferred polyamides are copolymers and interpolymers. One such commercially available polyamide is prepared from approximately equal portions of hexamethylene adipamide, hexamethylene sebacamide and caprolactam (sold under the trade designation nylon 61 by Du Pont).

The selection of a suitable solvent for use with a particular polyamide in forming the gel may also be of importance. Generally, the solvent is selected for its ability to solvate the polyamide at elevated temperatures as well as for its ability to form a relatively strong, stable gel. In some instances, it may be advantageous to use a mixture of solvents to obtain the advantages of both. As examples of solvents that are suitable for use in the practice of this invention, there may be mentioned alcohols, and especially the polyhydric alcohols such as ethylene, propylene and hexylene glycol, glycerine, and especially triethylene glycol. Also, while perhaps not solvents in the true sense, swelling agents such as epoxies and diocetylphthalate may be used effectively in some instances.

In addition to the above described methods for forming a porous polyamide cloth, it is sometimes useful to prepare an intermediate product that may be stored and used from time to time as may be required. In this case, the polyamide is dissolved in the solvent at elevated temperatures and the solution allowed to cool to form the gel-like structure. The resulting gel is then comminuted to a convenient size and stored for further use. As needed, the desired quantity of comminuted gel may be heated to above its melting point to reform the liquid solution, and this in turn applied to a surface or a mold to form an article.

Many techniques may be used for forming articles in accordance with this invention. In addition to preparing continuous lengths of sheet and cloth as illustrated in the drawings, articles may be formed by casting techniques, extrusion, injection molding, spraying, and the like. As an example of the latter technique, the solution

may be sprayed over a last to form the upper part of a shoe in a single operation. This further may be enhanced by first covering the last with a suitable cloth material and then spraying the solution thereover. These and other similar techniques will occur to one skilled in the art, and it is intended that they be included within the scope of this invention.

I claim:

1. A method for making a vapor-pervious polyamide fabric comprising the steps of dissolving an irregular, unsymmetrical polyamide by mixing said polyamide with a liquid that is a solvent at elevated temperatures above room temperature and a non-solvent at temperatures below said elevated temperatures; heating the mixture to a temperature at least as high as the elevated temperatures, thereafter cooling the solution to form a gel-like structure; comminuating the gel-like structure; melting the gel-like structure by means of heat and distributing the melt over a form; cooling and solidifying the distributed melt; and removing at least a substantial portion of said liquid from the solidified material.

2. A method of making a fabric comprised of a moisture pervious polyamide comprising the steps of mixing a powdered irregular, unsymmetrical polyamide with a liquid which is a non-solvent for the polyamide at room temperatures but is a solvent for the polyamide at elevated temperatures above room temperature, heating the mixture to a temperature above room temperature at which the liquid is a solvent and for a time sufficient to dissolve the polyamide, cooling the mixture below the elevated temperature to produce a form stable gel and thereafter comminuting the form stable gel, heating the comminuted gel to form a melt, distributing the melt over a form, thereafter cooling the melt to a temperature at which the liquid is a non-solvent and thereafter removing substantially all of the liquid from the solidified material while maintaining the polyamide at a temperature at which it is in a non-solvent state.

3. A method for making a moisture pervious polyamide article comprising the steps of dissolving an irregular, unsymmetrical polyamide at a temperature at least as high as an elevated temperature, which elevated temperature is above room temperature, in a liquid that is a non-solvent for the polyamide below the elevated temperature and a solvent for the polyamide at and above the elevated temperature, forming a layer from the solution by distributing the solution over a surface while the solution is heated to at least the elevated temperature, cooling the layer of solution below the elevated temperature to form a stable gel of the liquid and the polyamide and removing the liquid from the stable gel while the gel is maintained below the elevated temperature.

4. A method according to claim 3 in which the stable gel is embossed before removal of the liquid.

5. A method according to claim 3 in which the heated solution is distributed over cloth.

6. A method according to claim 5 in which the cloth is impregnated with the solution.

7. A method according to claim 6 in which the impregnation of the cloth is aided by means of pressure.

8. A method according to claim 3, wherein said solvent is selected from the class comprising polyhydric alcohols, epoxies and dioctylphthalate.

9. A method according to claim 3 in which the solvent is an epoxy or dioethylphthalate.

10. A method for making a moisture pervious fabric comprised of a cloth base coated with a non-fibrous protective layer of polyamide, comprising the steps of: selecting an irregular unsymmetrical polyamide; selecting a liquid that is a solvent for the polyamide at and above an elevated temperature, which temperature is above room temperature, and which solvent is a non-solvent for the polyamide below the elevated temperature; mixing the polyamide with the liquid and heating the mixture to a temperature at least as high as the elevated temperature for a time sufficient to dissolve the polyamide; coating a cloth with the solution while the solution is heated at least as high as the elevated temperature; cooling solution to below the elevated temperature to form a stable gel of the liquid and the polyamide; and removing the liquid from the stable gel while the gel is maintained below the elevated temperature.

11. A method according to claim 10, wherein the irregular, unsymmetrical polyamide is a randomly oriented copolymer.

12. A method according to claim 10 in which said solvent is a polyhydric alcohol.

13. A method according to claim 10 in which said removal is accomplished by leaching.

14. A method according to claim 13 in which said leaching is accomplished by means of a hot water bath.

15. A method according to claim 10 in which said removal is accomplished by vacuum distillation.

16. A method according to claim 10 in which said gel-like structure is embossed.

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U.S. Cl. X.R.

117—63, 65.2, 102, 119, 119.2, 161; 264—212, 216