This invention relates to the manufacture of vapor permeable, water repellent fabrics, and more particularly to the combination of glass fibers and resinous materials or elastomeric materials or both in the manufacture of a product possessing the desirable properties of leather. Materials forming the subject matter of this invention are primarily laminates that are characterized by high resistance to water while permitting transmission of vapors to enable the material to breathe in a manner desirable for the material when used as wearing apparel in the form of shirts, jackets, and the like or when used as a leather substitute in the manufacture of purses, luggage, and the like.

It has been found that when a vapor permeable, water repellent fabric is in the form of a structure having substantially large cross section, it is expedient to have a reinforcing fabric which is sufficiently deformable without fiber disintegration to conform to the greater or lesser dimension occasioned by bending the product in one direction or the other. This will be readily understood when it is realized that the fabric constituting the outer layer of the structure must apparently become elongated when the structure is bent in one direction, while the fibrous fabric constituting the opposite wall of the structure is stretched when the structure is bent in the opposite direction. In the event that the fibers in the particular fabric are unable to realign themselves responsive to such operating forces, the product will be substantially inflexible and unsuitable for many of the uses for which it is intended.

An object of this invention is to provide an extensible fabric containing glass fibers for treatment with resinous or elastomeric materials or combinations thereof in the manufacture of vapor permeable, water repellent fabrics of substantial thickness.

Another object is the manufacture of a material having the desirable properties of leather with increased resistance to water penetration.

A further object is to produce a vapor permeable, water repellent fabric having leather-like characteristics with increased flexibility notwithstanding variation in thickness and which may be varied to have a high degree of vapor permeability to a low degree of vapor permeability, from high flexibility to relative stiffness, from high resistance to water penetration to water generation under fluid pressure, from a high degree of voids of pore-like dimensions to a substantially fully impregnated product which still retains vapor permeable characteristics, and from substantial hardness to relative softness.

These and other objects of this invention will hereinafter appear and for purposes of illustration but not of limitation, embodiments are shown in the accompanying drawings, in which:

Figure 1 shows a knitted fabric of glass fibers which is particularly well adapted as a reinforcing member in the manufacture of structures embodying features of our invention;

Figure 2 is an enlarged detail view showing the arrangement of fibers in a fabric woven of yarns of glass and resinous fibers;

Figure 3 shows the arrangement of fibers of Figure 2 after shrinking;

Figure 4 is a plan view of the fabric of which the fibers of Figure 3 are a part;

Figure 5 is a top plan view of a laminate which is produced by the invention;

Figure 6 is an enlarged sectional view through a section of the treated fabric prior to lamination; and

Figure 7 is an enlarged sectional view through a part of the laminate shown in Figure 6.

The objects of this invention are achieved by the use of a glass fiber fabric in which the fibers are arranged to permit some degree of elongation or stretchability of the fabric in planar directions.

The desired flexibility in a thick or laminated structure is secured when the fibrous base is a knitted fabric of glass fibers having the desired characteristics of stretchability or elongation in planar directions. A suitable knitted fabric may be produced of "continuous" glass fibers arranged in bundles or strands which may be further combined to form twisted or untwisted yarns suitable for knitting purposes. Yarns may also be formed of " staple" glass fibers which are collected in bundles and drafted to suitable dimension for knitting purposes.

When staple glass fibers are used, the yarns may be formed of superfine fibers of less than 0.0003 inch in diameter, or by mixtures of superfine with conventional staple fibers of larger dimension.

The desired flexibility in a thick laminated structure is secured by use of a fibrous base formed of a fabric prepared by integrating staple or continuous glass fibers with a small proportion of a synthetic organic fiber contractible to shorter lengths upon molecular activation by heat or solvent means. Since the glass fibers integrated with the organic fibers are relatively unaffected by the activating conditions, it will be apparent that the length of the glass fibers will ultimately exceed that of the retracted synthetic organic fibers whereupon the stretch fibers will become loomed to compensate for their differences.

By this technique an exceptionally useful fabric is secured in a simple and economical manner, a fabric having considerable stretch in one or elongation in another direction without imposing strain upon the glass fibers.

One such fabric is prepared as shown in Figures 2, 3 and 4 of the drawing. In its original form, the fabric is woven of 1 to 10 strands of staple or continuous glass fibers 10 twisted or untwisted with one or more strands of a contractable synthetic organic fiber 11 to form a yarn which may comprise the warp 12 or weft 13 or both of a woven fabric or one or more yarns of a knitted fabric.

By way of explanation, a certain amount of molecular orientation takes place in the synthetic fibers as the fabric is stretched incident to its manufacturing process. This orientation sets the molecules in strained condition and they constantly strive to return to their original relaxed condition. As soon as the fibers are softened by heat, solvent or other means enabling molecular rearrangement, the molecules rearrange themselves and the fiber returns rather quickly to the shorter lengths originally possessed. This characteristic is known as "elastic memory" and it is this feature which comes into play in the manufacture of a fabric which has been found particularly well adapted for the manufacture of vapor permeable, water repellent fabrics having substantial cross section.

Thus, whenever the fabric so formed is exposed to elevated temperatures capable of softening the synthetic fibers of which the fabric is constituted, molecular rearrangement and contraction takes place causing shrinkage of the synthetic resinous fiber with corresponding looping 15 of the then lengthier glass fibers. Representative of suitable contractible synthetic organic fibers are the Vinyon fibers formed of the copolymer of vinyl acetate and vinyl chloride. When Vinyon is used it may be effected anywhere from a temperature of 150°F. to a temperature below which resinous decomposition takes place. For practical purposes it is preferred to use a temperature of 180°F. to 300°F. with corresponding exposures of about 20 to 5 seconds.

Instead of Vinyon, other synthetic fibers may be used, such as nylon (polymide for the reaction of dibasic acids, diamines and amino acids). "Saran" (poly-vinylidene chloride and copolymers thereof with vinyl chloride or vinyl acetate), rayon (cellulose acetate), viscose (cellulose xanthate), casein, zein, soy bean and the like, and fibers which may
be formed of set elastomeric compositions. Temperatures for effecting contraction of particular resins depend primarily on the specific structure and its degree of molecular growth. For example 250°F. to 350°F. is sufficient for Saran.

Of weaving the yarns of combined glass and synthetic fibers, they may be knitted into a fabric. Yarns of glass fibers may be interwoven or knitted with yarns of the synthetic resin fibers in the described proportions. Bundles or individual glass fibers and synthetic fibers may be laid down from above in mixture to form fibrous mats or webs which may have a small amount of binder incorporated to impart greater self-sufficiency to the mat and to integrate the fibers to the extent that contraction of the synthetic fibers will cause corresponding looping of the glass fibers.

A looped fiber fabric 16 of the type described is particularly well adapted as an element for impregnation to form a vapor permeable water repellent fabric of substantial cross section because the glass strands and the fibers stand apart in looped form in a manner to make a greater portion of their surfaces available for coating with the treating or impregnating composition; whereas, in a woven or knitted fabric, the fibers and strands are closely associated together in compact bundles which militate against full impregnation and wetting of the fiber surfaces.

The following examples demonstrate the principles of manufacture by shrinkage of a resinous fiber component.

Example 1

Continuous strands of Saran (polyvinylidene chloride) and glass fibers in the ratio of about 1 to 4 in haphazard distribution, were fed down an oven a collecting belt traveling substantially at right angles to the oncoming fibers at a linear speed which is less than the rate at which the fibers are fed. As a result, the separate strands form into natural spirals upon the belt to form what will hereinafter be referred to as "swirl mat." Integration of fibers one with another is effected by an adhesive of the type of butadiene-acrylonitrile elastomer in combination with equal parts compatible phenolic resin. Ordinarily, 5 to 20 per cent by weight solids adhesive is sufficient. The dien is removed by air drying or it may be driven off at a temperature below 200°F.

Subsequently, the "swirl mat" is heated to a temperature of 300°F. for 8 seconds during which the Saran fibers shrink to much smaller lengths, with a resulting looping of the glass fibers between anchored junctures.

Example 2

(FIGURES 3 AND 4)

A woven fabric, having about 14 yarns per inch, is manufactured with yarns consisting of one end of continuous Vinyon fiber 11 (vinyl acetate-vinyl chloride copolymer) of 160 denier and 112 filaments, and 3 ends of continuous glass strands 10 of 100 denier and 150 filaments in each strand. The woven fabric is heated to 250°F. for 5 seconds to shrink the Vinyon fibers 11 while the unshrinked glass fiber becomes looped as at 15, as shown in Figure 3. This results in a novel, flexible fabric 16 having a very attractive appearance and properties ideally suited for subsequent treatment to form leather-like products.

Example 3

Instead of subjecting the woven fabric of Example 2 to elevated temperature for causing shrinkage, some degree of shrinkage may instead be secured upon immersion of the fabric in water or softening solvents. Alternatively, partial immersion of the described fabrics to deposit less than the full complement of solids may be made with a variety of resins and elastomeric compositions, depending chiefly on the characteristics desired in the final product. Ordinarily, it is of a composition capable of subsequent flow or cure under laminating conditions to integrate the layers and to reduce the openings to pore-like dimensions.

Suitable elastomers include butadiene-acrylonitrile copolymer (Buna N), butadiene-styrene copolymers (Buna S or GRS), isoprene (neoprene), rubber hydrochloride, natural rubber, chlorinated rubber, and derivatives thereof. Suitable thermosetting resinous materials for use in the impregnation step are the type phenol formaldehyde, which are compatible with the elastomer, but may also include the furfural resins, resorcinol resins, amine resins, and the like. Depending upon the degree of hardness or flexibility, the ratio of elastomer to resin may vary from 3 parts of elastomer and 1 part resin to 3 parts of resin and 1 part elastomer.

Instead of using thermosetting resins, the rubbery plastic resins may be used alone or in combination with a phenolic or urea type thermosetting resin embodied while in an intermediate state of resinous cure. Suitable thermoplastic resinous materials include the vinyl derivatives, such as polyvinyl chloride, polyvinyl acetate, vinyl chloride-acetate copolymers, polyvinyl acetics, polyvinyl chloride and copolymers thereof with vinyl chloride; polyacrylates, such as methyl methacrylate, ethyl acrylate, butyl methacrylate, and the like; polyamides, polyethylene, polystyrene and chlorinated poly-styrene, and the like.

Instead of relying on the amount of phenolic or resinous components to govern the softness and flexibility of the resins, elastomeric compositions may be arranged to impart the desired characteristics by proper selection of polymers depending on the modifying groups and the degree of polymerization, or by plasticizing the polymer with resins and plasticizing agents which may be selected as to type and amount from suitable tables available to the resins and plastic arts.

Impregnation or treatment of the glass fibers may be accomplished by known techniques, such as spraying and dip coating with dilute solutions or suspensions of the composition. In such instances, the treating composition may have a solids content of about 5 to 45 per cent by weight. When a knife coating, roller coating process or the like is used, higher solids compositions may be employed ranging from 75 to 90 per cent by weight (hydrorsols). Coating compositions of 100 per cent concentration (hydrorsils) may also be used in such processes.

The treated fabric may be air dried or subjected to elevated temperatures for driving off the diluent at an accelerated rate. However, if a heat hardenable polymer is employed as a constituent in an impregnating composition, care should be taken during the drying not to exceed temperatures, such as 250°F. or conditions which will advance the resinous material beyond flowable condition.

The ratio of impregnating material to glass fibers depends to a great deal upon the type of fabric which is used. More polymer is required for fabrics having a high degree of openness, and less for denser woven fabric or felted mat. Volumetrically, the final product may be constituted of about 20 to 65 per cent solids with the solids being present in the ratio of about 10 parts by volume of glass fibers to 5 to 20 parts by volume of polymeric substances.

Although an impregnated fabric of the type described may alone be treated to provide vapor permeability and water repellency, it is expedient to combine two or more of the fabrics in the manner of a laminate during which the polymeric materials are caused to flow sufficiently to integrate the layers and to reduce the openings and voids to pore-like dimension through which vapors but not liquids are able to pass. Lamination may be effected at any time subsequent to the drying of the individually treated fabrics by subjecting a required number of layers to suitable heat and pressure conditions which may include room condition under catalytic activation, but more often under the conditions call from 220°F. to 400°F. for 5 to 30 minutes under 100 to 1000 psi pressure, depending primarily upon the type fabric which is used and the polymeric materials with which it is impregnated.

Water repellency of the fabric may be increased further by use of a water repellent or hydrophobic substance which preferably is embodied coating the original fabric before impregnation, but may instead be applied to the impregnating composition or by later treatment of the laminate with hydrophobic agent which has been incorporated in the impregnating composition or otherwise applied to the untreated or treated fabrics, concentrations of water repellent substance in the range of 1 to
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2 per cent by weight are sufficient to impart greater hydrophobicity to the surfaces of the finished product.

Suitable water repellent substances for imparting hydrophobic characteristics to the exposed surfaces comprise dilute water or solvent solutions, emulsions, or dispersions of one or more of the following materials or mixtures thereof:

A. An organosilicon of the type silane, represented by chlorosilane, alkyl halogen silanes, such as methyl trichlorosilane, octadeclitetrichloro silane, didecyldichlorosilane; polyisoxane fluids of low molecular weight, such as methyl polyisoxane, methyl ethyl polyisoxane, methyl phenyl polyisoxane, and the like.

B. Werner or chrome complexes of the type described in the patent to Sloan, No. 2,356,542, in which the organic group associated with the trivalent chromium atom has more than eight carbon atoms.

C. Cationic active amine complex compounds of the type described in the patent to Sloan, No. 2,356,542, in which the organic group associated with the basic nitrogen, phosphorous, or sulfer atom has more than eight carbon atoms.

D. Metallic soaps, oils, waxes, and mixtures thereof.

The following examples, given by way of illustration but not of limitation, demonstrate means for effecting this invention:

**Example 4**

A fabric knitted with yarns formed by twisting together four strands of glass fibers and one strand of cellulose acetate rayon is impregnated with the following composition:

- 3.0% butadiene-acrylonitrile (40% aqueous emulsion)
- 2.0% phenol formaldehyde “A” stage resin (40% solution)
- 1.0% diethyl siloxane (25% water emulsion)
- Balance water.

Following impregnation by a dipping process, the fabric is heated for about ten minutes at 225° F. to drive off the water diluent and, at the same time, to shrink the rayon fibers in a manner to form the glass fibers into multiple loops in the manner previously described. Five plies of the treated looped fabric are laminated together under 120 pounds per square inch pressure for twenty minutes at 352° F. The product is flexible and has leather-like characteristics. From a volumetric standpoint, the laminate consists of 48% glass, 13.5% resin and resin-like material with 38.5% of the fabric constituting voids of substantially pore-like dimension through which the vapors but not fluids are able to pass.

**Example 5**

(FIGURES 1 AND 2)

A fabric 20 knitted of staple glass yarns 21 may be impregnated with the following compositions:

**A**

- 2.5% butadiene-acrylonitrile copolymer (Hyca OR-25)
- 7.5% oil modified phenol formaldehyde resin
- 25.0% polymethyl siloxane
- 87.5% methyl ethyl ketone.

**B**

- 7.5% butadiene-acrylonitrile copolymer (Hyca OR-25)
- 5.0% oil modified phenol formaldehyde resin
- 3.0% copolymer of methyl phenyl siloxane and methyl siloxane
- 83.8% methyl ethyl ketone.

**C**

- 2.5% butadiene-acrylonitrile copolymer (Hyca OR-25)
- 2.5% oil modified phenol formaldehyde resin
- 1.0% polymethyl siloxane
- 94.0% dibutyl phthalate.

**D**

- 2.5% butadiene-acrylonitrile copolymer (Hyca OR-25)
- 7.5% oil modified phenol formaldehyde resin
- 25.0% polymethyl siloxane
- 8% polyvinyl chloride
- 86.7% methyl ethyl ketone.

15.0% phenol formaldehyde “A” stage resin
10.0% polymethyl siloxane
75.0% water.

The fabric 23 impregnated with composition A, is air dried at room temperature, and when four plies are laminated together under 120 pounds per square inch pressure for thirty minutes at 320° F., a laminate 24 is secured having 37.4% by volume glass, 28.0% resin 22, and 34.6% porosity.

When the same fabric is impregnated with composition B and five plies are laminated together under 120 pounds per square inch pressure for forty-five minutes at 320° F., the resulting product is constituted of 34% by volume glass, 46% by volume resin elastomer 22, and 20% by volume porosity. Although permeable to water vapor, the product is able to withstand a water pressure of 20 pounds per square inch without wetting through. In view of the greater amount of elastomer in the instant formulation when compared with the first, the resulting product exhibits considerably more flexibility which adapts it for certain purposes wherein softness and flexibility are more critical.

When the same fabric is impregnated with composition C and three plies are laminated together under 120 pounds per square inch pressure for forty-five minutes at 320° F., a product is obtained having by volume 12.2% glass, 22.4% resin, and 65.4% porosity.

When a knitted fabric of the type described is impregnated with composition D and six plies of the air dried fabric are laminated together under 120 pounds per square inch pressure for forty-five minutes at 320° F., a product is secured having 38% by volume glass, 36% by volume resin, with 26% porosity. The addition of vinyl chloride to the impregnating solution imparts a smooth and tough finish to the product.

When a knitted fabric of the type described is impregnated with composition E and two plies of the air dried treated fabric are laminated together under 120 pounds per square inch pressure for forty-five minutes at 370° F., the product therof, though somewhat stiffer, has properties similar to leather. From a volumetric standpoint, the laminate is constituted with 34.5% glass, 33.5% resin and 32% porosity.

**Example 6**

A fabric of the type described in Example 1 is treated with a 3% solution of dimethylpolysiloxane followed by air drying at room temperature. The mat is then impregnated with a composition constituted of a 5% solution of GRS latex (butadiene styrene copolymer in water emulsion), 5% polystyrene (40% water dispersion at 230° F.), and the remaining being water. After drying at a temperature of about 200° F. for about ten minutes, seven plies of the treated material are laminated together under 200 pounds per square inch pressure at 250° F. for twenty minutes. The resulting laminate has considerable porosity of pore-like dimension through which vapors but not fluids are able to pass. It is also flexible and well adapted as a leather substitute in the manufacture of leather-like articles.

**Example 7**

A knitted fabric of glass fibers is impregnated with a 20% solution of vinyl chloride-vinyl acetate copolymer in a combination of solvents, including toluene and ethyl acetate. After the treated fabric is air dried, five layers are laminated together under heat and pressure and the laminate is treated with an aqueous dispersion containing 1% cationic-active amine, such as octadecyl ammonium chloride, and 4% polysiloxane fluid, such as diethyl polysiloxane, to impart hydrophobic characteristics to the surfaces upon air drying.

It has been found that less impregnant is required and a better leather-like product is produced when relatively short discontinuous fibers of small dimension are incorporated in a manner to block the interstices between the fabric fibers. The interstitial closing fibers may be deposited on the fabric prior to impregnation or treatment or they may be incorporated into the treating composition.

It will be understood that numerous changes may be made in treating compositions, their method of application, the order of application, and in fabricating steps
to produce a product having the desirable characteristics without departing from the spirit of the invention, especially as defined in the following claims.

1. A vapor permeable, water repellent fabric formed of glass fiber threads intermixed uniformly with threads of shrinkable synthetic organic polymeric fibers, the threads of synthetic fibers being shrunkken in the fabric relative the glass fibers which retain their original lengths and form into loops in the fabric, and a water resistant polymeric resinous material impregnating the fabric substantially completely to fill the interstices thereof except for microporous openings through which vapor but not water is able to pass.

2. A vapor permeable, water repellent fabric formed of glass fiber threads woven with threads of shrinkable synthetic organic polymeric fibers, the threads of synthetic fibers being shrunkken in the fabric relative the glass fibers which retain their original lengths and form into loops in the fabric, and a water resistant, organic polymeric resinous material impregnating the fabric substantially completely to fill the interstices thereof except for openings of microporous dimension through which vapor but not water is able to pass.

3. A vapor permeable, water repellent fabric formed of glass fiber threads knitted in combination with threads of shrinkable synthetic organic polymeric fibers, the threads of synthetic fibers being shrunkken in the fabric relative the glass fibers which retain their original lengths and form into loops in the fabric, and a water resistant, organic polymeric resinous material impregnating the fabric substantially completely to fill the interstices thereof except for openings of microporous dimension through which vapor but not water is able to pass.

4. A vapor permeable, water repellent fabric as claimed in claim 1 in which the synthetic organic fibers and the glass fibers are mixed one with the other to form the thread.

5. A vapor permeable, water repellent fabric as claimed in claim 1 in which a plurality of such resinous impregnated fabrics are joined together as plies in a laminated structure.

6. A vapor permeable, water repellent fabric as claimed in claim 1 having a coating of a water repellent material on the surfaces of the impregnated fabric.

7. The method of forming a vapor permeable, water repellent fabric comprising weaving a fabric of threads formed of glass fibers and of heat shrinkable synthetic organic polymeric fibers substantially uniformly distributed with the glass fibers, heating the woven fabric to shrink the synthetic organic fibers independently of the glass fibers which retain their original lengths and form into loops in the woven fabric, impregnating the fabric with a flexible, water repellent, synthetic organic polymeric material substantially completely to fill the interstices between the fibers of the fabric except for openings of microporous dimension through which vapor but not water is able to pass.

8. The method as claimed in claim 7 which includes the additional step of laminating a plurality of the impregnated fabrics produced in accordance with claim 6 under heat and pressure to form a consolidated structure.

9. The method as claimed in claim 8 which includes the additional step of treating the surfaces of the laminate with a water repellent to improve the water repellency of the fabric without interfering with the ability of the vapor to pass therethrough.

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