

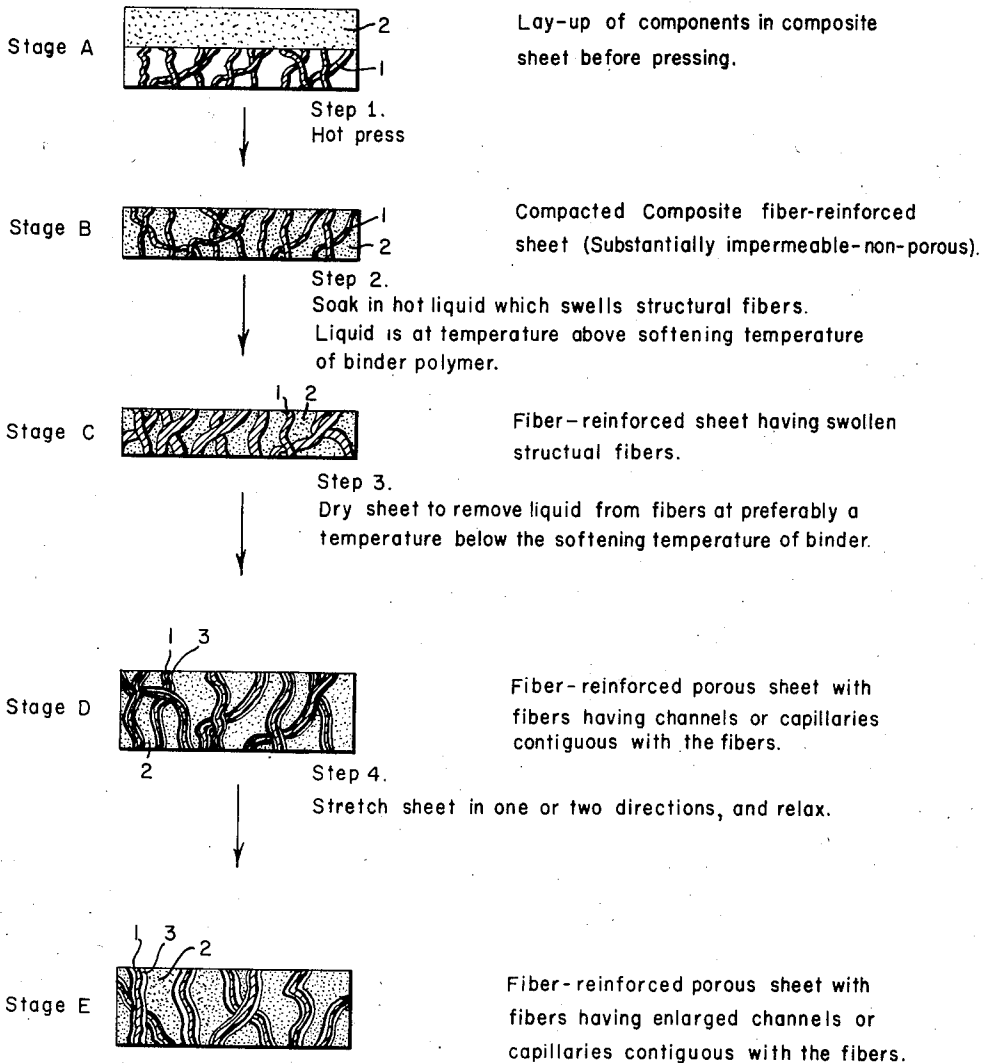
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H. R. MIGHTON

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PROCESS OF PREPARING FIBROUS, NON-WOVEN, POROUS SHEETS

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INVENTOR

HAROLD R. MIGHTON

BY

A. Ralph Snyder

ATTORNEY

1

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PROCESS OF PREPARING FIBROUS, NON-WOVEN, POROUS SHEETS

Harold R. Mighton, Kenmore, N. Y., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention relates to a process of preparing leather replacement compositions, and, more specifically, to a process for forming leather replacement compositions by treating a fiber-reinforced polymeric sheet.

Patents relating to methods and techniques of preparing leather replacement compositions have been granted to inventors as far back as 1850; and even before that time, a great number of attempts have been made to devise a simple and rapid technique of producing leather replacement compositions. In most of the early art, pyroxylin was used to coat or impregnate various types of fibrous base materials to prepare leather substitutes. As time went on, pyroxylin/oil/pigment compositions were widely used as coating or impregnating compositions for various woven or non-woven fibrous base materials. In the early stages of the synthetic leather industry, the main objective was to simulate the general appearance of leather.

In today's markets, coated fabrics, particularly the vinyl-coated fabrics, are outstanding as leather substitutes in such applications as handbags, bookbinding, brief cases, card table covers, luggage, etc. In such applications, the coated fabrics are satisfactory because the general appearance of leather is simulated; and the coated fabrics possess some of the desirable properties of leather. However, as compared to genuine leather, the coated fabrics lack good tear strength, softness, and the ability to "breathe" or transpire water vapor and air; and although the coated fabrics are used in such applications as chair coverings, much is left to be desired, especially with respect to water vapor and air permeability. Up to the present time, leather replacement compositions have made little or no inroads into the boots, shoes, and gloves markets, mainly because of their inability to breathe, in addition to lack of good tear strength and softness. As used hereinafter, the term "breathe" means transpire water vapor and air.

In general, the use of leather replacement compositions in boots, shoes, gloves, etc., is mainly dependent upon its ability to breathe, usually expressed in terms of water vapor permeability or "leather permeability." Physical tests on the water vapor permeability of leather indicate that leather transpires water vapor about two-thirds as readily as free air. In general terms, shoe upper leather samples having a thickness of 0.016"—0.104" have a leather permeability within the range of 2,000—18,000 grams/100 sq. meters/hour when tested according to the method of Kanagy and Vickers Journal of American Leather Chemists Association 45, 211—242 (April 1950) in an atmosphere of 23° C. and 90% relative humidity. Hereinafter, the ability of leather replacement compositions to transpire water vapor will be expressed in terms of leather permeability in the units of grams/100 sq. meters/hour. Based upon comfort tests, the minimum tolerable leather permeability for shoe upper leather is about 2,000 grams/100 sq. meters/hour. Preferably, for shoe upper leather, the permeability value

2

should be 4,000—20,000 when tested at 23° C. and not greater than 90% relative humidity.

Recently, various techniques and processes have been developed for preparing leather replacement compositions which not only have the appearance of leather but are also capable of breathing. Comparisons of the leather permeability of these synthetics compared with genuine leather have shown that the leather permeability of the synthetics in many cases is superior to that of shoe uppers fabricated from genuine leather. Furthermore, the flexibility of these recently developed techniques provides for tailoring the compositions for particular end uses, that is, produce a product having the desired water vapor permeability, tear strength, softness, etc. However, in many cases, as a result of these techniques, flex life and tensile strength are imparted to the leather replacement compositions at the sacrifice of water vapor-permeability.

An object of the present invention, therefore, is to provide a process of preparing leather replacement compositions having increased water vapor-permeability in addition to having good flex life, tear strength, tensile strength and a relatively low tensile modulus. Other objects will become apparent from the following description.

These objects are realized by the present invention which, briefly stated, comprises forming a compact, essentially water vapor-impermeable, composite sheet by hot-pressing a composite comprising a liquid-swellaable structural fiber component and a soft, elastomeric, initially thermoplastic polymeric binder component having a softening temperature below that of the structural fiber component, and thereafter swelling the liquid-swellaable fibers by soaking the sheet, at a temperature between the softening temperature of said binder and of said liquid-swellaable structural fibers, in a liquid which swells the liquid-swellaable structural fibers and stretching the sheet within the limits hereinafter set forth, followed by relaxing and drying the sheet.

Swelling the fiber component of a substantially impermeable compacted sheet composed of a mat of non-woven fibers thoroughly impregnated with a soft, initially thermoplastic polymer, swelling being effected at or above the softening temperature of the polymeric binder, results essentially in stretching the softened binder polymer. That is, as the polymer-encased fibers are swelled, the softened binder polymer around each fiber is deformed in the direction of swelling; and thereafter the composite sheet is subjected to a temperature essentially below the softening point of the polymer, this serving to set the binder polymer in deformed condition. This step is followed by removal of liquid from the swelled fibers which results in shrinkage or deswelling of the fibers to substantially the original dimensions thereof. The net result of this step is the production of a porous structure in which the pores are interconnecting channels contiguous with structural fibers. This process is described and claimed in the copending application of J. C. Richards, U. S. Serial No. 325,689 filed December 12, 1952, now abandoned.

On the other hand, stretching a substantially water vapor-impermeable composite sheet comprising an extensible or stretchable binder material and structural fibrous component also results in the formation of a sheet which is permeable to water vapor and air. Generally, the degree of permeability imparted to a sheet which has only been subjected to a stretching step substantially depends upon the particular fiber component employed; the particular relatively extensible binder material employed; the ratio of fibrous component to binder material in the initial sheet; the extent of stretch (either in one direction or two

directions); and the degree of adhesion between the two major components of the sheet. Stretching the initial compacted sheet appears to pull the extensible binder component away from the fibrous components, and this results in the formation of voids or capillaries contiguous with the fibers. Hence, a stretched sheet has a cross-sectional structure essentially consisting of a binder polymer reinforced with fibers, areas immediately adjacent the fibers being voids. This process is described and claimed in the copending application of V. L. Simril, U. S. Serial No. 318,732 filed November 4, 1952, now U. S. Patent No. 2,757,100.

The process of the present invention comprises combining the steps of swelling structural fibers and stretching the fiber-reinforced sheet to form a porous leather replacement composition having leather permeability or LPV, which in most cases is greater than the sum total of the LPV's of individual sheets, one sheet produced solely by a stretching process and the other sheet being produced solely by the swelling-deswelling process. Furthermore, the process of the present invention contemplates no restrictions with respect to the order in which the essential steps thereof are carried out. In other words, the compacted fiber-reinforced sheet may first be subjected to soaking in a liquid which swells at least a part of the structural fibers, and this may then be followed by deswelling the swollen fibers by drying the sheet at a temperature which is no greater than the softening temperature of the binder polymer and is usually below the softening temperature of the binder polymer. Thereafter, the resulting porous sheet may then be subjected to stretching in one direction or two directions, followed by relaxing, to produce a final sheet having a vastly increased LPV. On the other hand, the initial compacted sheet may be soaked in a hot liquid for a short period of time, and then while maintained in the liquid, the sheet may be stretched in one or two directions and thereafter relaxed and subjected to drying conditions at a temperature no higher than the softening temperature of the binder to remove liquid from the sheet. Lastly, the initial compacted sheet may be first stretched in one or two directions, relaxed, and thereafter permitted to soak in a hot liquid at a temperature above the softening temperature of the binder polymer followed by drying the sheet to remove liquid. In most cases, the resulting leather permeability value (LPV) is greater than that of a sheet subjected to only one or the other of the essential component steps of the process of the present invention.

The expression "substantially water vapor-impermeable" as applied to the initial composite sheet (i. e., before swelling and stretching) means that the sheet has a leather permeability value (LPV) of less than 1,000 grams/100 sq. meters/hour, measured at 23° C. and 90% relative humidity. In general terms which may be applied to any combination of non-woven fibers and soft thermoplastic polymers useful in the present process, the water vapor-permeability of the initial composite base sheet is substantially no greater than that of homogeneous sheets of the fiber components or binder polymer, whichever has the higher water vapor-permeability. Usually, providing the initial composite base sheet is prepared in such a manner that there are substantially no voids present in the sheet, the water vapor-permeability of such a base sheet is intermediate between the permeabilities of homogeneous sheets of the two major components of the base sheet. Actually, the leather permeability value (LPV) of the initial compacted, substantially water vapor-impermeable sheets which are transformed into the permeable sheets by following the present process are low not only because the sheet is compacted by hot-pressing, but also because of the thickness of the sheets which are useful for converting to synthetic leather sheets. That is, the initial compacted sheets are usually between

0.015"-0.05"

in thickness; and homogeneous sheets of either the binder polymer or the structural fiber having thicknesses within this range have low LPV's. Normally, the LPV is appreciably less than 1,000 and is in no case greater.

The term "liquid-swellaable structural fiber," as employed herein, denotes fibers which swell in contact with a liquid by absorption of the liquid into the fibers and which, upon removal of the liquid by drying, shrink back to substantially their original dimensions. The liquid used should not dissolve the binder material although it may be absorbed to a limited extent by the binder.

The "softening temperature" of the thermoplastic polymeric binder is the "second order transition temperature" (T_m) in the case of a normally amorphous polymer; or, in the case of a crystalline polymer, the softening temperature is the beginning of the melting point range or the temperature at which the crystalline phase begins to disappear as determined by X-ray examination or any other suitable technique. The "second order transition temperature" of an amorphous polymer is defined as the temperature at which a discontinuity occurs in the curve of a first derivative thermodynamic quantity of the polymer with temperature. It can be observed from a plot of density, linear expansion, specific volume, specific heat, sonic modulus, or index of refraction against temperature. The method of determining the second order transition temperature of a polymer is described in U. S. Patent 2,556,295 to Pace.

The total volume of voids produced in products resulting from the process of the present invention depends primarily upon the content of structural fibers in the fiber/binder sheet. It should be pointed out that all or only a portion of the structural fibers may be liquid-swellaable. Normally, however, all of the structural fibers will be liquid-swellaable, e. g., will absorb a liquid such as water to such an extent that swelling takes place. Other factors which affect the number of voids produced in the final sheet composition include the degree to which the sheet is stretched and the amount of recovery of the binder polymer upon relaxing. Normally, the binder polymer after stretching does not recover completely, i. e., 100%, especially after being stretched as much as 40%-50% in one or both directions. Incomplete recovery is evidenced by an increase in the thickness of the sheet after stretching and relaxing. However, as long as the adhesive bonds between fiber and binder are broken in stretching, it may be desirable to obtain almost complete recovery or a high degree of recovery because the resulting sheet would be softer and yet highly permeable as a result of the internal surface area formed by breaking the adhesive bonds between binder polymers and structural fibers. On the other hand, with regard to the step of swelling the fibrous components, the volume of voids formed in the final composition further depends upon the degree to which the fibers swell upon soaking in a liquid. Hence, with reference to the present overall process, the greater the actual number of individual structural fibers present in the initial sheet, the greater the volume of voids formed and the greater the internal surface area regenerated.

Usually, the weight ratio of fibrous component to binder polymer in the initial compacted sheet to be subjected to the present process varies from 30:70 to 70:30. However, the optimum quantity of binder material in the initial composite sheet ranges from 40-60%, based upon the total weight of the two major components. Normally, the densities of the binder polymer and the fibrous component are relatively close; and in such cases, the ratio of the two components may be expressed on either a volume or weight basis. Generally, as the quantity of extensible or binder material in the compositions is reduced, the initial composite sheet becomes more and more permeable to water vapor, but the other properties and characteristics of the sheet as finally treated in accord-

ance with the present process are not satisfactory for use as a leather replacement, for example, in boots, shoes, gloves, chair coverings, etc.

Any fiber capable of being swollen by a liquid and shrinkable to substantially its original dimensions on removal of the liquids, and having a deformation temperature higher than the softening temperature of the binder employed, may be used as the structural fibers in the non-woven porous compositions produced by the present process. The particular choice of fiber depends mainly upon the end use of the product and the particular binder being employed. Fibers of nylon, i. e., synthetic linear polyamides such as polyhexamethylene adipamide, polyhexamethylene sebacamide, polycapromide and interpolymers thereof, etc., are outstanding for use in the present compositions. Various other types of polyamides and synthetic linear condensation polymers which may be employed in the form of fibers in this invention are described in U. S. Patents Nos. 2,071,250, 2,171,251, 2,071,253, 2,130,948, 2,224,037 and 2,572,844. In general, nylon structural fibers produce permeable compositions having high tear strength, tensile strength and flex life. Other fibers useful for purposes of this invention include polyethylene terephthalate, viscose rayon, acetate rayon, polyacrylonitrile, acrylonitrile copolymers, cellulose acetate, polyvinyl acetals, cotton and wool, and mixtures of two or more varieties of fibers. It should be emphasized that the use of a blend of fibers which are swollen to different extents by certain liquids, for example, by water, are very useful in making leather replacement sheets in accordance with the process of this invention. For example, a blend of nylon fibers and rayon fibers may be highly advantageous, in that the rayon fibers are more readily swollen by water, these fibers imparting increased porosity to the final composition, and the nylon fibers, while also forming the nuclei of pores, impart superior strength properties to the final compositions.

Since the structural fibers are serving to reinforce the binder material and provide for formation of interconnecting capillaries or pores having substantially the same interconnecting network pattern as that of the structural fibers, selection of fibers having particular physical characteristics as well as selection of fibers of a particular length and denier must be considered with these two functions in mind. For the purpose of providing adequate tensile strength, tear strength, and flex life, the structural fibers should be at least 0.5" in length. As a general observation, the strength properties of the final permeable compositions do not increase appreciably when using structural fibers greater than about 1.5" in length. On the other hand, from the standpoint of handling non-woven mats of fibers on standard textile machines, it may be more convenient to use longer fibers, for example, as long as 8". With respect to the network of interconnecting pores formed throughout the cross-section of a sheet treated in accordance with this invention, the use of very short fibers, e. g., 0.01" flock, does not produce a composition having optimum permeability. When the length of a structural fiber is increased from 0.25" to 0.5", the permeability appears to increase; but no appreciable increase is obtained when fibers longer than 0.5" are employed.

It is within the scope of the present invention to employ fibers having a denier within a relatively wide range. Normally, textile fibers having a denier within the range from 1-3 denier/filament are employed. On the other hand, fibers having a denier as low as 5.5×10^{-5} denier/filament have been used in conjunction with fibers of greater denier, e. g., 1-3 denier/filament. Usually, it is entirely practical to employ very thin denier fibers so long as the cohesive bonds within the fibers are greater than the adhesion between fiber and binder, or, in other words, so long as the fibers are distinguishable as such in the fiber/binder composite. It is especially advantageous to position very thin denier fibers at the surface of the present compositions in order to produce sheeting

which will retain its original surface appearance after repeated abrasions. Extreme condition with respect to employing fibers of higher denier is the use of fibers substantially greater than about 16 denier per filament, these fibers being relatively stiff and bristle-like.

It is to be understood that the non-woven fibrous mats employed in preparing the polymer-impregnated, substantially impermeable, initial compacted sheets should be fabricated in accordance with any well known batch-wise or continuous techniques such as by carding machines, air deposition apparatus and water deposition or paper making techniques. Furthermore, the resulting fibrous mats may have their component fibers oriented substantially in one direction or randomly arranged. Individual mats having the fibers oriented in one direction may be cross-laminated. In any event, the fibers must be interconnecting so that the resulting capillaries or void spaces contiguous with the fibers may be interconnecting.

As mentioned hereinbefore, the initial composite, uncompact sheet is subjected to a hot-pressing or consolidating operation which causes the binder to melt and flow, this resulting in thoroughly impregnating the fibrous components therein and redistributing the polymeric binder to form a continuous solid polymeric film or sheet. The hot-pressing step must be carried out at a temperature above the flow temperature of the polymeric binder (flow temperature, for example, may be measured by ASTM Test D-569-48) and below the deformation temperature or softening temperature of the fibrous components. Generally, the compositions are hot-pressed at a temperature within the range from 120°-200° C. under pressures varying from 50 p. s. i. to 2,000 p. s. i. In all cases, the temperature at which the fiber/binder sheet is consolidated must be below the degradation temperatures of the fibrous components and the binder polymer or polymers. During the hot-pressing step, the fibrous component, which must not be deformed to such an extent as to lose its identity as fibers, or be transposed to the extent that a greater proportion of fibers are concentrated in one portion of the sheet than in other portions, serves as a lattice, around which the polymeric binder flows to impregnate each and every fiber. Hence, after consolidation, the sheet takes the form of a fibrous lattice which is completely embedded or surrounded by the binder polymer. In this form, the compacted fiber-reinforced polymeric film or sheet is ready to be subjected to the process steps of the present invention.

The binder polymer must be thermoplastic at least in the sense that it must flow under the initial hot-pressing step which compacts the initial sheet composing non-woven fibers impregnated with a binder. Furthermore, it must be thermoplastic in the sense that it is capable of being deformed at its softening point by the swelling fibers; and the deformation must be substantially permanently set upon subsequent drying of the sheet at a temperature at or below the softening temperature of the binder polymer. The binder polymer may be selected from the large class of soft, thermoplastic polymers, and, more specifically, from the class of polymers which may be generally classified as elastomers or elastomeric materials, as set forth by H. L. Fisher (Industrial and Engineering Chemistry, August 1939, page 42). The binder polymer employed should not be chemically similar to the structural fibers, and the degree of adhesion between the binder polymer and fibers after hot-pressing should not be too great. The lower the adhesion between binder polymer and fibers, the less drastic the treatment necessary to break the bonds between the fibers and binder to form interconnecting pores in the compacted sheet. Copending application U. S. Serial No. 325,689, filed December 12, 1952 in the name of J. C. Richards, discloses a screening process which may be employed to determine the relative adhesion of various binder polymers and fibers.

The addition polymers are preferred for use as the binder material. A particularly outstanding group are the addition polymers containing in combined form the ethylenically unsaturated monomers including both the mono- and diene-type monomers. The most outstanding group of these addition polymeric binders are the vinylidene polymers and copolymers including both the monoene and diene types. This class of polymers is characterized by having in each polymerizable monomer therein involved as the only polymerizable ethylenic unsaturation, terminal ethylenic groups wherein the terminal carbon is a methylene carbon, i. e., those containing one or more vinylidene ($\text{CH}_2=\text{C}=\text{}$) groups. Included in this most preferred class are the great majority of commercially available addition polymers. Specific examples of such polymers include the various vinylidene hydrocarbon polymers such as butadiene/styrene, polyethylene, polyisobutylene, polyisoprene, both synthetic and natural; the various negatively substituted polymers such as the vinylidene halide including vinyl halide polymers, e. g., polyvinylidene chloride, polyvinyl chloride and polyvinyl fluoride; derivatives of such polymers as halogenated vinyl and vinylidene polymers, e. g., chlorinated polyethylene, and chlorinated polyvinyl chloride; the various vinylidene polymers wherein one or both of the indicated free valences of the 2-carbon of the vinylidene group are bonded directly to carboxyl groups or groups hydrolyzable to carboxyl groups either directly to the acyl carbon or the oxy oxygen thereof, such as polymers of various vinylidene esters, including vinyl acetate and ethylidene diacetate; vinylidene carboxylic acids and their derivatives such as acrylic acid, acrylonitrile, and methacrylamide.

Also included in this most preferred group are the various copolymers of such vinylidene monomers, including specifically the various monoene and diene copolymers of this class such as 2,3-dichlorobutadiene-1,3/2-chlorobutadiene-1,3 copolymers; the various monoene/vinylidene copolymers such as the commercially important vinyl and vinylidene chloride copolymers, e. g., vinyl chloride/vinyl acetate, vinyl chloride/vinylidene chloride, and vinyl chloride/vinyl acetate/acrylonitrile copolymers; the various vinylidene hydrocarbon negatively substituted vinylidene copolymers, e. g., ethylene/vinyl acetate and the hydrolyzed products therefrom; ethylene/vinyl chloride, and butadiene/acrylonitrile copolymers. In the case of those binder components containing in combined form appreciable proportions of diene monomers, particularly the vinylidene diene monomers, it is frequently desirable to have present in the solution, dispersion, or bulk treating material, whichever is used, suitable amounts of chemical agents for effecting under controlled conditions, after the fiber has been impregnated with the binder and the whole mat suitably compacted, the cross-linking of the diene copolymer component. These chemical systems for effecting such controllable cross-linking are well known in the rubber art and in the case of the diene hydrocarbon polymers and copolymers, such as 2-chlorobutadiene-1,3 (chloroprene), normally function through a disulfide formed cross-link arising from the presence of mercaptans and/or sulfur in the diene polymer composition; and in the case of such polymers as chlorosulfonated polyethylene, curing may be carried out in the presence of metallic oxides such as zinc or magnesium oxides.

Various polyesters containing terephthalic acid or derivatives thereof as essential components are useful as binder polymers, these including polyethylene terephthalate and copolyesters made from ethylene glycol, terephthalic acid and sebacic acid of the general type described and claimed in U. S. Patents No. 2,623,031 and 2,623,033 in the name of M. D. Snyder. Polyamides useful as a binder polymer include N-methoxymethyl polyhexamethylene adipamide and other similar polymers disclosed and claimed in U. S. Patent 2,430,860.

Also included among useful binder polymers are the polyvinyl acetals, such as polyvinyl butyral, polyvinyl laural, etc.

Included among other elastomeric polymers which may be employed as binders in the present invention are the polyurethanes which are essentially reaction products of (1) an organic polyisocyanate or polyisothiocyanate with (2) a compound obtainable by reacting (a) one or more polyhydric alcohols with (b) one or more polycarboxylic acids (either in the presence or absence of one or more monocarboxylic acids). Specific products of this type are described and claimed in U. S. Patent 2,333,639 to R. E. Christ and W. E. Hanford. Still other types of elastomeric polymers which may be used as binders include reaction products of polyalkylene ether glycols and organic diisocyanates.

In many instances, it is desirable to have present in the binder composition appreciable proportions of plasticizers, now well known in the art, for the binder polymers. This is particularly important in the case of the vinylidene resins, to prevent formation of products of too great stiffness, especially with the higher molecular weight, negatively substituted vinylidene polymers and copolymers, such as the vinyl chloride/vinylidene chloride and vinyl chloride/vinyl acetate copolymers, so as to produce leather-like products of good drape and high pliability. Suitable examples of these include the higher molecular weight mono- or dicarboxylic acid/alcohol or/polyesters such as glycerol mono-oleate, glycerol sebacate, dioctyl phthalate, and ethylene octanoate; or the lower molecular weight polyesters and polyethers such as the polyalkylene oxides and their esters, e. g., polyethylene oxide, methoxypolyethylene glycol; and the lower molecular weight condensation polyesters such as polyethylene glycol adipate.

As pointed out previously, the critical factor in the choice of a preferred polymeric binder is the fact that it should not be chemically similar to the structural fiber. This is quite important since it has been found that where the polymeric binder is chemically similar to the structural fiber, the resulting sheet material, while occasionally adequate in tensile strength, is generally deficient in drape, hand, and flex life, and, more importantly, is usually particularly deficient in tear strength. A convenient rule for characterizing the chemically dissimilar polymeric binders is that they be incompatible in the melt with the structural fibers.

The polymeric binder in general should be tough, pliable, and elastic, and it should be at least initially thermoplastic and should melt and flow at a temperature below the deformation (softening) temperatures of the structural fiber and pore-forming fiber. By the term "initially thermoplastic" is meant that the binder material must melt and flow under the conditions of the hot-pressing step. When the binder material is in the form of individual fibers, the length of the fibers has no effect upon the properties of the extracted sheet, provided that the binder fibers have been strategically uniformly dispersed through the composition before heat and pressure are applied. In describing the binder material as a tough, pliable, at least initially thermoplastic, polymer, the following more specific requirements apply to those binder materials that are preferred:

1. Tensile strength should be at least 500 p. s. i.
2. The elongation must be at least 100%.
3. Materials not having a tensile strength and elongation greater than the above minimum specifications may be satisfactory if the product of their tensile strength and elongation (where 100% equals 1) is at least 1,000.
4. Tensile modulus must not be more than 25,000 p. s. i. and, preferably, not more than 5,000 p. s. i.

The binder material may be incorporated into the initial impermeable composite sheet in a variety of ways,

several of which have been illustrated hereinbefore. The binder material may be in the form of fibers which may be carded along with the structural fibers and the pore-forming fibers to form a composite sheet by pressing the carded mixed fibers at elevated temperatures. Webs or mats of mixtures of structural fibers, pore-forming fibers and binder polymers may be formed by mutual coagulation of a mixed dispersion of the three components. A fibrous mat of a mixture of structural and pore-forming fibers may be impregnated with a binder polymer which may be dispersed in a non-solvent, e. g., aqueous medium, or may be in a solvent solution. On the other hand, a fibrous mat containing both structural and pore-forming fibers or just structural fibers may be impregnated with a binder polymer in the form of a hot melt. A fibrous mat of structural and pore-forming fibers or structural fibers alone may be impregnated with a binder polymer by calendaring techniques or by spraying the binder material from an aqueous dispersion or solvent solution onto one or both sides of the fibrous mat, followed by the application of heat and pressure to impregnate the fibrous portion of the mat with the binder material. Regardless of the technique employed to form a composite sheet, the sheet is compacted prior to extraction of the soluble or pore-forming fibers by pressing at a temperature above the flow temperature of the binder and below the softening or deformation temperature of the structural fiber and pore-forming fiber.

The main objective in subjecting the initial compacted sheet to the soaking and drying steps (swelling-deswelling) of the present process is to bring about a reversible dimensional change in the liquid-swellaible structural fibers thereby producing a permanent deformation of binder material in the portions contiguous with the structural fibers. Therefore, at least a portion of the fibers employed must become readily swollen in the particular liquid employed, e. g., water, which liquid must not dissolve the fibers or the binder material to any appreciable extent. On the other hand, the liquid may effect some swelling of the binder material so long as the net result is permanent deformation of the binder material to form annular capillaries or voids around the structural fibers. The preferred liquid in which the initial composite sheets are soaked to swell the structural fibers is water. In instances where the softening temperature of binder material is above 95–100° C., other suitable liquids may be employed so long as they are readily removed from the fibers and surfaces of the treated sheets. For example, various water-soluble dihydric and trihydric alcohols and aqueous solutions thereof may be employed, such as ethylene glycol and various polyethylene glycols and glycerin. Various organic acids, such as acetic and other aliphatic carboxylic acids, may be used alone or in aqueous solution. On the other hand, in order to employ liquids which are readily removable from the surfaces of the sheets by water and yet maintain a temperature above 100° C., solutions may be prepared by dissolving various salts such as sodium chloride, sodium acetate, etc., in water. Such swelling media are non-toxic and cheap. To maintain water at temperatures above 100° C., swelling may be effected in a pressure tank or vessel. As a general requirement, the liquid employed for soaking the initial sheets should not dissolve the structural fiber or binder material to any appreciable extent; and the swelling produced must be due to the presence of the liquid within the fibers so that shrinkage of the fibers may be effected by removal thereof from within the fibers.

The improvement in the water vapor permeability of the initial compacted sheet, as effected by stretching the sheet in one or two directions, is directly related to the degree to which the sheet is stretched, i. e., the degree to which the sheet is elongated. At very low elongation,

i. e., 5–10%, the improvement in water vapor permeability is low, even though the sheet may be stretched 5–10% in two directions. However, as the amount of elongation is increased, the water vapor permeability increases; and the improvement is outstanding when the sheets are stretched in two directions. Generally, the nature of the extensible and relatively non-extensible material employed in the initial composition determines the amount of stretch required to effect the desired improvement in water vapor permeability. However, in all cases, stretching in two directions, that is, biaxially, appears to produce the greatest improvement in water vapor permeability for a given extent of stretch or elongation, i. e., 50% and above, although imparting excellent porosity or breathing qualities, usually degrades the other physical properties necessary to produce a good leather replacement composition. Specifically, the tensile strength decreases appreciably at high elongation. In general, as the extensible material or binder polymer is extended to the limit of its extensibility, the binder ruptures; and from this point, in the case of a fiber-reinforced composition, only fiber-fiber separation is measured. Preferably, the initial sheet should be stretched biaxially from 10–40%, the degree of stretching being substantially the same in each direction.

Color may be imparted to the leather replacement sheet produced by the process of this invention by incorporating dyes or pigments in the polymeric binder, or by dyeing after finishing or using pre-dyed or pre-pigmented structural fibers. Preferably, colored sheet material is prepared by the use of dyed or pigmented structural fibers or by incorporating coloring mat in the polymeric binder, since the sheet material is then uniformly colored throughout and thus unlike colored natural leather, it will not exhibit any marked or undesirable color changes if scuffed or abraded. When pigments are incorporated into the polymer binder for the purpose of preparing colored sheets, the concentration of pigments should be kept at a minimum, less than 5–10%, by weight of the total sheet, in order that the physical properties of the sheet, particularly tensile strength, tear strength, and abrasion resistance are not materially affected.

A clearer understanding of the present process and embodiments thereof for forming leather replacement compositions may be had by referring to the flow diagram set forth in the accompanying drawing wherein is illustrated an embodiment of the present invention wherein a consolidated fiber/binder sheet is subjected to the steps of swelling and then deswelling the structural fibers, followed by stretching the sheet in one or two directions and relaxing the sheet.

Referring to the drawing, stage A represents the initial composite of alternate layers of fibers and binder polymer. Layer 1 is composed of structural fibers, e. g., nylon fibers, in the form of a non-woven mat; and layer 2 is a homogeneous film or sheet of a binder polymer, e. g., plasticized polyvinyl chloride. Step 1 involves hot-pressing the composite of stage A to form stage B which represents a compacted composite fiber-reinforced sheet which is substantially impermeable, i. e., non-porous, to water vapor and air. Step 2 involves soaking the sheet of stage B in a hot liquid, e. g., water at 95° C., to swell the structural fibers at a temperature which is above the softening temperature of the binder polymer. The resulting sheet is stage C which is a fiber-reinforced sheet having swollen structural fibers. This sheet is then subjected to step 3 which involves drying the sheet at a temperature preferably below the softening temperature of the binder polymer to remove liquid from the structural fibers and from the binder material if some liquid has been absorbed. The resulting sheet is then in stage D, which is a fiber-reinforced porous sheet having channels or capillaries 3 contiguous with the fibers. At this stage, the sheet has an LPV which is comparable to many types of shoe upper

leathers. Finally, the sheet in stage D is subjected to step 4 which involves stretching the sheet in one or two directions, that is, stretching the sheet usually at least 15%–20% (elongation) in two directions and thereafter permitting the sheet to relax. The final sheet is then in stage E which represents a fiber-reinforced porous sheet having enlarged (over those of the sheet in stage D) channels or capillaries contiguous with the fibers. The resulting sheet in stage E will have an LPV which is substantially greater than the sum total of LPV's for individual sheets treated solely by a swelling-deswelling process and a sheet treated solely by a stretching process. For simplicity, the initial composite is shown as consisting of a single layer of structural fibers and a single layer of binder polymer. It is to be understood, however, that any desired number of layers may be employed and that in practice, a plurality of layers of fibers and of binder polymer will generally be employed.

The terms "contiguous channels," or "channels contiguous with fibers," as applied to the interconnecting pores formed in the fiber-reinforced strata of the leather replacement sheets of this invention, mean that the channels or pores are immediately adjacent the structural fibers. It should be emphasized that the pores or channels are not necessarily wholly annular; that is, the structural fiber is not necessarily entirely broken away from the surrounding binder polymer. In some cases, for example, a continuous pore or capillary may spiral around a continuous length of fiber; whereas, on the other hand, the capillary, formed by the fiber's breaking away from the surrounding binder polymer, may take the form of a "hair-line crack" running substantially parallel and immediately adjacent a structural fiber.

The following examples of the process will serve to

Table I

Composition	Parts By Weight, of Fibrous Components	Parts By Weight, of Polyethylene Binder	LPV, Gms./100 Sq. Meters/Hr.
Sheet 1-----	4.4	4.4	1,100
Sheet 2-----	4.8	4.8	6,000
Sheet 3-----	5.0	5.0	10,000

EXAMPLE 2

Composite sheets comprising alternate layers of polyhexamethylene adipamide fibers (2½" in length and 3 denier/filament) in the form of non-woven mats and homogeneous sheets of a plasticized vinyl chloride/vinyl acetate copolymer were pressed together at 160–165° C. under 500–600 p. s. i. for 12 minutes to form a compacted fiber-reinforced sheet similar to stage B of Figure 1. One sheet (sheet 4) was subjected only to a swelling-deswelling process; a second sheet (sheet 5) was stretched in two directions (elongated 20% in both directions), and a third sheet (sheet 6) was soaked (swelled) in water at 95° C. for 35 minutes, dried at room temperature and thereafter stretched 20% in two directions and permitted to relax. Pertinent physical properties of the resulting sheets are given in Table II below. The tear strength given in Table II is the tongue-tear strength (average resistance to propagation of a pre-cut slit in the Instron tensile tester). Tongue-tear strength is measured by cutting a 1" slit in the sheet to be tested, and thereafter measuring the average force in pounds required to propagate the tear. The test is carried out in a manner similar to ASTM Test D-39-39.

Table II

Parts by Weight of Fiber	Parts by Weight of Binder	Method of Introducing Porosity	Thickness of the Final Sheet (mils)	Tenacity, p. s. i.	Tensile Modulus, p. s. i.	Tongue-Tear Strength, pounds	LPV, gms./100 sq. meters/hour
4.6 6.06	4.5 6.06	Swelling-Deswelling-----	20	4,000	16,000	10	2,700 8,500
6.4	6.7	Stretched-20% in Two Directions. Swelling-Deswelling followed by stretching 20% in Two Directions.	37	4,244	11,000	31	12,000

further illustrate the principles and practice of the present invention:

EXAMPLE 1

Layers of polyhexamethylene adipamide fibers (1½" in length and 3 denier/filament) in the form of non-woven fibrous mats were composited with alternate homogeneous films of polyethylene in a manner similar to that illustrated by stage A of the drawing. This composite contained equal weights of fibers and binder polymer, and the composite was hot-pressed at 120–125° C. under a pressure of 500–600 p. s. i. for 7 minutes. Individual samples of the resulting compacted, substantially impermeable sheets were subjected to one of three different processes, one of the processes being that of the present invention. One sheet (sheet 1) was soaked in hot water at 95° C. for 45 minutes and thereafter dried at room temperature. The second sheet (sheet 2) was stretched in two directions so that the sheet was elongated 30% in both directions, and the sheet was permitted to relax. The third sheet (sheet 3) was soaked in hot water at 95° C. for 20 minutes and thereafter dried at room temperature. This sheet was then stretched in two directions to an elongation of 30% in both directions, and the sheet was permitted to relax. Table I below indicates the LPV's of the sheets resulting from the present process having an LPV which is substantially greater than the sum total of the LPV's of the other two porous sheets.

Example 3

This example illustrates employing the process of the present invention for preparing porous leather replacement sheets from combinations of fibers and a binder which adhere strongly to one another. Normally, under these circumstances, that is, when the fiber and binder adhere strongly to one another after being hot-pressed, it is extremely difficult, and in most cases not possible, to improve the leather permeability value of a compacted fiber-reinforced sheet by solely a swelling-deswelling process or by solely a stretching process. This is the case when polyhexamethylene adipamide fibers (2½" in length and 3 denier/filament) are hot-pressed with a binder polymer of N-methoxymethyl polyhexamethylene adipamide. The initial compacted fiber-reinforced sheet is substantially impermeable to water vapor, the initial compacted sheet having an LPV appreciably less than 1,000 grams/100 sq. meters/hour. When this compacted sheet is subjected to solely a swelling-deswelling process, the improvement in LPV is negligible. On the other hand, when the sheet is stretched in one or two directions, the fibers tend to break; and the resulting sheet shows negligible improvement in LPV in addition to having poor strength properties. On the other hand, by soaking the sheet in hot water at about 95° C., stretching the sheet 50% in both directions while hot, and thereafter drying the sheet at room temperature, the

resulting porous fiber-reinforced sheet has an LPV of 1,500 grams/100 sq. meters/hour.

Example 4

A composite of nylon fibers (polyhexamethylene adipamide) was formed by superimposing three mats of non-woven nylon fibers (2½" in length and 3 denier/filament), each mat weighing approximately 11 grams per square foot, and a mat of non-woven nylon fibers of fine denier (less than 0.5 denier per filament) was placed uppermost. In this initial composite, there were 11.53 parts by weight of the denier per filament fibers and 1.51 parts of the fine denier fibers. This composite of fibrous mats was impregnated with 24.17 parts of polyvinyl chloride binder in accordance with the following procedure.

The impregnating solution was comprised of the following:

7.8 parts of polyvinyl chloride,
5.2 parts of dioctyl phthalate,
200 parts of a solution of 98% tetrahydrofuran and 2% of dimethylformamide.

The composite of fibers was placed between metal screens and immersed in the impregnating solution. Thereafter, the composite was removed from the solution while being held between the screens, and the composite was sprayed on both sides with cold water. After removing the impregnated composite of fibers from the screen, it was washed in cold water for 1 hour and dried in air. The impregnated composite was finally pressed between two pieces of chip board for 10 minutes at 140° C. under 500 p. s. i. pressure. The pressed structure was cooled under pressure until the temperature was below 90° C. This pressed structure was substantially impermeable to water vapor, and samples of this structure were treated as indicated in the following table.

Table III

Treatment	Weight	Thickness (Inches)	LPV of Treated Sheet
(1) Immersed in boiling water 45 minutes and dried in air.....	527	0.0238	1,433, 1,256
(2) Immersed in boiling water 45 minutes and dried in air.....	528	0.0241	1,080, 1,032
(3) Same treatment as in (1) and thereafter stretched 30% in both directions.....	467	0.0258	5,687, 7,000
(4) Same as in (2) and thereafter stretched 30% in both directions.....	449	0.0261	8,900, 9,632

I claim:

1. The process which comprises associating liquid-swellaable structural fibers and soft, elastomeric, initially thermoplastic polymeric binder material, having a softening temperature below the softening temperature of said fibers to form an initial sheet, hot-pressing said initial sheet at a temperature above the softening temperature of said binder and below the softening temperature of said fibers whereby to form a substantially water vapor-impermeable composite sheet, and thereafter rendering said composite sheet water vapor-permeable by (1) soaking said composite sheet at a temperature between the softening temperature of said binder and of said fibers in a liquid which swells said fibers and thereafter drying said composite sheet at a temperature no higher than the softening temperature of the binder to remove said liquid, and (2) stretching said composite sheet and thereafter relaxing the same.

2. The process of claim 1 wherein said fibers constitute from 30% to 70% of the total weight of said initial sheet.

3. The process of claim 1 wherein said fibers consti-

tute from 40% to 60% of the total weight of said initial sheet.

4. The process of claim 1 wherein said fibers are at least 0.5 inch in length.

5. The process of claim 1 wherein said composite sheet is stretched in two directions.

6. The process of claim 1 wherein said composite is stretched in both directions from about 10% to about 40% of its original dimensions.

7. The process which comprises associating water-swellaable structural fibers and soft, elastomeric, initially thermoplastic polymeric binder material having a softening temperature below the softening temperature of said fibers to form an initial sheet, hot-pressing said initial sheet at a temperature above the softening temperature of said binder and below the softening temperature of said fibers whereby to form a substantially water vapor-impermeable composite sheet, and thereafter rendering said composite sheet water vapor-permeable by (1) soaking said composite sheet in water at a temperature between the softening temperature of said binder and the softening temperature of said fibers, and thereafter drying said composite sheet at a temperature no higher than the softening temperature of the binder to remove water, and (2) stretching said composite sheet and thereafter relaxing the same.

8. The process of claim 7 wherein said fibers constitute from 40% to 60% of the total weight of said initial sheet.

9. The process of claim 7 wherein said composite is stretched in both directions from about 10% to about 40% of its original dimensions.

10. The process which comprises associating synthetic linear polyamide structural fibers and soft, elastomeric, initially thermoplastic polymeric binder material, having a softening temperature below the softening temperature of said fibers to form an initial sheet, hot-pressing said initial sheet at a temperature above the softening temperature of said binder and below the softening temperature of said fibers whereby to form a substantially water vapor-impermeable composite sheet, and thereafter rendering said composite sheet water vapor-permeable by (1) soaking said composite sheet at a temperature between the softening temperature of said binder and of said fibers in a liquid which swells said fibers and thereafter drying said composite sheet at a temperature no higher than the softening temperature of the binder to remove said liquid, and (2) stretching said composite sheet and thereafter relaxing the same.

11. The process of claim 10 wherein said binder is an addition polymer.

12. The process of claim 10 wherein said liquid is water.

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