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POROUS ELASTOMERIC COATING

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ABSTRACT OF THE DISCLOSURE

Coating, coating process and coating composition in which the composition includes a latex of elastomeric polymer in which are suspended droplets of a water-immiscible volatile organic liquid to form the coating, the composition is spread on a surface, the polymeric material is coalesced and the water or organic liquid are removed leaving pores where the organic liquid had been.

This invention relates to coating compositions and coated sheet material and to a process for coating and particularly to a coating composition and process for forming a coated sheet material having an appearance comparable to grain leather when stretched, as in lasting of a shoe, and on flexing and creasing.

Leather historically is the primary material for making shoe uppers because of its good appearance and its combination of durability, protective action and comfort. Leather comprises a number of different zones including the main body which is a porous mass of intertwined fibers and a grain layer which is also porous and in which the fibers are more tightly associated. On stretching and flexing of leather there is an interaction of these two zones in which the tightly intertwined fibers of the grain layer acts to compensate for the irregularities developed in the coarser fiber structure of the main body. Particularly, in a sharp bend with the grain layer on the inner surface of the bend, a good leather will develop a series of closely spaced creases and fine folds. The nature of the creases and fine folds developed is called the "break" of the leather. The fineness of the ridges is in some degree a measure of the quality of the leather and reflects both the tight association of the grain layer with the main body and the compaction of the grain layer.

Leather substitute materials heretofore known have comprised a carrier layer and a resinous layer on a surface of the carrier layer. It has been a characteristic of these resinous layers that they have been compounded to be resiliently compressible so that their appearance when sharply bent does not correspond to the appearance of leather but more nearly to that of a fabric-backed vinyl material. Some of these materials have been treated in various ways as by mechanical means or electric discharge perforation of the resin layer, or by mechanical or chemical development of pores or cells in the resin layer to provide porosity with the object of permitting escape of moisture in order to avoid foot discomfort within a shoe. There is some question as to whether simple porosity is effective for this purpose; and the porosity developed in the readily compressible materials ordinarily used does not alter the character of crease appearance.

It is an object of the present invention to provide a coating composition and to form a sheet material coated with this composition in which sheet material, as in leather, a relatively tough, fine surface layer possesses strength and integrity to compensate for irregularities developed in the coarser structure in a carrier layer and in which there are provided pores or spaces of controlled size having a character and relation in the coating allowing compaction in a manner to develop a surface appearance when sharply bent resembling the appearance of leather when sharply bent.

To those ends and in accordance with a feature of the present invention there is provided a novel coating composition including a fluid dispersion such as an aqueous emulsion or latex of a tough, strong film-forming polymeric material in which are suspended controlled size droplets of a water-immiscible volatile organic liquid having at most only limited solvent or swelling action on the polymeric material. The coating composition is coated on the surface of a fibrous base and caused to set up; and the droplets maintain spaces in the coating until the coating becomes stable. Thereafter, the organic liquid is removed leaving void spaces of controlled size and character. The coating possesses the toughness and strength to distribute applied stresses and to reduce or eliminate surface irregularities from coarse fibrous structure in layers beneath the coating when the coated article is stretched. The coating is also capable of limited compaction because of the void spaces so that a sharp bend of a coated article does not result in buckling or in simple resilient compression of the coating material. Rather there is a squeezing-together of the openings left by the droplets of the organic liquid so that a desirable surface "break" is obtained.

In securing the desired structure it appears to be important that the droplets suspended in the coating composition be sufficiently large to prevent complete coalescence of the polymer particles so as to retain the openings or pores. The minimum droplets or globule size depends on the nature of the polymer and also in some degree on the polymer particle size. In general, larger droplet sizes are preferred with larger sizes of the polymer particles.

It is also important that gel strength be developed by the coalescence of the polymer particles at a stage on heating or other treatment of the polymer dispersion prior to exudation or volatilization of the suspended liquid to an extent which will prevent collapse of the openings after removal of the liquid.

It has been found for instance that suspensions of the non-solvent liquid if carried on with a very severe agitation or with particularly active emulsifying agents will form droplets so small that pores or openings are undesirably small and not as effective as desired for the intended purposes. Also organic liquids having a substantial aromatic content appear particularly susceptible to undesirably fine droplet formation and are less satisfactory for securing the desired character of openings or pores. A suitable range of droplet sizes small enough to give stability and uniformity for application and large enough to give desirable porosity may have from about 30% to 60% of the particles in the range of about 0.001 to 0.003 mm. in diameter, with substantially all of the remainder in the range of from 0.003 to 0.010 mm. It is preferred that the remaining droplets comprises 90% to 70% in the range from about 0.003 to about 0.006 mm. in diameter and from about 10% to about 30% in the range of from about 0.006 to 0.010 mm.

The action of the non-solvent liquid is primarily physical, that is, the non-solvent liquid is a readily removable space filler which is only present until the coating at least partially solidifies, and is then removed. Suitable liquids may readily be selected by a chemist on the basis of the known physical properties of liquids. Any liquid having water immiscibility and non-solvency for the film-forming polymeric material together with suitable volatility characteristics may be used. Liquid petroleum hydrocarbon fractions, particularly those commercially available as mineral spirits, petroleum naphtha and kerosene which are largely or completely aliphatic in composition are generally preferred because of their low cost and satis-

factory behavior in the coating composition; but other organic liquids such as halogenated hydrocarbons and nitroparaffins may be used. To avoid premature evaporation from the coating so that it can serve its space filling function until the coating has solidified, the non-solvent liquid should preferably have a boiling point of at least about 100° C. and preferably at least 130° C. On the other hand the liquid will be chosen with low enough boiling point for removal without heat injury to the coating and the base on which it is disposed. Thus the liquid should ordinarily not contain substantial quantities of high boiling or low volatility components, and preferably should not contain over 90% of components boiling at a temperature of over 450° F. It is to be understood that other means than evaporation may be used to remove high boiling liquid and in such cases the upper limit of boiling point does not apply.

Maintaining the openings or pores within the body during and after removal of the droplets of organic liquid depends on the structural stability of the polymer material under the conditions of removal of the liquid. That is, for example with a latex it is important that in the course of evaporating the water component a gel strength be developed sufficient at the time a temperature causing volatilization of the liquid is reached to prevent the collapse and sealing up of the openings or pores left by removal of the organic liquid.

A wide variety of latices of water-insoluble elastomeric synthetic film-forming polymers and copolymers have been found useful. The term "film-forming" is used to refer to the ability of a polymeric material dispersed in the aqueous continuous phase of the latex to join together in coherent films as water is removed from the latex. In particular there have been used butadiene acrylonitrile copolymer latices including the carboxy modified copolymer materials known as Hycar 1570X20 and Hycar 1571, acrylic polymer, and copolymer emulsions including the commercially available material known as Hycar 2671, vinyl chloride polymer latices and latices of copolymers of vinyl chloride with vinyl acetate and other monomers, for example a material known commercially as Geon 552 and latices or aqueous emulsions of elastomeric polyurethanes such as the latices from Wyandotte Chemicals Corporation known as "E–204" "E–207" and "E–406" and from Thiokol Corporation as "D–407JL." These are formed by condensation of at least one aromatic or aliphatic polyester polyol or polyether polyol with at least one aromatic or aliphatic polyisocyanate in amount providing active —NCO groups in excess of those required to react with the active hydrogen atoms of the polyols thereby forming —NCO terminated adducts which are chain extended with compounds having more than one active hydrogen such as a polyol, a polyamine or an amino alcohol.

The coating systems will be used in the range of polymer solids concentration based on the combined weight of polymer solids and aqueous phase in the range of polymer concentrations in polymer latices normally used to form continuous films. Ordinarily this is between 25% and 50% polymer solids by weight based on the combined weight of polymer and aqueous phase.

While all of these materials retain porosity to varying extents after removal of suspended water-immiscible volatile organic liquid non-solvents from coalesced polymer, the gel strength for preventing collapse and closure of the openings left by removal of the organic liquid may be improved by addition of various modifiers. These gel strength improving modifiers cooperate with the polymeric material to reduce or prevent viscous flow and collapse of the openings. Casein rendered water-soluble by treatment with an alkaline material such as ammonia or borax has been found effective; but other materials such as polyvinyl alcohol and methyl cellulose and harder resins such as the gasoline-insoluble residue from the distillation of pine tar resin, (Vinsol), can be used. Methyl cellulose offers a particular advantage in that it develops a gel when its aqueous solution is heated and this gel is available to aid in preventing collapse of the pores and openings in the polymer material during evaporation of the water content of a polymer latex. The amount or modifier will vary with the modifier selected, but suitably is an amount to give an over all coating composition viscosity from 500 to 100,000 centipoises as determined by the Brookfield Viscometer at 25° C. using a #4 spindle at 4 r.p.m. This can usually be obtained by adding from about 0.5 to about 15 parts per hundred parts by weight of latex solids.

A variety of other materials may be included such as waxes or wax-like substances, coloring agents and mineral fillers including carbon black.

The concentration of organic liquid required to give the desired openings or porosity depends on the nature of the polymeric material and on the conditions of coalescence of the particles and drying. Substantial development of openings or porosity is observable with as low as 25 parts of the organic liquid on 100 parts of the polymer and coherent porous films have been obtained with as much as 300 parts of organic liquid per 100 parts of the polymer material. Higher percentages could be used but would be uneconomical. Presently the preferred range is from about 60 parts to about 200 parts of organic liquid per 100 parts of polymeric material.

The base on which a coating of the material is deposited may have some effect on the operation of the system. Particularly when the base preferentially absorbs either the water component or the organic liquid component, local conditions adjacent the surface may cause a different character of polymer structure adjacent that surface. For example, where the volatile organic liquid is more readily absorbed by the base, the polymer material adjacent the surface of the base may become less porous. This factor may be controlled by a preliminary coating of the base, e.g. with a discontinuous deposit of a natural or synthetic rubber or resin such as an acrylic ester polymer or copolymer, to control the absorption action or by a prewetting of the base with that component i.e. water or organic liquid which tends to become absorbed more readily.

Preparation of the compositions involves introducing the organic liquid into the liquid dispersion of polymer particle material in a manner to distribute it uniformly through the liquid phase of the polymer dispersion in the form of droplets or globules of a desirable size. In practice it has been found that there is ordinarily a sufficient content of wetting and dispersing agent in commercially available latices so that additional dispersing agent has not been necessary. It is to be understood of course that if additional dispersing agent is needed it may be added with proper precautions for selecting a surface-active agent which will not coagulate the polymer dispersion on the one hand nor produce such fine droplets of the added organic liquid as to give undesirably low porosity. The addition of modifiers such as casein or methyl cellulose and the use of such materials as gums to increase viscosity, pigments to give color or modify the mechanical properties of the deposited polymer may be achieved by simple mixing.

The coating material may be applied to surfaces by any of a variety of means including spraying, brushing, dipping, knife spreading and so on. Coating thicknesses may range from very thin but continuous deposits, e.g., 8 mils wet thickness, up to as high as 100 mils wet thickness.

Surfaces which may be coated include casting surfaces from which the resultant film may be stripped after solidification and porous bases on which the deposited material will form a permanent coating. A preferred base is a tough, open-fibered, flexible sheet material obtained by impregnating an intermeshed fiber mat with an aqueous dispersion of collagen fibers of microscopic size followed

by treatment of the impregnated sheet to reaggregate the collagen fibers into a larger collagen fiber structure reinforcing the intermeshed fibers and the initial mat against displacement. Manufacture of such a sheet is described in the patent application of Shu-Tung Tu Serial No. 256,225, filed Feb. 5, 1963 and entitled Leather-Like Material and Method of Making Same. The coating may also be applied to other woven and non-woven fibrous bases including cloth, felt and leather, particularly to the flesh of leather or the leather splits.

After depositing the desired coating on a base, the coating is caused to coalesce as by evaporation of water where the polymer dispersion is a latex or aqueous dispersion to form a gel of at least partially coalesced polymer particles. This gelling or partial coalescence is ordinarily effected by subjecting the coating to heat to drive off the water. Where the organic liquid has a boiling point above that of water and a relatively low vapor pressure, evaporation of the water will cause at least partial coalescence of the polymer particles to shape retaining state before substantial loss of organic liquid, so that when the coating is subjected to further heat to volatilize the organic liquid, the polymer structure will resist collapse of the openings or pores left by departure of the organic liquid. Evaporation of the water may be carried out at room temperatures or elevated temperatures which do not cause bubbling, ordinarily below 100° C. After removal of water to effect gelling or partial coalescence the temperature may be raised to from 60° C. to 160° C. to drive off the organic liquid.

Temperatures employed for driving off the organic liquid must be such as not to harm the base material under the conditions existing. For example, depending on the degree of tannage of the collagen material present in an open-fiber sheet final temperatures must be controlled to avoid subjecting the collagen material to a sufficient temperature or sufficient time of heating to shrink or otherwise degrade the collagen material.

In a modification of the process of porous sheet to be coated is laid on a porous surface and held in position on that surface by vacuum, suitably 5 to 25 inches, acting through the porous surface. The coating composition is then applied. As applied, the consistency of the composition and control of the vacuum prevent undue penetration, e.g. more than one-fourth of the thickness into the porous sheet. When coalescence of a polymeric component of the coating begins the water component and the organic liquid become free to move and at least some portion of each may be pulled into and through the porous sheet by the vacuum on the face of the sheet opposite the coated surface. Any remaining liquid may be evaporated.

The coating after removal of the organic liquid is a tough, flexible material with a high degree of porosity so that water vapor penetrates the layer at a desirable rate for example to carry off perspiration. This water vapor penetration is a measure of permeability and is one means of characterizing the coating as having the percentage, size and character of spaces therein giving desirable flexing characteristics and appearance of surfaces of creased portions of the coating.

The following examples are given as of assistance in understanding the invention but it is to be understood that the invention is not restricted to the particular materials, conditions, proportions or procedures set forth in the examples.

EXAMPLE I

100 parts of a 43% solids aqueous emulsion of a carboxylated butadiene acrylonitrile copolymer (Hycar 1570X20) was placed in a mixing vessel and the pH adjusted by addition of sodium hydroxide to about 8.5 A 100% paraffin petroleum fraction having an initial boiling point of about 340° F. and an end point of about 410° F. was slowly added with agitation to the dispersion in the mixer to the extent of 86 parts on the 100 ports of the latex. 3 parts of a 60% aqueous dispersion of zinc oxide was added and stirred in and finally 25 parts of a 3% aqueous solution of methyl cellulose (1,500 centipoises grade) was added and stirred in. During addition of the methyl cellulose only mild agitation was employed in order to avoid inclusion of air bubbles. The resultant mixture was a smooth liquid material having a viscosity somewhat thicker than heavy cream.

An open-fibered flexible sheet material obtained by impregnating an intermeshed fiber mat with an aqueous dispersion of collagen fibers of microscopic size and reaggregation of the collagen fibers into a collagen fiber structure reinforcing the fibers against displacement was prepared as described in the patent application of Shu-Tung Tu above referred to. This material was held flat on a porous bed by 15 inches of vacuum applied through the bed and a coat of uniform thickness applied to the exposed surface of the sheet material using a knife coating applicator set to form a coating of .033" wet thickness.

The coated sheet material was dried at 20° C. for 3 hours during which time the coating lost its liquid appearance and developed a smooth matte finish. Thereafter, the coated sheet was subjected to a temperature of 80° C. with circulation of air over its surface for two hours to drive off residual liquid petroleum fraction.

The coating on the resulting sheets was tough, flexible and firmly adherent to the underlying fibrous material. The water vapor permeability was slightly better than two grams of water for an area of 30 square centimeters per 24 hours. On flexing the coating exhibited desirable fine creasing comparable to the creasing action of a good grade of leather.

EXAMPLE II

100 parts by weight of an aqueous dispersion of an elastomeric polyether polyol urethane (Wyandotte Polyurethane Latex E–204) having a solids content of 50% was placed in a mixer and 200 parts by weight of the same paraffinic petroleum fraction used in Example I was added and dispersed therethrough by agitation. 12 parts of a commercial dispersion of carbon black pigment in water diluted to 12.5% solids was added and stirred in and thereafter 40 parts by weight of a 3% solution of methyl cellulose (1,500 centipoises) was added and stirred in with mild agitation to avoid air bubble inclusion. The composition was applied to a fibrous base as in Example I and dried for 3 hours at 20° C. Thereafter the coated sheet was subjected to further heating with circulation of air over its surface at 100° C. for two hours.

The product thus attained had a smooth black matte finish and was tough and abrasion resistant. On bending the finish displayed a pattern of fine creases comparable to the "break" of a good grade of leather. On stretching of the coated sheet material the surface retained its smooth state, i.e. the tough coating material was effective to distribute the stresses so that irregularities in the base did not develop to an extent to markedly distort the surface of the coating. This coated material had a water-vapor permeability of nearly 2.5 grams of water for an area of 30 square centimeters for 24 hours.

EXAMPLE III

A 10% solids solution of casein in water was prepared with the aid of ammonium hydroxide in dissolving the casein. 100 parts of the polyurethane dispersion of Example II was placed in a mixer and casein solution added in amount to provide 10 parts by weight of casein to 100 parts by weight of solids in the polyurethane dispersion. Thereafter 100 parts by weight of a petroleum fraction having a naphthene content of 26% and a paraffin content of 74% and having an initial boiling point of 376 to 392° F. and an end point of 480 to 500° F. was added and mixed in with agitation. The composition was coated on a fibrous base and subjected to the two stage drying and heating as in Example II. A coating comparable to that of Example

II was obtained having to give a sheet material having a vapor permeability of about 2.2 grams for an area of 30 square centimeters for 24 hours.

EXAMPLE IV

100 parts of a 55% solids polyvinyl chloride latex (Geon 552) was introduced into a mixer and there was then added a weight of petroleum naphtha equal to the weight of the polyvinyl chloride in the latex. 40 parts by weight of 3% solution of methyl cellulose (1,500 centipoises) was added stirred in with mild agitation.

The coating was applied to a fibrous base as in Example I, dried at 65° C. for 3 hours and then subjected to heating with circulation of air at 160° C. for 10 minutes.

A tough matte finish was obtained on the coated sheet material. The sheet material had a water vapor permeability of 1.6 grams of water for an area of 30 square centimeters per twenty-four hours.

EXAMPLE V

100 parts of a 50% solids aqueous emulsion of a polyacrylic ester latex (Hycar 2671) was placed in a mixing vessel and there was added 80 parts by weight of a 10% solids borated casein solution of 60 parts of water. Thereafter, 86 parts of a 100% paraffin petroleum fraction having an initial boiling point of about 340° F. and an end point of about 410° F. was slowly added with agitation to the mixing vessel with agitation to disperse the petroleum fraction. The resultant mixture was a smooth liquid having a viscosity comparable to heavy cream.

The composition was applied to a fibrous base as a coating having a wet thickness of 0.033 inch and dried overnight at 20° C. Thereafter, the coating was subjected to a temperature of 60° C. for two hours to drive off residual petroleum fraction.

The coating on the resulting sheet was tough, flexible and firmly adherent to the underlying fibrous material. The water vapor permeability was about 1.3 grams of water for an area of 30 square centimeters in 24 hours.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent of the United States is:

1. The process of forming a permeable film comprising the steps of spreading on a surface a composition including a latex of a film-forming elastomeric polymer selected from the group consisting of butadiene-acrylonitrile copolymer latices, latices of elastomeric polyurethanes from chain extension of an —NCO terminated condensate of at least one polyol and at least one polyisocyanate, vinyl chloride polymer latices and vinyl chloride-vinyl acetate copolymer latices and fine droplets of a water-immiscible volatile organic liquid having at most limited solvent action on the polymeric material, said liquid being selected from the group consisting of liquid petroleum hydrocarbon fractions, liquid halogenated hydrocarbons and liquid nitroparaffins, 30% to 60% of said droplets having dimensions in the range of from .001 to .003 mm. and substantially the remainder of said droplets are in the range of from .003 to .010 mm., said latex having from about 25% to about 55% by weight of dispersed film-forming polymer solids based on the weight of said polymer solids and the aqueous phase of said latex, said liquid being suspended in the aqueous phase of said latex and being present in amount from 25% to 300% based on the weight of said polymeric material, coalescing said polymeric material to shape retaining state with said organic liquid held in the coalesced material and removing water and organic liquid to form a continuous layer in which the spaces occupied by said organic liquid provide pores and discontinuities in the layer constituting passageways for air and vapor through the polymer material.

2. The process of forming a permeable coating on a porous fibrous sheet comprising the steps of spreading on a first surface of said sheet a coating composition comprising a latex of a film-forming elastomeric polymer selected from the group consisting of butadiene-acrylonitrile copolymer latices, latices of elastomeric polyurethanes from chain extension of an —NCO terminated condensate of at least one polyol and at least one polyisocyanate, vinyl chloride polymer latices and vinyl chloride-vinyl acetate copolymer latices and with fine droplets of a substantially water-immiscible organic liquid suspended uniformly throughout the aqueous phase of said dispersion, said organic liquid being selected from the group consisting of liquid petroleum hydrocarbon fractions, liquid halogenated hydrocarbons and liquid nitroparaffins and having a boiling point higher than water and having at most limited solvent action on said polymeric material, from 30% to 60% of said droplets having dimensions in the range of 0.001 to 0.003 mm. and substantially the remainder of the droplets having dimensions of from 0.003 to about 0.010 mm., said dispersion having a polymer solids content of from 25% to about 50% based on the weight of the polymeric material and aqueous phase and said organic liquid being present in amount of from 25% to 300% by weight based on the weight of said polymeric material, heating said coating to evaporate water and coalesce said polymeric material to shape retaining state with said organic liquid held therein applying vacuum to the surface of said sheet opposite said first surface and removing residual water and said organic liquid to form a continuous layer in which the spaces occupied by said organic liquid provide pores and discontinuities in the coalesced polymer material constituting passageways for air and vapor through said coating.

3. The process of forming a permeable coating on a porous fibrous sheet comprising the steps of spreading on a first surface a layer having a wet thickness of 0.02 to 0.1 inch comprising latex of a film-forming elastomeric copolymer of butadiene and acrylonitrile with fine droplets of a substantially water-immiscible organic liquid suspended uniformly throughout the aqueous phase of said dispersion, said organic liquid being selected from the group consisting of liquid petroleum hydrocarbon fractions, liquid halogenated hydrocarbons and liquid nitroparaffins and having a boiling point higher than water and having at most limited solvent action on said polymeric material, from 30% to 60% of said droplets having dimensions in the range of 0.001 to 0.003 mm. and substantially the remainder of the droplets having dimensions of from 0.003 to about 0.010 mm., said dispersion having a copolymer solids content of from 25% to about 50% based on the weight of the copolymeric material and aqueous phase and said organic liquid being present in amount of from 25% to 300% by weight based on the weight of said copolymeric material, coalescing said copolymeric material to shape retaining state with said organic liquid held therein, applying vacuum to the surface of said sheet opposite said first surface and removing water and said organic liquid to form a continuous layer in which the spaces occupied by said organic liquid provide pores and discontinuities in the coalesced copolymer material constituting passageways for air and vapor through said coating.

4. The process of forming a permeable coating on a porous fibrous sheet comprising the steps of spreading on a first surface a layer having a wet thickness of 0.02 to 0.1 inch of a coating composition having a viscosity of from 500 to 10,000 centipoises and comprising a latex of a film-forming elastomeric copolymer of butadiene and acrylonitrile with fine droplets of a substantially water-immiscible organic liquid suspended uniformly throughout the aqueous phase of said latex, said organic liquid being selected from the group consisting of liquid petroleum hydrocarbon fractions, liquid halogenated hydrocarbons and liquid nitroparaffins and having a boiling point higher than water and having at most limited solvent action on said polymeric material, from 30% to 60% of said droplets having dimensions in the range of 0.001

to 0.003 mm. and substantially the remainder of the droplets having dimension of from 0.003 to about 0.010 mm., said dispersion having a copolymer solids content of from 25% to about 50% based on the weight of the copolymeric material and aqueous phase and said organic liquid being present in amount of from 25% to 300% by weight based on the weight of said copolymeric material, heating said coating to evaporate water and coalesce said copolymeric material to shape retaining state with said organic liquid held therein, applying vacuum to the surface of said sheet opposite said first surface and removing residual water and said organic liquid to form a continuous layer in which the spaces occupied by said organic liquid provide pores and discontinuities in the coalesced copolymer material constituting passageways for air and vapor through said coating.

5. The process of forming a permeable coating on a porous fibrous sheet as defined in claim 4 in which said coating composition includes a gel strength improving modifier.

6. The process of forming a permeable coating on a porous fibrous sheet as defined in claim 5 in which said gel strength improving modifier is methyl cellulose.

7. The process of forming a permeable coating on a porous fibrous base as defined in claim 5 in which said gel strength improving modifier is casein rendered water soluble by alkaline material.

8. The process of forming a permeable coating on a porous fibrous sheet comprising the steps of spreading on a first surface of said sheet a layer having a wet thickness of 0.02 to 0.1 inch of a coating composition having a viscosity of from 500 to 10,000 centipoises, and comprising a latex of a film-forming elastomeric polyurethane from chain extension of an —NCO terminated condensate of at least one polyol and at least one polyisocyanate with fine droplets of a substantially water-immiscible organic liquid suspended uniformly throughout the aqueous phase of said latex, said organic liquid being selected from the group consisting of liquid petroleum hydrocarbon fractions, liquid halogenated hydrocarbons and liquid nitroparaffins and having a boiling point higher than water and having at most limited solvent action on said polymeric material, from 30% to 60% of said droplets having dimensions in the range of 0.001 to 0.003 mm. and substantially the remainder of the droplets having dimensions of from 0.003 to about 0.010 mm., said dispersion having a polymer solids content of from 25% to about 50% based on the weight of the polymeric material and aqueous phase and said organic liquid being present in the amount of from 25% to 300% by weight based on the weight of said polymeric material, coalescing said polymeric material to shape retaining state with said organic liquid held therein, applying vacuum to the surface of said sheet opposite said first surface and removing residual water and said organic liquid to form a continuous layer in which the spaces occupied by said organic liquid provide pores and discontinuities in the coalesced polymer material constituting passageways for air and vapor through said coating.

9. The process of forming a permeable coating on a porous fibrous sheet comprising the steps of spreading on a first surface of said sheet a layer having a wet thickness of 0.02 to 0.1 inch of a coating composition having a viscosity of from 500 to 10,000 centipoises and comprising a latex of a film-forming elastomeric polyurethane from chain extension of an —NCO terminated condensate of at least one polyol and at least one polyisocyanate with fine droplets of a substantially water-immiscible organic liquid suspended uniformly throughout the aqueous phase of said latex, said organic liquid being selected from the group consisting of liquid petroleum hydrocarbon fractions, liquid halogenated hydrocarbons and liquid nitroparaffins and having a boiling point higher than water and having at most limited solvent action on said polymeric material, from 30% to 60% of said droplets having dimensions in the range of 0.001 to 0.003 mm. and substantially the remainder of the droplets having dimensions of from 0.003 to about 0.010 mm., said dispersion having a polymer solids content of from 25% to about 50% based on the weight of the polymeric material and aqueous phase and said organic liquid being present in amount of from 25% to 300% by weight based on the weight of said polymeric material, heating said coating to evaporate water and coalesce said polymeric material to shape retaining state with said organic liquid held therein, applying vacuum to the surface of said sheet opposite said first surface and removing residual water and said organic liquid to form a continuous layer in which the spaces occupied by said organic liquid provide pores and discontinuities in the coalesced polymer material constituting passageways for air and vapor through said coating.

10. The process of forming a permeable coating on a porous fibrous sheet as defined in claim 9 in which said coating composition includes a gel strength improving modifier.

11. The process of forming a permeable coating on a porous fibrous sheet as defined in claim 10 in which said gel strength improving modifier is methyl cellulose.

12. The process of forming a permeable coating on a porous fibrous sheet as defined in claim 10 in which said gel strength improving modifier is casein rendered water soluble by alkaline material.

13. Flexible sheet material comprising a porous fibrous base and a fine porous layer of synthetic elastomeric polymeric material united to a surface of said fibrous base, said porous layer having been formed by the process of claim 1.

14. A coating composition for depositing a porous film on a surface comprising a latex of a tough, strong film-forming elastomeric polymeric material selected from the group consisting of butadiene-acrylonitrile copolymer latices, latices of elastomeric polyurethanes from chain extension of an —NCO terminated condensate of at least one polyol and at least one polyisocyanate, vinyl chloride polymer latices and vinyl chloride-vinyl acetate copolymer latices and fine droplets of a water-immiscible volatile organic liquid having at most limited solvent action on the polymeric material, said liquid being selected from the group consisting of liquid petroleum hydrocarbon fractions, liquid halogenated hydrocarbons and liquid nitroparaffins, 30% to 60% of said droplets having dimensions in the range of from .001 to .003 mm. and substantially the remainder of said droplets are in the range of from .003 to .010 mm., said latex having from about 25% to about 55% by weight of dispersing film-forming polymer solids based on the weight of said polymer solids and the aqueous phase of said latex, said liquid being suspended in the aqueous phase of said latex and being present in amount from 25% to 300% based on the weight of said polymeric material.

15. A coating composition for depositing a porous coating on a fibrous base, said composition having a viscosity of from 500 to 10,000 centipoises and comprising a latex of a tough, strong film-forming elastomeric polymeric material selected from the group consisting of butadiene-acrylonitrile copolymer latices, latices of elastomeric polyurethanes from chain extension of an —NCO terminated condensate of at least one polyol and at least one polyisocyanate, vinyl chloride polymer latices and vinyl chloride-vinyl acetate copolymer latices and droplets of a water-immiscible volatile organic liquid having at most limited solvent or swelling action on the polymeric material, said liquid being selected from the group consisting of liquid petroleum hydrocarbon fractions, liquid halogenated hydrocarbons and liquid nitroparaffins and being dispersed in the aqueous phase of said dispersion as droplets of which 30 to 60% have dimensions in the range of .001 to .003 mm. and substantially the remainder of said droplets are in the range of from .003 mm. to .010 mm., said dispersion having a polymer solids content of

from about 25% to 50% based on the weight of the polymeric material and aqueous phase and said volatile organic liquid being present in amount from 25% to 300% based on the weight of said polymeric material.

16. A coating composition as defined in claim **15** in which said latex is a butadiene-acrylonitrile copolymer latex.

17. A coating composition as defined in claim **3** in which said latex is a latex of an elastomeric polyurethane from chain extension of an —NCO terminated condensate of at least one polyol and at least one polyisocyanate.

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U.S. Cl. X.R.

117—135.5, 161; 260—29.6, 29.7