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SUEDE-LIKE SHEET MATERIAL OF AN ACRYLONITRILE/BUTADIENE POLYMER CONTAINING AN ADDITIVE

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ABSTRACT OF THE DISCLOSURE

An improved supple, synthetic, microporous vapor permeable suede sheet material of a non-woven synthetic flexible fibrous web that is impregnated with a polymeric binder of butadiene and acrylonitrile and the polymeric binder contains about 0.1–20 parts of additive per 100 parts of binder where the additive is either a hydrocarbon oil or a silicone oil.

BACKGROUND OF THE INVENTION

This invention relates to a novel suede-like microporous sheet material and in particular to a synthetic suede-like microporous vapor permeable sheet material that has a substantially improved nap over prior art synthetic suede products.

Leather-like sheet materials that can be formed into a suede-like sheet material have been prepared by a variety of processes as disclosed in the following patents: Graham et al. U.S. 2,715,588, issued Aug. 16, 1955; Gaylord U.S. 2,917,405, issued Dec. 15, 1959; Proctor U.S. 2,994,617, issued Aug. 1, 1961; Hollowell Patents U.S. 3,067,482 and 3,067,483, both issued Dec. 11, 1962; British Patent 986,437, published Mar. 17, 1965 and FitzGerald et al. U.S. 3,228,786, issued Jan. 11, 1966. These sheet materials have a very wide variety of uses from shoe uppers to apparel suede. However, while these materials have been considered acceptable suede-like materials after buffing, the surface of the material does not approach that of a natural leather suede as closely as is desired. The density and fiber length of the fibers that form the suede-like surface of these prior art products are insufficient to form a product which very closely resembles a natural leather suede.

A synthetic material that would closely resemble natural leather could be used as an apparel suede, a brushed casual shoe upper, as a felt-like men's hat material and the like.

The novel suede-product of this invention surprisingly has a surface which more closely approaches that of natural suede leather than the aforementioned prior art products which are of a high quality and are excellent for many purposes. Along with this improved property, the novel product of this invention still is highly flexible, soft, supple and has a high water vapor permeability. This is accomplished by using a particular additive with the polymeric binder used to form the sheet that will give a nap on the novel product with a high fiber density and a greater fiber length than previously has been possible with prior art products.

SUMMARY OF THE INVENTION

The supple synthetic microporous vapor permeable suede sheet material comprises

(a) a non-woven synthetic flexible fibrous web that is impregnated with

(b) a polymeric binder which consists essentially of a polymer of acrylonitrile and butadiene and contains 0.1–20 parts of a nap improving additive per 100 parts of polymeric binder which is either a hydrocarbon oil

which consists essentially of paraffinic and naphthenic hydrocarbon constituents and has a Saybolt viscosity at 99° C. of 20–200 seconds or a silicone oil which has a viscosity at 25° C. of at least 10 centistokes;

wherein said microporous sheet material has a water vapor permeability value of at least 100 grams of water/100 square meters/hour and a binder to fiber ratio of about 0.2–3.0.

DESCRIPTION OF THE INVENTION

The novel sheet material of this invention is prepared by forming a non-woven porous substrate or web, impregnating this web with a polymeric binder, and a coagulating this polymeric binder, preferably into a microporous form. The non-woven web is impregnated with sufficient polymeric binder to give the final product a binder/fiber ratio of about 0.2–3.0. For best results, a binder/fiber ratio of 0.5–2 is preferred.

The term "microporous" refers to a porous material in which the individual pores are not discernible to the naked eye.

Preferably, the novel sheet material of this invention has a flexural rigidity at a 50 mil sheet thickness of about 1,000–80,000 milligrams-centimeters, and more preferably, 4,000–30,000 milligrams-centimeters, measured according to the method of ASTM–1388–D–64. A sheet having a flexural rigidity within the above ranges indicates that the sheet is supple and flexible and not stiff and board-like.

Water vapor permeability of the novel sheet material of this invention is determined by sealing the sheet on top of a cup containing $CaCl_2$. This sealed cup is stored at 90% relative humidity at 72° F. and the weight increase of the cup due to moisture permeating through the material is determined and the water vapor permeability value of the sheet is calculated in

$$\frac{\text{grams of water}}{\text{100 square meters of material/hour}}$$

Preferably, the novel sheet material of this invention has a water vapor permeability of 2,000–15,000 grams/100 square meters/hour.

The non-woven porous fibrous substrate or web used to form the novel sheet material of this invention prefebably has a density of about 0.01–1.0 grams per cubic centimeter (gm./cc.), and more preferably, about 0.1–0.4 gm./cc. The method used to prepare the non-woven web and the fibers from which the web is prepared art not critical.

Generally, the non-woven web is prepared by forming fibers into a loose batt by any known method, such as carding, blowing the fibers, dropping the fibers and the like. Preferably, a batt of about 4–20 ounces per square yard is formed by air-blowing the fibers. The batt is then compacted by any of the well-know techniques, such as mechanical needling. Preferably, the resulting web is further compacted by heat shrinking, for example, which can be accomplished by immersion in hot water. A web having properties of stretchability or shrinkability balanced in each direction is formed by cross-lapping the fibers into layers of dissimilar orientation within the plane of the web. When unidirectional stretchability or shrinkability is preferred, the crosslapping is omitted and most of the fibers are laid so that they have a similar orientation to the plane of the web.

The choice of the particular fibers from which the substrate used in this invention is made is not critical; for example, fibers of polyamides, polyesters, polyesterimides, polyurethanes, chain-extended polyurethanes, acrylic polymers, acetate polymers, viscose rayon, glass and mixtures thereof, can be used. Elastomeric fibers can be used to form the web or can be blended with any of the aforementioned webs.

One particularly preferred non-woven substrate used to form the novel product of this invention which gives a high quality suede-like material is a non-woven web of needed, heat shrunk about 1–2 denier polyethylene terephthalate fibers having a density of about 0.15–0.30 gm./cc.

A non-woven porous fibrous substrate that is impregnated with a polymeric material that has a binder to fiber ratio of less than 1.0 can also be used as a substrate to form the novel product of this invention. This substrate is reimpregnated with sufficient polymeric binder to give a product with a final binder fiber ratio of less than 3, preferably 1–2. After impregnation, the polymer is coagulated in a microporous form. One preferred substrate of this type is a non-woven needled heat shrunk batt of polyethylene terephthalate fibers that has been impregnated with a mixture containing up to 50% by weight polyvinyl chloride and at least 50% by weight of a chain-extended polyurethane polymer. One preferred polyurethane is the reaction product of an aromatic diisocyanate and poly(alkyleneether) glycol which is chain-extended with a diamine that has at least one active hydrogen attached to each nitrogen atom.

The acrylonitrile/butadiene polymeric binder used to impregnate the non-woven fibrous substrate to form the novel sheet material of this invention should be tough and durable, and preferably, should form a microporous structure. These characteristics are necessary to form a product which is a suede leather replacement for shoe uppers, for wearing apparel, such as hats, coats, vests and the like. Acrylonitrile/butadiene polymers that form sheet materials that have these described characteristics preferably contain 25–50% by weight acrylonitrile and 75%–50% by weight butadiene and generally have a tensile stress at 5% elongation of about 4–150 p.s.i., and preferably 8–72 p.s.i.

Tensile stress at 5% elongation is the force in pounds which is required to elongate a sample 5% divided by the cross-section of the sample with the results being expressed in pounds per square inch (p.s.i.). Preferably, an 8–12 mil thick film is prepared from the acrylonitrile/butadiene polymer used to prepare the novel sheet material of this invention. Test samples of about ½ inch by 4 inches are cut, conditioned at 50% relative humidity and tested at 23° C. The samples are tested at the above temperature and humidity conditions on an Instron Tensile Tester using about 1 inch between grips on the sample, a cross-head speed of 1 inch per minute and a chart speed of 10 inches per minute.

One preferred acrylontrile/butadiene polymeric binder used to prepare the novel sheet material of this invention contains in addition to acrylonitrile and butadiene about 0.1–5% by weight of an α,β-ethylenically unsaturated carboxylic acid. One particularly preferred binder of this type which provides excellent adhesion to the non-woven substrate and is readily cured by conventional techniques consists essentially of 25–50% by weight acrylonitrile, 75–50% by weight butadiene and 0.1–5% by weight of one of the following carboxylic acids: acrylic acid, methacrylic acid or itaconic acid.

The above acrylonitrile/butadiene polymeric binder can be in a solution or a dispersion to impregnate the non-woven substrate to form the novel sheet material of this invention. Preferably, dispersions of the above polymer either using an organic or an aqueous phase as the dispersing medium are used to impregnate the non-woven substrate to form the novel sheet material of this invention. Dispersions can readily be formed that contain a high polymer solids content but have a low viscosity and are readily adaptable to an impregnation process. Aqueous dispersions or latices of the above acrylonitrile/butadiene polymeric binders are particularly preferred since there are no problems such as occur with solvent dispersions, such as the high cost of solvents which require solvent recovery. Moreover, latices are

readily coagulated after impregnating the non-woven substrate by heat or cold or by chemicals into a microporous structure.

Preferably, for best results, the latex of the acrylonitrile/butadiene polymeric binder used in this invention has a low viscosity of 1–300 centipoises and a polymer solids content of about 20–70% by weight and more preferably, a 40–60% polymer solids content is used.

To give a novel suede-like sheet material of this invention a dense nap with long fibers, an additive of a hydrocarbon oil or silicone oil is added to the polymeric binder in an amount of 0.1–20 parts of additive per 100 parts of polymeric binder. For best results, about 1–15 parts of additive per 100 parts of binder are used.

The hydrocarbon oil used as an additive in this invention is a petroleum oil fraction which consists essentially of paraffinic and naphthenic hydrocarbon constituents and has a Saybolt viscosity at 99° C. of 20–200 seconds. Preferred hydrocarbon oils are the white-non-staining oils which have a Saybolt viscosity at 99° C. of 40–90 seconds. These preferred hydrocarbon oils typically contain about 40–100% by weight of a paraffins constituent and 60–0% by weight of a naphthenic constituent. Since these oils are petroleum fractions, they generally contain other constituents which may be aromatic or aliphatic in character. One particularly preferred oil contains about 43–47% by weight of a paraffinic constituent, 38–42% by weight of a naphthenic constituent and 13–17% by weight of an aromatic constituent and has a Saybolt viscosity at 99° C. of about 52–56 seconds.

The silicone oils that are useful additives in this invention are of the formula.

$$\text{-}[\text{Si}(\text{R})_2\text{—O}]\text{-}_n$$

where R is an alkyl group of 1–4 carbon atoms or a phenyl group or a mixture of alkyl and phenyl groups, and the oil has a kinematic viscosity at 25° C. of at least 10 centistokes and may have a viscosity up to 2.5×10^6 centistokes. Preferably, the oil has a kinematic viscosity of 50–30,000 centistokes. The aforementionel R group can be methyl, ethyl, propyl, isopropyl butyl, isobutyl or phenyl. One preferred silicone oil, since it gives a high quality product, is polydimethylsiloxane which has a kinematic viscosity at 25° C. of about 20–100 centistokes.

Often it is desirable to add pigments, extender pigments and dyes to the binder used to form the novel sheet material of this invention to give the product the desired color. About 0.1–20% by weight pigment, based on the weight of the polymeric in binder, and preferably, 2–10% by weight can be used. Typically useful pigments are, for example, metal oxides, such as titanium dioxide, zinc oxide, metal hydroxides, chromates, silicates, sulfides, sulfates, carbonates, carbon blacks, organic dyes, such as β-copper phthalocyanine, lakes and metal flake pigments, ferric yellow (yellow iron oxide pigment), burnt sienna, (an orange brown mineral pigment containing iron oxide, manganese dioxide and clay) and the like.

Thickening agents can be added to a latex used in this invention to prepare the novel product to give the desirable impregnating viscosity. The useful viscosity range for the latices used to form the novel sheet material of this invention is about 1 to 300 centipoises (c.p.s.) with the preferred range being about 10 to 100 (c.p.s.). Thickening agents most commonly used are ammonium casinate, ammonium alginate, methyl cellulose (25 c.p.s. to 50,000 c.p.s. viscosity, measured as a 2% aqueous solution at 25° C.) and sodium polyacrylate. Other thickening agents, such as polyacrylic acids, polyvinyl alcohol, carboxymethyl cellulose, polyvinyl pyrrolidone, maleic acid copolymers, gelatine, and the like, can also be used. It is desirable, but not absolutely necessary, to remove the thickener from the latex after it has been coagulated; this is accomplished by washing the coagulated latex with water. If the thickener is retained in the sheet, subsequent rewet-

ting of the material causes the thickener to come to the surface and makes the material feel slimy. This washing step may be eliminated from the process by cross-linking and insolubilizing the thickener and can be accomplished by adding a cross-linking agent such as polyacrylamide and an agent which insolubilizes the thickener, such as bis-hydroxy methyl urea. The subsequent drying and curing of the polymer after coagulation at an elevated temperature aids in the cross-linking and insolubilization of the thickener.

Antioxidants are generally added in small amounts to the latex used in this invention of an unsaturated polymers, such as 4,4' - butylidene-bis-(6 - tertiary-butyl-m-cresol), 2,2'-methylene-bis-(4 - methyl - 6 - tertiary-butyl-phenol), 4,4'-thio-bis-(6-tertiary-butyl-m-cresol) and the like.

Plasticizers may be added in small amounts to the latex to form the novel sheet material of this invention. The type of plasticizer used is dependent on the latex polymer.

Curing agents are generally added in small amounts to the latex used to form the novel sheet material of this invention, such as zinc oxide; sulfur plus an accelerator like zinc dibutyl dithiocarbamate; melamine-formaldehyde polymer; phenolformaldehyde polymer. Curing or vulcanization of the latex polymer after it is coagulated in the non-woven substrate is carried out at about 100–160° C. and preferably, at 110–150° C.

If the latex is coagulated by heat, generally heat sensitizers, such as polyvinylmethylether, ammonium sulfate, zinc ammonium acetate, methylcellulose and the like, are added. Heat coagulation can be accomplished by hot air, steam, microwave, infrared heat and the like. A temperature of about 40–100° C. is usually required with the preferred temperature range being about 60–90° C.

If the latex is coagulated by chemical means, the impregnated sheet is immersed in a liquid, for example, an acetic acid bath containing about 1 to 10% by weight acid. Solutions of the following can be used to coagulate the latex: calcium chloride, barium chloride, zinc acetate, formic acid, aluminum sulfate and the like.

Preferably, after the non-woven web is impregnated with the latex, the latex is coagulated by freezing the latex at about —20° C. to —100° C. for about 10 minutes to 2 hours. After coagulation, the novel sheet material is dried, preferably at a temperature of about 30–150° C. However, it is possible to dry the product at a lower temperature, for example, room temperature about 22° C.

If a colored product is desired, the novel sheet material of this invention can be dyed by ordinary techniques after the polymer has been coagulated. Manwaring U.S. Patent 3,337,289, issued Aug. 22, 1967, teaches a dyeing process that can be used on the novel product of this invention. Preferably, the non-woven web is dyed and then a colored polymeric binder is used to form the novel sheet material of this invention. The binder is colored as aforementioned by the addition of dyes or pigments.

Printing, stencilling, embossing, preferential dyeing, and other known techniques for surface decoration can be used to modify the novel product of this invention.

When a denser product is wanted, the dried sheet is pressed between two smooth heated surfaces. The time, temperature and pressure of pressing are controlled to maintain product permeability and suppleness, as will be apparent to those skilled in the art.

The suede surface of the novel sheet material of this invention is formed by raising a nap on one or both sides of the smooth, supple microporous sheet in any suitable manner known in the art of napping fabrics and tanned skins. A preferred napping process involves buffing with emery covered rolls followed by brushing. Buffing also improved the suppleness of the product besides softening its surface feel.

Another optional feature is to treat the novel product with known fabric softeners, or to likewise treat the mat at any stage of the process.

In general, the product of this invention is a versatile material with many uses. The novel product of this invention, because of its desirable properties, may be buffed on one side and coated on the other, for example, coated with a microporus layer.

The following examples illustrate the invention. All parts and percentages are by weight unless otherwise specified.

Example 1

Latex A is formulated by blending the following ingredients:

	Parts by weight
A latex—50% solids dispersion of a carboxy modified polymer of about 30% by weight acrylonitrile and about 70% by weight butadiene	200.0
Ammonia solution—14% by weight aqueous solution	1.4
Zinc oxide dispersion—50% zinc oxide solid	10.0
Antioxidant dispersion—40% aqueous dispersion of 2,2'-methylene-bis(4-methyl - 6 - t - butyl phenol)	2.5
Lampblack dispersion—50% aqueous dispersion	4.0
"Primol" D emulsion—50% aqueous emulsion of a mineral oil that has naphthenic and paraffinic constituents and has a Saybolt viscosity at 99° C. of 54 seconds	30.0
Solution of sodium salt of sulfated methyl oleate—20% aqueous solution	5.0
Total	252.9

A dried coalesced non-porous polymer film of the latex has a tensile stress at 5% elongation of about 10 p.s.i., determined at 23° C. and 50% R.H. on a 0.5 inch wide sample on an Instron Tensile Tester using 1 inch between jaws and an elongation rate of 1 inch per minute.

An 18 inch by 18 inch by ¼ inch web prepared by needling and heat shrinking a batt of 1.8 denier polyethylene terephthalate fibers 1.5 inches in length and have a density of about 0.2 gram/cubic centimeters is immersed in the above prepared latex binder. The amount of latex binder picked up by the web is about 280% by weight. This impregnated web is placed between two aluminum sheets and this assembly is immersed in pulverized Dry Ice for about 30 minutes to coagulate the latex binder. The web is then thawed and washed with warm water and cured one hour in a circulating air oven held at about 120° C. The resulting material is a soft flexible substrate which has excellent scuff resistance and an excellent water vapor permeability.

Latex B is formulated using the identical ingredients and in the same amounts as used to formulate Latex A except the mineral oil emulsion is omitted. The latex polymer has a tensile stress at 5% elongation of 15 p.s.i. A non-woven web of polyethylene terephthalate fibers described above is impregnated following the above procedure.

Each of the above prepared sheets are split to a 70–75 mils thickness and buffed on both sides with 120 grit emery paper to a thickness of about 60–65 mils; about 5 mils are buffed from each surface of the sheet.

The resulting sheets have the following properties:

	Latex	
	A	B
Mineral oil (parts oil per 100 parts polymer)	15	0
Density, grams/cc	0.57	0.60
Thickness, mils	60	63
Water vapor permeability (grams/100 square meters/hour)	8,900	10,700
Nap length (mils)	50-65	8-20
Nap density [1]	High	Low

[1] Low nap density indicates relatively few fibers protruding from the buffed surface, a high nap density indicates that the surface is completely covered with nap.

The above results indicate that the mineral oil additive greatly improves the length and density of the nap

without adversely affecting other properties of the sheet such as water vapor permeability.

Example 2

Latex C is formulated by using the identical ingredients and in the same amounts as used to formulate Latex A except that 50 grams of the following silicone oil dispersion is substituted for the mineral oil dispersion used in Latex A: 10% aqueous emulsion of silicone compound "Dow Corning Antifoam B" which is believed to be a thickened dimethyl siloxane oil that has a viscosity at 25° C. of at least 20 centistokes. A non-woven web of polyethylene terephthalate fibers identical to the web described in Example 1 is impregnated with Latex C, the latex is coagulated and the web is split and buffed as in Example 1.

The resulting web has the following physical characteristics:

Density grams/cc.	0.59
Thickness (mils)	64
Water vapor permeability (grams/100 square meters/hour)	8100
Nap length (mils)	20–80
Nap density	High

Example 3

A heat shrunk non-woven web of needled polyethylene terephthalate fibers is impregnated with a chain-extended polyurethane solution described in Example 1 of Holden U.S. 3,100,321, issued Aug. 13, 1963, to form an impregnated sheet that is split to a thickness of about 70 mils. This sheet has a binder/fiber ratio of about 0.5 and a density of about 0.35 g./cc.

The above impregnated sheet material is reimpregnated with a latex binder having the following composition:

	Parts by weight
A latex—50% polymer solids of a carboxy modified copolymer of about 70% by weight of butadiene and about 30% by weight of acrylonitrile	200
Aqueous zinc oxide dispersion—50% zinc oxide solids	10
Antioxidant dispersion—40% aqueous dispersion of 2,2'-methylene-bis-(4-methyl - 6 - t - butylphenol)	2.4
"Primol" D oil emulsion—described in Example 1	20
Nonionic surfactant solution—25% aqueous solution of the condensation product of octylphenol and 9–10 moles of ethylene oxide	8
Pigment dispersion—50% beige pigment solids	20.8
Water	161.2
Total	422.4

Excess latex binder is squeezed from the sheet by a pair of nip rolls. The resulting product is dried at 110° C. Both sides of the sheet are buffed with 120 grit sand paper, yielding a suede-like material useful, for example, for shoe uppers.

This final product has the following properties:

Thickness—61 mils
Binder/fiber ratio—1.08
Density—0.49 g./cc.
Water vapor permeability—6200 g./100 m.^{2}/hr.
Tensile strength at break, M/T—1640/1000 p.s.i.
Elongation at break, M/T—210/230%
Stitch tear strength, M/T—320/520 lb./in.
Nap length—40–50 mils
Nap density—High

The above prepared polyurethane impregnated sheet is reimpregnated as above with a latex that does not contain the mineral oil additive. The sheet is dried and buffed as above but the resulting material has a low nap density and a nap length of 6–15 mils, which illustrates that mineral oil additive greatly improves nap length and nap density.

What is claimed is:

1. A supple synthetic microporous vapor permeable suede-like sheet material consisting essentially of
   (a) a non-woven synthetic flexible fibrous web impregnated with
   (b) a polymeric binder which consists essentially of a polymer of acrylonitrile and butadiene and contains a nap improving additive about 0.1–20 parts of additive per 100 parts of polymeric binder selected from the group consisting of a hydrocarbon oil which consists essentially of naphthenic and paraffinic hydrocarbon constituents and has a Saybolt viscosity at 99° C. of 20–200 seconds or a silicone oil which has a kinematic viscosity at 25° C. of at least 10 centistokes;

said microporous sheet material having at least one suede-like surface, a water vapor permeability of at least 1000 grams/100 square meters of sheet material/hour and a binder/fiber ratio of 0.2–3.0.

2. The microporous suede-like sheet material of claim 1 in which the binder contains 1–15 parts of additive per 100 parts of polymer, the water vapor permeability is about 2,000–15,000 grams/100 square meters/hour, and the binder/fiber ratio is about 0.5–2.

3. The microporous suede-like sheet material of claim 2 in which the polymeric binder consists essentially of 25–50% by weight acrylonitrile, 75–50% by weight butadiene and 0.1–5% by weight of an α,β-unsaturated carboxylic acid.

4. The microporous suede-like sheet material of claim 2 in which the additive is a hydrocarbon oil which consists essentially of 40–100% by weight of a paraffinic constituent and 60–0% by weight of a naphthenic constituent and has a Saybolt viscosity at 99° C. of 40–90 seconds.

5. The microporous suede-like sheet material of claim 2 in which the additive is a silicone oil of the formula

$$\text{-Si(R)}_2\text{—O-}_n$$

where R is selected from the group consisting of an alkyl group having 1–4 carbon atoms and a phenyl group and said silicone oil has a kinematic viscosity at 25° C. of about 50–30,000 centistokes.

6. The microporous suede-like sheet material of claim 2 in which said non-woven web consists essentially of polyethylene terephthalate fibers.

7. The microporous suede-like sheet material of claim 3 in which the α,β-unsaturated carboxylic acid is selected from the group consisting of acrylic acid, methacrylic acid and itaconic acid.

8. The microporous suede-like sheet material of claim 7 in which the non-woven web consists essentially of polyethylene terephthalate fibers and in which the additive is a hydrocarbon oil which consists essentially of 40–100% by weight of a paraffinic constituent and 60–0% by weight of a naphthenic constituent and has a Saybolt viscosity at 99° C. of 40–90 seconds.

9. The microporous suede-like sheet material of claim 7 in which the non-woven web consists essentially of polyethylene terephthalate fibers and in which the additive is a silicone oil of the formula

$$\text{-Si(CH}_3)_2\text{—O-}_n$$

and has a kinematic viscosity of 25° C. of about 20–100 centistokes.

10. The microporous suede-like sheet material of claim 1 in which the non-woven synthetic flexible fibrous web contains an impregnant of a polymeric material and has a binder/fiber ratio of less than 1.

11. The microporous suede-like sheet material of claim 10 in which the impregnant of a polymeric material consists essentially of at least 50% by weight of a chain-

extended polyurethane and up to 50% by weight of polyvinyl chloride.

12. A process for forming a supple synthetic microporous vapor permeable suede-like sheet material which comprises

(a) impregnating a non-woven synthetic flexible fibrous web with

(b) a polymeric binder which consists essentially of a polymer of acrylonitrile and butadiene and contains a nap improving additive about 0.1–20 parts of additive per 100 parts of polymeric binder selected from the group consisting of a hydrocarbon oil which consists essentially of naphthenic and paraffinic hydrocarbon constituents and has a Saybolt viscosity at 99° C. of 20–200 seconds or a silicone oil which has a kinematic viscosity at 25° C. of at least 10 centistokes;

(c) removing excess liquid from the web and drying the web; and

(d) napping at least one side of the impregnated web to form a suede-like surface;

said microporous sheet material having a water vapor permeability of at least 1000 grams/100 square meters of sheet material/hour and a binder/fiber ratio of 0.2–3.0.

13. A process for forming a supple synthetic microporous vapor permeable suede-like sheet material which comprises the following steps:

(a) forming a microporous sheet having a binder/fiber ratio of less than 1 by impregnating a non-woven synthetic fibrous flexible web with a polymeric binder, coagulating said binder and washing and drying said sheet;

(b) reimpregnating the microporous sheet formed in step (a) above with a latex of a polymeric binder which consists essentially of a polymer of acrylonitrile and butadiene and contains a nap improving additive about 0.1–20 parts of additive per 100 parts of polymeric binder selected from the group consisting of a hydrocarbon oil which consists essentially of naphthenic and paraffinic hydrocarbon constituents and has a Saybolt viscosity at 99° C. of 20–200 seconds or a silicone oil which has a kinematic viscosity at 25° C. of at least 10 centistokes; coagulating the latex and washing and drying said sheet material; and

(c) napping at least one side of the impregnated sheet to form a suede-like surface;

the resulting sheet material having at least one suede surface, a water vapor permeability of at least 1000 grams/100 square meters of sheet material/hour and a binder/fiber ratio of 0.2–3.0.

References Cited

UNITED STATES PATENTS

2,715,588	8/1955	Graham et al.	162—135
2,993,811	7/1961	Smith et al.	117—139.5
3,067,482	12/1962	Hollowell	28—74
3,167,448	1/1965	Hirshfield	117—138.8
3,400,013	9/1968	Harrison	117—140X

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