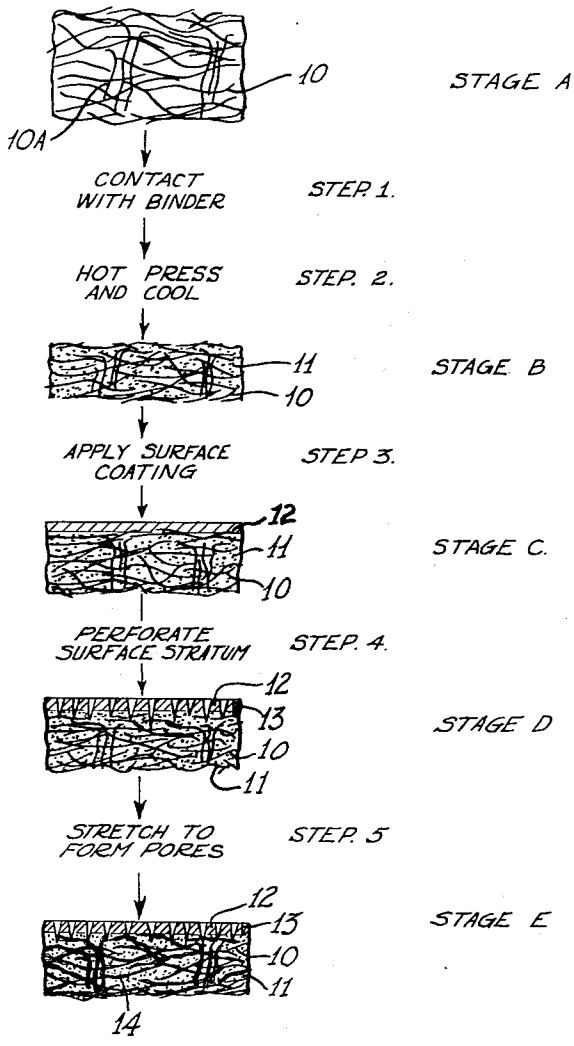
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LEATHER SUBSTITUTE

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# LEATHER SUBSTITUTE

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This invention relates to leather replacement materials, and more particularly to multi-layer, water-vapor permeable, scuff resistant sheet materials comprising a compressed interconnecting pore-containing layer of non-woven matted fibers bound together with an extensible polymeric binder and adhered thereto a surface layer of a perforated, extensible, scuff-resistant polymeric material.

The sheet materials of the invention and methods for their manufacture will be described in detail by reference to the drawing in which a representative process is illustrated by means of a flow diagram.

Stage A in the drawing represents a portion of a cross-section in greatly enlarged form of a non-woven mat of fibers **10**. Such mats, or bats as they are also called, the formation of which may be considered as the starting point in forming the base layer or stratum of the products of the invention, are readily prepared by known methods for laying down and interlacing fibers, such as the techniques used in wool carding and paper making. Preferably, the well-known felt making technique is followed by superposing a plurality of single webs or slivers of fibers from a carding machine in parallel or cross-lapped piles. Added strength can be imparted to the fiber mats by passing them thru a needle loom. Needle looming tends to orient some of the fibers in a direction generally perpendicular to the surfaces of the mat as illustrated by fibers **10**A in the drawing.

Most fibers can be used in preparing the non-woven mat. Illustrative of suitable fibers are those made of synthetic linear polyamides such as polyhexamethylene adipamide, polyhexamethylene sebacamide, polycaproamide and interpolyamides; and polyesters, and polyesteramides, and mixtures or blends thereof such as dibasic diamide or amino acid polyamides, dibasic dihydroxy acid/polyester; and the intermixed polyester/polyamide products described in U.S. Patents 2,071,250, 2,071,251, 2,071,253, 2,130,948, 2,224,037 and 2,572,833 fall in this category of linear condensation polymers. Other fibers which can be used, preferably as mixtures with fibers of the polyamide, polyester or polyesteramide types, include cotton, ramie, viscose rayon, acetate rayon, wool, polyacrylonitrile, acrylonitrile copolymers, polyurethanes, polyvinyl acetals and glass. Preferred are the syntheic linear polyamide fibers.

The denier and the length of the fibers used in making the mats can be varied widely. Ordinarily, the length will be in the range of from about 0.01 inch up to 8 inches. About 1.5 inches is preferred. The denier will ordinarily be within the range of from 0.5 to 15 denier per filament. About 3 denier is preferred.

Having formed the mat of fibers, it is then brought together with an extensible polymeric binder. This contacting step, represented by step 1 in the drawing, can be effected in any convenient manner. Thus, for example, the mat can be permeated with a solution or suspension of the binder. Alternatively, the binder can be spread on to or distributed thruout the mat in the form of finely divided particles. If the binder is of a kind that can be made in sheet or film form, such sheets or films can be laid in contact with the fiber mats. Also, if the binder is one that can be made in fiber form, fibers of the binder can be mixed with the fibers used



to form the mat during the mat forming step. Still another method involves the use of structural or mat forming fibers that have been coated with the binder material prior to forming the mat.

The extensible polymeric binder used can be any of a great variety of soft, elastic, initially thermoplastic (i.e., flows under the conditions of the subsequent hot pressing step), synthetic polymers which may be classified generally as elastomers. Care should be taken, however, to select a polymeric binder that is chemically different from the structural fiber used in making the non-woven mat. A convenient rule is that the binder when softened or melted in the subsequent hot pressing step be incompatible with the structural fibers. Additionally, the binder selected should be relatively fusible with respect to the structural fiber which, in terms of practical commercial operation, means that the differential in the temperature at which the fiber and the binder soften and develop adhesive properties is preferably not substantially less than about 50° F. In other words, the binder should flow at a temperature at least 50° F. below the deformation temperature of the structural fiber.

Among the extensible polymeric materials which can be used as binders in making the products of this invention are those classified as elastomers by H. L. Fisher in Industrial and Engineering Chemistry, August 1939, page 942.

In the most preferred products of this invention, the polymeric binder is a linear addition polymer. Because of their availability and particularly their low cost and desirable polymer properties, the most outstanding are the vinylidene polymers including both the monoene and diene types. This class of polymers is characterized by having in each polymerizable monomer 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 ($CH_2=C<$) groups. Specific examples of such polymers include the various vinylidene hydrocarbon polymers such as butadiene/styrene, 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 to carboxyl groups, or groups hydrolyzable to carboxyl groups, either directly to the acyl carbon thereof (e.g. polymethyl acrylate) or to the oxy oxygen thereof (e.g., polyvinyl acetate); 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, dis-

persion, 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. The agents for effecting such controllable cross-linking are well known in the rubber art. In the case of the diene hydrocarbon polymers and copolymers, the presence of mercaptans and/or sulfur in the diene polymer composition provides cross-linking by disulfide formation. In the case of negatively substituted diene polymers and copolymers such as the 2-chlorobutadiene-1,3 (chloroprene) polymers, the presence of metallic ovides such as zinc or magnesium oxides provides cross-linking by removal of halogen.

Various polyesters containing terephthalic acid or derivatives thereof as essential components are also useful as binder polymers. These include polyethylene terephthalate and copolyesters made from ethylene glycol, terephthalic acid and sebacic acid of the general type described and claimed in United States Patents Nos. 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 the United States Patent No. 2,430,860.

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

Still other elastomeric polymers which can 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). Specified products of this type are described and claimed in United States Patent No. 2,333,639 to R. E. Christ and W. E. Hanford.

Other types of elastomeric polymers which can be used as binders include reaction products of polyalkylene ether glycols and organic diisocyanates, such as described in U.S. patent application S.N. 365,270, filed June 30, 1953, now U.S. Patent No. 2,929,800 by F. B. Hill, Jr.

In many instances, it is desirable to have appreciable proportions of plasticizers for the binder polymers in the binder composition. This is particularly important in the case of the vinylidene resins. Plasticizers provide high pliability and desirable drape in products that might otherwise be too stiff. This is particularly true of the higher molecular weight, negatively substituted vinylidene polymers and copolymers, such as the vinyl chloride/vinylidene chloride and vinyl chloride/vinyl acetate copolymers. Suitable examples of plasticizers include the mono- or dicarboxylic acid/alcohol or/polyol-esters such as glycol dibenzoate, dioctyl sebacate, dioctyl phthalate, and polypropylene sebacate; or the polyesters of the lower polyalkllene oxides such as methoxypolyethylene glycol octoate.

The weight ratio of binder polymer to structural fibers in the base layer is in general between 30:70 and 70:30, and more preferably, the binder amounts to from 40 to 60% by weight of the base layer. Products made containing too low a quantity of binder polymer feel more like felt than leather and those containing too much binder are ordinarily stiff or brittle and hence undesirable.

Having brought together the non-woven mat of structural fibers and the binder polymer therefor in a suitable manner, as indicated above, the resulting composite is then hot-pressed, that is, it is heated under pressure, and then cooled to form a compacted unitary base structure in which the mat of fibers is substantially embedded in and the fibers thereof are bound by the binder polymer.

The hot-pressing and cooling operation is represented by step 2 in the drawing and the resulting structure is represented by stage B which shows the fibers 10 that constitute the non-woven mate embedded in and bound by the binder 11.

In the hot-pressing step, the temperature used can be varied as desired keeping in mind the requirement that it must be high enough to cause the binder polymer to flow but not so high as to fuse or transpose the structural fibers of the non-woven mat appreciably. This requirement also makes apparent the need, as indicated heretofore, in selecting the structural fiber and the binder to be used, to choose a fiber that is, with respect to the binder, relatively non-fusible, which in terms of practical commercial operations means that the differential in the temperature at which the fiber and the binder soften and develop adhesive properties is preferably not substantially less than about 50° F. With most combinations of fiber and binder a temperature in the range 100°–250° C. will be satisfactory in the hot-pressing step, and with the preferred combinations temperatures of 150°–200° C. are preferred.

The pressure used in the hot-pressing step can be varied widely to give the degree of compacting required. Ordinarily, the pressure applied will be between 50 p.s.i. and 1500 p.s.i., the higher pressures, of course, giving a more dense, tougher structure. For most uses it is preferable to prepare a compacted base stratum having a thickness from about 10 to 70 mils.

The hot-pressing step is ordinarily of short duration, in the order of 3 to 20 minutes depending upon the nature of the fiber and binder composition used, the temperature, and pressure, but other times can be used as may be desired with varied combinations of ingredients and processing conditions.

The hot-pressing step can be carried out using conventional apparatus. For example, the material to be processed can be passed between heated calender rolls under pressure or pressed between heated plates.

Having carried out the hot-pressing step as mentioned above and then cooling under pressure to solidify the binder and form the desired compacted base stratum, a surface coating of an extensible, abrasion resistant, polymeric material is then applied to at least one surface of the base stratum. This surface coating operation is represented by step 3 in the drawing and the resulting coated structure is represented by stage C which shows a compacted mat of fibers **11** bound by binder **10** and coated on one surface with a coating **12**.

Any of the wide variety of extensible abrasion resistant polymeric materials that are compatible with the binder polymer can be used to provide the surface coating. Illustrative of such materials are polyvinyl chloride, chlorosulfonated polyethylene such as described in McQueen U.S. Patent 2,212,786, polyurethanes such as described in Rodman U.S. 2,723,935, neoprene (polychlorobutadiene), polyacrylic esters (for example, isobutyl acrylate), N-methoxypolyadipamides, butadiene/acrylonitrile copolymers, polyvinyl chloride/methyl methacrylate copolymers, and the like. In the most preferred embodiment of the invention, the same polymeric material, perhaps with slight modifications such as added plasticizers, coloring agents, etc., is used in the surface layer as in the base stratum. The most preferred of such polymeric materials is polyvinyl chloride.

The surface coating can be applied by any of the methods known in the art for applying coatings to sheet-like materials. Thus, the coating material can be applied as a preformed film or a powder followed by heating, or more preferably from solutions, or from suspensions of the coating polymer composition in a non-solvent, a plasticizer or partial solvent by spraying or flowing the solution or dispersion on to one surface of the base stratum, or on to both surfaces if desired. Well-known calendering methods can be used for applying the surface coating.

In general, the surface coating composition is applied in one or more applications as desired in amount to

give a surface layer or stratum having a total thickness of from about 1 to 20 mils and more preferably from about 1.5 to 5 mils.

After applying a surface coating composition, the resulting composite is preferably heated under moderate pressure to remove any volatile solvents present, to level or to emboss the coating surface if desirable, and to improve adhesion of the surface coating polymer to the base stratum.

It should be noted that color can be imparted to the sheet material of this invention, if desired, by incorporating dyes or pigments into the surface coating composition, or in the binder for the fibers, or alternatively by dyeing the structural fibers prior to forming the non-woven mat of fibers. When pigments are incorporated into the surface coating material or binder of the base stratum, the concentration of pigments is preferably kept below 5 to 10% by weight of the total sheet in order to minimize the adverse effect on the physical properties of the sheet, particularly the tensile strength, the tear strength, and abrasion resistance of the sheet.

The sheet material of stage C, the surface coated bound fiber mat, is then treated to make it permeable to water vapor. This is done by perforating the surface coating to form channels that connect with interconnecting pores that are formed in the base stratum. The interconnecting pores can be formed first according to any of the techniques described hereinafter and the surface coat subsequently perforated to form channels connecting therewith. Preferably, however, as shown in the drawing, step 4, the surface coat is first perforated and the product so obtained is subsequently treated to form interconnecting pores in the base stratum.

According to the preferred method of processing, having obtained the sheet material represented by stage C in the drawing, the next step in preparing the sheet materials of this invention is to perforate the surface stratum (or strata, if both surfaces of the base stratum have been coated) as represented by step 4 in the drawing to obtain the product represented by stage D in which the surface layer **12** contains many perforations **13** in which the perforations extend completely thru the surface stratum **12** and part way into the base stratum.

The step of perforating the surface stratum can be carried out in conventional apparatus designed for making fine perforations in sheet materials and is preferably carried out using what is commonly known as a needle punching apparatus. The punching apparatus is preferably adjusted so that the punches or needles will not extend more than about half way into the base stratum, and still more preferably, so that they will penetrate not more than about one-third the thickness of the base stratum. The punches or needles can be adjusted so that they all penetrate to the same depth or, as illustrated in stage D in the drawing, they can be adjusted to provide varied degrees of penetration.

The number of punches or perforations made in the surface layer can vary widely, as desired, from about 300 to 30,000 or more per square inch depending largely upon the diameter of the perforations made, the degree of water vapor permeability desired, and the surface appearance sought. In the preferred products of the invention, the perforations will be in the range of from about 10,000 to 20,000 per square inch.

Best results are obtained using punches or needles having a diameter of from about 1 to 10 mils and, most preferably, from about 2 to 5 mils. Needle diameter, thus used means the diameter of the needle measured at the top surface of the surface stratum at the time the needle has reached its maximum penetration. Thus if the tip of the needle is to be inserted 0.01 inch into the material being perforated, then the needle diameter is measured at a point 0.01 inch from the tip.

A sheet material of stage D is then treated to form interconnecting pores in the base stratum. There are various ways for doing this, but a preferred way for doing this when the binder polymer used is more extensible or stretchable than the structural fiber polymer is to stretch the sheet material as indicated by step 5 in the drawing to obtain the product sheet material represented by stage E.

The stretching is ordinarily carried out by stretching the stage D sheet material from 10 to 50% in one or more directions. This causes a substantial portion of the fibers in the base stratum to break away from the binder polymer. The result is that a network of channels or pores **14** are formed more or less contiguous with the fibers along a major portion of a substantial number of the fibers. Since the fibers in the base stratum are tightly compacted, there results an interconnecting of a substantial number of the channels or pores that are contiguous with adjacent or substantially touching or intersecting fibers. Porosity and water-vapor permeability is thereby imparted to the base stratum. Simril U.S. Patent 2,757,100 describes such a method in detail.

The term "contiguous" as applied to the pores or channels in the base stratum refers to channels or pores adjacent to portions of fibers throughout the structure. The channels are not necessarily completely annular. In some cases, the channel may spiral around part of the length of the fiber or may take the form of a "hairline crack" substantially parallel to or immediately adjacent to the fiber. They are formed by breaking away fibers from the binder, and this breaking away occurs especially at points where fibers cross or otherwise contact each other. In general such pores, channels, or cracks form a capillary network in the base stratum.

Another method for forming the interconnecting pores in the base stratum is first to soak the stage D sheet material in a liquid at a temperature above the softening temperature of the binder and below the softening temperature of the fibers to swell the fibers and deform the binder in the direction of swelling of the fibers. The sheet material is then cooled to set the binder while the fibers remain in swelled condition. The liquid is then removed from the swelled fibers whereupon the fibers shrink away from the binder to form channels or pores more or less contiguous with the fibers, much the same as is obtained by the stretching method. Water is the liquid preferably used for swelling the fibers, although other liquids can be used so long as they can be readily removed from the fibers and the surfaces of the treated materials. The liquid is most conveniently removed from the treated material by evaporation.

Alternatively, the interconnecting pores in the base stratum can be obtained by first forming the non-woven mat of a mixture of structural fibers with from 40 to 70% by volume of soluble fibers such as those made from polyvinyl alcohol, cellulose acetate, sodium alginate, or carboxymethyl cellulose, and then subsequently treating the sheet material with a liquid which is a solvent for the soluble fibers and a non-solvent for the structural fibers to dissolve the soluble fibers.

The sheet material of this invention is suitable for those uses in which leather is commonly used, for example, upholstery, luggage, handbags, gloves, boots, and shoe uppers, because of its high flex life, tensile strength, extensibility, and especially because of its scuff resistance. The breathability, or permeability to water vapor and air, coupled with the scuff resistant properties make the sheet material of the invention especially suitable for making shoe uppers.

In order that the invention may be better understood, the following examples illustrating sheet materials of the invention, their preparation and properties, are given in addition to the examples already given above. Parts are by weight unless otherwise specified.

*Example 1*

Dyed staple fibers of polyhexamethylene adipamide (nylon) 1.5 inches long and 3 denier per filament, are

treated with a sizing agent of alkyl aryl polyether alcohol ("Triton" X–100, a Rohm & Haas Co. product) in water solution to a weight increase of about 1% when dried. The treated fibers are carded to form uniform slivers on conventional garnett equipment which are then sprayed with an equal weight of a plastisol binder of the following composition:

| | |
|---|---|
| Polyvinyl chloride ("Geon" 121, a B. F. Goodrich Co. product) | 55.5 |
| Dioctyl phthalate | 20.9 |
| Dioctyl azelate | 20.9 |
| Stearic acid | 0.5 |
| Stabilizer for polyvinyl chloride plastisol ("Barca" 10, Deecy Products Co.) | 2.2 |
| | 100.0 |

The sprayed slivers are then superposed in a cross grain fashion to build up a pile of about 50 slivers having a weight of about 26 ozs./yd.$^2$. The structure is placed between a smooth steel plate and a perforated sheet of cellophane on a paper board pad and placed in a press for 12 minutes at 185° C. and 1200 p.s.i. to form a compacted fiber/binder sheet as a base structure.

After cooling under pressure the base structure is coated on one surface by spraying in three stages with a modified 3.37% solution of polyvinyl chloride ("Geon" 121) in a 3/1/1 mixture of methyl ethyl ketone, methyl isobutyl ketone and acetone. In addition to the polyvinyl chloride the first spray solution (the color coat) contains 37.5 parts of dioctyl phthalate, 37.5 parts of dioctyl azelate, 40 parts of burnt sienna pigment and 4 parts of a vinyl stabilizer ("Barca" 10) per 100 parts of the polyvinyl resin; the second spray solution (depth coat) contains 33 parts of plasticizer polypropylene sebacate ("Paraplex" G–25, a Rhom and Haas Co. product) and 1.5 parts of stearic acid as a lubricant per 100 parts of the polyvinyl resin; and the third spray solution (gloss coat) contains 33 parts of polymethyl methacrylate, 1.4 parts of stearic acid and 6.6 parts of a silica flatting agent ("Santocel" silica aerogel, a Monsanto Chemical Company product) to 100 parts of the polyvinyl resin. A total topcoat or surface stratum thickness of about 4 mils is applied.

The coated sheet material is dried and then pressed at 150° C. and 800 p.s.i. for 5 minutes and cooled under pressure. The surface coating is needle-punched with 10,000 holes per sq. in. to a depth of about 5 to 7 mils. The structure is then stretched 25% in two directions, 90° to each other, to form interconnecting pores in the base stratum connecting with the perforations in the surface stratum. The product of this example is about 40 mils thick.

The leather replacement material of thie example is suitable for making shoe uppers, gloves, upholstery, and the like. It is scuff resistant and has breathability. A numerical measure of the breathability of the product was obtained by measuring its water vapor permeability to obtain a so-called leather permeability value, or LPV, according to the test described by Kanagy and Vickers in Journal of American Leather Chemists Association, 45, 211–242 (April 19, 1950).

Briefly, this test for determining LPV involves covering a small dish or cup, such as a crystallizing dish, filled with 12 mesh calcium chloride with the product to be tested and then suspending the container in an inverted position in an atmosphere of 90% relative humidity and a temperature of 23° C. The increase in weight of the calcium chloride provides a measure of the moisture vapor permeability of the substance under test. The LPV is expressed in terms of grams of water per 100 square meters of substance under test per hour. It has been determined from prior experience that an LPV of over 1500 grams of water per 100 square meters per hour is necessary for comfort in shoe uppers.

The product of the present example has an LPV of 2000.

*Example 2*

Viscose rayon staple, 1.5" long 3 denier per filament pre-sized with 3.0% dry weight of a silicone oil (DC1107), and a crimped polyadipamide (nylon) staple, 1.5" long, 3 denier per filament, pre-sized with 1% by dry weight of an alkyl aryl polyether alcohol ("Triton" X–100) are carded together on a conventional combination garnetting and cross-lapping machine to form a uniform non-woven sliver containing 60 parts of nylon and 40 parts of rayon fiber and weighing about 2.5 oz. per square yard. The sliver is then sprayed with an organosol binder of the following composition to a dry weight pick-up of 100% and dried 2 hours at 240° F.

| | |
|---|---|
| Polyvinyl chloride ("Geon" 121) | 23.8 |
| Polypropylene sebacate | 25.2 |
| Stabilizer ("Barca" 10) | 1.0 |
| Xylene | 50.0 |
| | 100.0 |

The dried sprayed sliver is then cross lapped to form six plies and pressed between cellophane sheets for 12 minutes at 185° C. and 1200 p.s.i. followed by cooling under pressure.

After removal of the cellophane, one side of the resulting compacted base stratum is coated by spraying on in three stages a modified 3.37% solution of polyvinyl chloride in a 3/1/1 mixture of methyl ethyl ketone, methyl isobutyl ketone and acetone. The first coat (color coat) is applied at a dry weight of 2.0 oz./yd.$^2$ and contained in addition to the polyvinyl chloride the following modifiers: 37.5 parts of dioctyl phthalate, 37.5 parts of dioctyl azelate, 40 parts of burnt sienna pigment, and 4 parts of a stabilizer ("Barca" 10) to 100 parts of the vinyl resin. The sheet material is then repressed for 5 minutes at 150° C. and 800 p.s.i. and cooled under pressure. The second coat (depth coat), applied at 0.8 oz./sq. yd., contains as modifiers for each 100 parts of the polyvinyl chloride, 33 parts of a polyester plasticizer ("Paraplex" G–25) and 1.5 parts of stearic acid. The final (gloss) coat, applied at 0.14 oz./sq. yd., contains as modifiers for each 100 parts of the polyvinyl chloride, 33 parts of polymethyl methacrylate ("Lucite" 41 acrylic resin, E. I. du Pont de Nemours & Co.), 7 parts of a flatting agent ("Santocel") and 1 part of stearic acid.

A decorative surface pattern is obtained in an embossing operation by heating for 5 minutes at 150° C. and 800 p.s.i., and then cooling under pressure.

The coated surface of the sheet is then perforated to provide 10,000 holes per sq. in. to a depth of 5–7 mils and then the sheet is stretched 25% in each of two directions, 90° to each other, to provide interconnecting pores in the substrate connecting with the perforated top layer.

The product has a thickness of about 50 mils and an LPV of 2500.

*Example 3*

Staple fibers of polyhexamethylene adipamide (nylon), 1.5 inches long and 3 denier filament, are carded to form a web or mat using a conventional wool carding method. The web is sprayed with a solution consisting of the following.

| | Parts |
|---|---|
| Polyvinyl chloride (binder) | 50 |
| Dioctyl phthalate (plasticizer) | 35 |
| Dinonyl sebacate (plasticizer) | 15 |
| Brown dye | 0.5 |
| Methyl ethyl ketone (solvent) | 2,000 |

The sprayed web is heated at 50–60° C. to remove the methyl ethyl ketone solvent. Four layers of the web are

then superposed, each one on top of the previous one, in cross-grain fashion to give a four-ply structure. The four-ply structure is placed between sheets of cellophane and pressed for 5 minutes at 175° C. and 500 pounds/square inch to form a compacted fiber-binder non-woven mat as a base stratum. This base stratum contains about 50% of the polyvinyl chloride binder.

The polyvinyl chloride solution tabulated above is then sprayed on the surface of the base stratum to provide a surface layer or stratum having a thickness of 1.7 mils. The coated structure is then pressed for 5 minutes at 140° C. and 500 pounds/square inch using an embossing plate to impart a graining effect to the surface.

After cooling, the resulting structure is stretched 40% in two directions at right angles to each other to make the base stratum permeable.

The top layer is then needle punched to provide 450 perforations per square inch. The perforations are about 3 to 5 mils in diameter at the surface and about 9 mils deep. The total thickness of the sheet material is about 25 mils and the thickness of the surface layer is 1.7 mils; therefore, the perforations extend into the base stratum about 7 mils or about 30% of the thickness of the base stratum.

The leather replacement product of this example is suitable for making shoe uppers. It has an LVP of 3300.

The product of this example has outstanding scuff resistance. A numerical measure of scuff resistance is obtained using an eccentric wheel scuff test. The test instrument used in this test consists of two wheels. One is a non-rotatable wheel, 6 inches in diameter and 1 inch wide. The second wheel is a 4 inch diameter, 1 inch thick felt disk mounted so as to rotate about an off-center axis. The smaller wheel is so arranged that at its maximum displacement it abrades strongly against the larger non-rotatable wheel. The sample to be tested is placed on the periphery of the non-rotatable wheel. A single rotation of the off-center wheel is referred to as a scuff. Using this test, the product of this example shows no fuzzing after being subjected to one thousand scuffs.

*Example 4*

A non-woven mat of polyhexamethylene adipamide fibers is made by cross lapping 4 carded webs of such fibers. The non-woven mat is sprayed with a solution consisting of the following:

| | Parts |
|---|---|
| Polyvinyl chloride (binder) | 100 |
| Dioctyl phthalate (plasticizer) | 37.5 |
| Dioctyl sebacate (plasticizer) | 37.5 |
| Pigment (burnt sienna) | 2.5 |
| Stabilizer | 4 |
| Lubricant (stearic acid) | 1 |
| Methyl ethyl ketone (solvent) | 1500 |
| Methyl isobutyl ketone (solvent) | 500 |

The sprayed mats are dried and pressed at about 180° C. and 750 pounds/square inch for 5 minutes and allowed to cool under said pressure. The resulting polyvinyl chloride bound non-woven fiber mat contains 45% polyvinyl chloride.

The compacted polyvinyl chloride bound non-woven mat is then coated on one surface by spraying in three stages with a modified 5% solution of polyvinyl chloride in a 75/25 mixture of methyl ethyl ketone and methyl isobutyl ketone. In addition to the polyvinyl chloride, the first spray solution (the color coat) contains 37.5 parts of dioctyl sebacate, 40 parts of pigment, 4 parts of a stabilizer and 1 part of lubricant; the second spray solution (the depth coat) contains 33 parts of a high molecular weight polypropylene sebacate and one part of lubricant; and the third spray solution (the gloss coat) contains 33.3 parts of polymethyl methacrylate, 1.4 parts of lubricant and 6.6 parts of a flatting agent.

The surface coated structure is then pressed at 140° C. under a pressure of 500 pounds/square inch for 2 minutes and cooled under pressure. The structure is then stretched 25% in two directions to form pores in the base stratum. The surface coating is needle-punched between 2500 and 5000 times per square inch using needles giving perforations of 3 to 5 mils in diameter at the surface of the material. The perforations so obtained pass completely thru the 4-mil thick surface coat and into the base stratum. The total thickness of the product of this example is 30 mils.

The product of this example has an LPV of 2690 and is suitable for use in making shoe uppers, gloves, upholstery, and the like.

*Example 5*

Four carded polyhexamethylene adipamide webs are sprayed with a solution consisting of the following ingredients:

| | Parts |
|---|---|
| Polyvinyl chloride (binder) | 100 |
| Dioctyl phthalate (plasticizer) | 50 |
| Dioctyl sebacate (plasticizer) | 50 |
| Stabilizer | 4 |
| Pigment | 5 |
| Dye | 4 |
| Anti-foaming agent | 0.1 |
| Methyl ethyl ketone (solvent) | 1500 |
| Methyl isobutyl ketone (solvent) | 500 |

The sprayed webs are cross-lapped and then consolidated by pressing for 5 minutes at 175° C. and 500 pounds/square inch. The compacted bound non-woven base stratum structure obtained contains 45% polyvinyl chloride.

Three coats are applied to the coated structure and the composite is pressed at 110° C. and 700 pounds/square inch. Each of these three additional coats contains 100 parts of polyvinyl chloride, 1500 parts of methyl ethyl ketone, 500 parts of methyl isobutyl ketone, and one or more modifying agents. The first of these coats (a color coat) contains as the modifying agents 50 parts of dioctyl phthalate, 50 parts of dioctyl sebacate, 4 parts of stabilizer, 5 parts of pigment, 4 parts of dye, and 0.1 part of anti-foaming agent; in the second (the depth coat) the modifying agents were 15 parts of dioctyl sebacate, 35 parts of a high molecular weight polyester plasticizer "Paraplex" G–25 and 4 parts of lubricating agent stearic acid; and the modifier in the third coat (a final gloss coat) was 7 parts of the flatting agent "Santocel" and 33 parts of polymethyl methacrylate. The total surface coating after final pressing was 3 mils thick.

The surface coated structure is then stretched 25% in each of two directions to form pores in the base stratum. The surface is then needle punched to provide 500 perforations per square inch. The perforations are about 5 mils in diameter at the surface and from about 3 to 5 mils deep. The product sheet is 40 mils thick.

The product of this example has an LPV of 1990. It is scuff resistant and has flex-strength and other properties making it suitable for use in shoe uppers.

*Example 6*

Six carded slivers of a "Triton" presized "Dacron" polyester 1½" staple fiber are alternately stacked with an equal weight of .0025" thick calendered vinyl films having the following composition:

| | |
|---|---|
| Vinyl chloride/vinyl acetate resin (VYNW-5 Bakelite) | 55.5 |
| Dioctyl phthalate | 20.9 |
| Dioctyl azelate | 20.9 |
| Stabilizer | 2.2 |
| Stearic acid | 0.5 |
| | 100.0 |

The stack is then placed in a press between smooth

steel plates and heated for 12 minutes at 180° C. and 1200 p.s.i. After cooling under pressure, the sheet then is surface coated on one side, perforated and stretched as indicated in Example 4. A soft pliable leather replacement material 40 mils thick having an LPV of 2100 results.

*Example 7*

Polyacrylonitrile fibers ("Orlon" acrylic fiber) of 1 denier per filament and 2½" long are carded on conventional equipment to give crosslapped sliver weighing 2.2 oz./sq. yd. and then sized with 4.0% by dry weight of a silicone oil (DC1107) from a methyl ethyl ketone solution. The slivers are then layered alternately with an equal weight of a binder of the following composition in thin films to a total of 25 oz./sq. yd.:

| | |
|---|---|
| Polyvinyl butyral 7200 | 65 |
| Dibutyl Cellosolve sebacate | 15 |
| Calcium carbonate | 10 |
| Urea-formaldehyde resin (RC718) | 10 |

The stack is then pressed at 120° C. and 100 p.s.i. for 5 minutes and then cured for 10 minutes at 150° C. at 500 p.s.i. and cooled under pressure. A colored film .005" thick of the following composition is then placed on one side of the sheet and the whole repressed for 5 minutes at 130° C. and 500 p.s.i. and again cooled under pressure:

| | |
|---|---|
| Polyvinyl butyral resin | 70 |
| Urea-formaldehyde resin (RC718) | 10 |
| Burnt sienna | 10 |
| Dibutyl Cellosolve sebacate | 10 |

This sheet is needle punched, stretched 20% in two directions and abraded on the unfinished side. A soft pliable leather-like sheet of 42 mils thickness and LPV of 1300 results.

I claim:

1. A process for making a water vapor-permeable, scuff-resistant, flexible sheet material suitable for use as a leather replacement which comprises bringing together a non-woven mat of polyhexamethylene adipamide fibers and a polyvinyl chloride plastisol in a polyvinyl chloride: fiber weight ratio of from about 30:70 to 70:30, forming a compacted base stratum in which the said mat of fibers is substantially embedded in and the fibers thereof are bonded by the polyvinyl chloride by heating the resulting mixture at 150° C.–200° C. under pressure of 50–1500 pounds per square inch followed by cooling under pressure, coating one surface of the base stratum with polyvinyl chloride to obtain an adherent polyvinyl chloride surface stratum 1–20 mils thick, needle punching thru the surface stratum and part way into the base stratum with needles of 1–10 mils diameter to provide from 300–30,000 perforations per sq. in. in the surface stratum, and stretching the surface coated base stratum from 10–50% in at least one direction to cause fibers to break away from polyvinyl chloride in said base stratum and form a network of interconnecting pores.

2. A water vapor-permeable, scuff-resistant, flexible leather replacement sheet material comprising a base stratum having a surface stratum adhered to at least one surface thereof, said base stratum being a compressed layer having a network of interconnecting pores and comprising as essential constituents a mat of non-woven synthetic linear polyamide fibers substantially embedded in and the fibers thereof bound together with a vinylidene polymer, the vinylidene polymer:fiber weight ratio being from 30:70 to 70:30, and said surface stratum comprising a vinylidene polymer film having from 300–30,000 perforations of 1–10 mils diameter per sq. in. connecting with pores in said base stratum.

3. A water vapor-permeable, scuff resistant, flexible leather replacement sheet material comprising a base stratum having a surface stratum adhered to one surface thereof, said base stratum being a compressed layer having a network of interconnecting pores and comprising as essential constituents a mat of non-woven polyhexamethylene adipamide fibers substantially embedded in and the fibers thereof bound together with polyvinyl chloride, the polyvinyl chloride:adipamide fiber weight ratio being from 30:70 to 70:30, and said surface stratum comprising a polyvinyl chloride film having from 300–30,000 perforations of 1–10 mils diameter therein connecting with pores in said base stratum.

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