SHEET MATERIAL AND PROCESS OF MAKING SAME

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This invention relates to a novel process for making non-woven fibrous sheet materials which have a unique combination of properties including high strength, suppleness, and air permeability. A preferred embodiment of the invention concerns the manufacture of sheet material having a soft and drapy hand similar to that of soft leather suedes.

This application is a continuation-in-part of my co-pending application S.N. 790,819, filed February 5, 1959, which is a continuation-in-part of S.N. 746,340, filed July 3, 1958, both now abandoned.

The limitations of soft suedes constitute a problem which has faced the suede industry for many years. Like most products of natural origin, their properties vary from batch to batch and piece to piece, making it difficult to produce a quality of products of similar texture and appearance. In addition, the size of the pieces obtainable is limited to the size of the animals from which the skins are taken, which necessitates costly piecing and matching to produce large articles. Soft leather suedes are also known to "crock," that is, they tend to shed their color when abraded. Moreover, laundering usually results in a shrunk and wrinkled product. Ease of soiling and difficulties in cleaning are further typical drawbacks.

Many unsuccessful attempts have been made to produce a man-made soft suede which overcomes these limitations in the natural product and yet retains the excellent hand and drape qualities. Prior attempts to make such a material have included such methods as treating woven or non-woven fabrics with plasticized resins and applying flocks to fabrics coated with initially tacky compositions. Heretofore, man-made suedes have usually been inferior to the natural material, and never have they been superior to it in most respects. For example, some have been poor in appearance and inferior in wear resistance. Others have turned stiff or brittle after a few months' time. Most have lacked the drape and hand characteristics required in good quality material, being either rubbery, boardy, papery or stiff. In many cases they have had little or no moisture permeability. Virtually none have been capable of withstanding repeated laundering or ordinary dry cleaning.

The primary object of this invention is to provide a method for producing a soft and drapy suede-like material having a thickness of .005 to .10 inch and a degree of suppleness within the range of 1.0 to 65 pounds per square inch as determined by the cantilever test of ASTM D1388—55T. The suppleness is expressed as bending stiffness in pounds per square inch obtained by dividing the cantilever value by the cube of the thickness of the material.

Other important objects will be apparent from the following description of the invention.

Briefly stated, the method of this invention comprises forming a non-woven mat or web of staple fibers, impreg-
the laminate is immersed in water to coagulate the impregnating polymer and extract the solvent from the impregnating solution. After substantially all the solvent has been extracted from the impregnating solution, the laminate is dried at 100° C. and if the impregnant is a curing type polymer it is cured by further heating.

Those combinations of polymers which produce an adhesion of the surface film to the impregnated mat less than about 0.5 pound per 1" strip when tested in accordance with ASTM D514-46T, paragraph 37-39, are considered to have substantially no adhesion to each other.

The following preferred embodiments, in which improved suede products are produced, are intended only to illustrate the invention and not to limit it in any way. Throughout the specification and claims, all parts and percents are by weight unless otherwise specified.

Example 1

A quantity of 0.5 denier polyethylene terephthalate filaments having the capacity to retract about 70% of their drawn length when boiled in water is prepared in the manner taught by H. J. Kolb in U.S. Patent 2,758,908. The uncrimped filament is treated with 0.2% of "Coranolite" HC, a cationic softener made by Sandoz Chemical Works, and cut into 1 inch staple fibers. Nine parts of fibers described above and one part of 1.5 denier 1.5 inch crimped staple fibers of polyethylene terephthalate are opened and blended on a roller card. The blended fibers are carded into a mat and cross-lapped into a loose layered mat having a thickness of about 1.5 inches, a weight of 5.5 ounces per sq. yd., and a specific gravity of 0.004.

The loose mat is placed on a carrier and fed into a needleloom.

The needles are mounted on the needle boards at a density of four per square inch. The loom operates at 240 perforation cycles per minute. The beam is set at 2\(\frac{3}{4}\) inches, and the stroke is 2\(\frac{1}{2}\) inches. While the needles are drawn clear of the mat, the mat advances at the rate of 0.285 inch per cycle.

After the first pass through the loom, the mat is removed from the carrier. Next, it is turned over and needled from the other side while supported on the carrier. This procedure of needling alternate sides is repeated until the mat has received a total of 16 passes through the loom at the above rate, 8 on each side. As the needles enter the mat, they force numerous closely spaced fibers, individually or in small groups, into and through the mat to assume positions substantially perpendicular to the mat faces. Thus the layers of fibers are bound together and compacted by the needling operation. Needling density or total punches per square inch, is 3100. The mat now has a thickness of 0.032 inch and a specific gravity of 0.13.

After needling, the mat is prepared for heat shrinking by being pretreated with water at 70° F. This is done by dipping the needled mat in water until it absorbs about 5 times its own weight in water. The wet mat, in a relaxed condition, is immersed in water at about 174° F., where it remains for a period of about 3 minutes. During this heating period the mat gradually shrinks, losing about 33% of its planar area. The shrinkage results from linear retraction and crimping of the highly retractable polyethylene terephthalate fibers. At this point these fibers have a residual shrinkage potential sufficient to cause a further area shrinkage of about 10 to 20% if the mat were dipped in boiling water.

The shrunk mat, while still relaxed, is removed from the hot water, cooled, and drained until relatively free of water. The wet shrunk mat is passed over drying cans heated to about 220° F. until substantially dry.

Dried and dried, the shrunk mat is 50 mile thick, with a specific gravity of 0.17. Smooth and uniform in appearance, it is also resistant to delamination and tearing. The needle-entry points are not discernible at this stage.

A polyurethane elastomer impregnating solution is prepared as follows: 73.5 parts of polytetramethylene ether glycol of 1000 molecular weight are dimerized with 6.4 parts of tolylene-2,4-diisocyanate by mixing together and heating for 3 hours at 194° F. The resulting dimer is capped with methylene diphenyl diisocyanate by mixing 6.4 parts of the former with 18.4 parts of the latter and heating for 1 hour at 176° F. The capped dimer, a prepolymer with isocyanate end groups, is dissolved in sufficient, N,N-dimethyl formamide (referred to hereinafter as "DMF") to form a 20% solution. Separately, a 20% solution of hydrazine (4-phenyl) is prepared by mixing the same solvent. Dibutyl amine is added to the DMF hydrate solution in the amount of 0.15% of the hydrate hydrate present; this serves as a chain-stopper. The two solutions are then mixed together to form a 20% elastomer solution. For the impregnating operation to follow, the solution is diluted with DMF to an elastomer content of about 7.5% which results in a viscosity of about one poise at 75° F.

The previously described densified and dried mat, (specific gravity of 0.17) is immersed in the 7.5% solution of the elastomer at 75° F., thereby becoming substantially saturated with the solution. As the mat leaves the impregnating solution, it passes between a pair of squeeze rolls, of which the bottom roll is driven and the top roll is free running and weighted to exert about 2 pounds of pressure per inch of mat width. Excess impregnating solution is removed from the mat's surface by the squeeze rolls, and sufficient elastomer remains within the mat after squeezing to yield an elastomer/fiber ratio of 35 parts of elastomer for each 100 parts of fiber. The residual shrinkability left in the fibers after the previously described shrinking step is neutralized by the solvent in the elastomer solution without casing further shrinkage of the mat.

The elastomer is precipitated uniformly throughout the fibrous structure of the mat to form a porous matrix for the fibers without any substantial adhesion between the fibrous mat and the non-fibrous matrix therefor by immersing the roller-squeezed mat in water at about 75° F., where it remains until the elastomer is precipitated throughout the mat. The material is passed through wringer rolls which exert sufficient pressure on the mat to remove about as much water and solvent as possible without crushing or otherwise damaging the mat. After passing between the wringer-rolls, the mat is washed in water until substantially free of DMF solvent for the non-fibrous matrix. It is important that substantially all the DMF be extracted from the impregnating solution before the mat is freed of water to prevent any substantial adhesion between the fibers and the non-fibrous matrix.

Next, the impregnated mat is dried by passing it around a series of six drums heated at 275° F. The smooth, heated drums effect a smoothing or ironing action on the mat as it dries. The dry sheet has a specific gravity of 0.24.

Employing a machine commonly used for raising a nap on fabrics and leather, both surfaces of the sheet are buffed with a #240 emory cloth covered roller until a fine uniform downy nap is produced. A brief brushing follows buffing to remove dust and enhance the nap. Then the suede-like sheet is dyed. This process consists of first scouring the sheet for \(\frac{1}{2}\) hour in water at 212° F. containing 1% of "Duponol" RA, a wetting agent, and 1% of 28% strength ammonium hydroxide. The sheet is scoured in 20 times its own weight of the above solution. Next, it is rinsed in water and immersed in a 5% aqueous dye solution for 120 minutes at a temperature of about 160° F. The dyeing process is completed by scouring the colored sheet for 30 minutes in a water bath at 212° F. containing "Duponol" RA surfacive active agent in the amount of 0.5% by weight of
the sheet, rinsing and drying. The dyed sheet has the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of non-fibrous matrix to fiber</td>
<td>35/1.00</td>
</tr>
<tr>
<td>Weight</td>
<td>6.0 oz./sq. yd.</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.039 inch</td>
</tr>
<tr>
<td>Specific gravity (Density)</td>
<td>0.24 gm./cc.</td>
</tr>
<tr>
<td>Bending stiffness (cantilever test ASTM D3188–55T)</td>
<td>7.3 p.s.i.</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>5.5 lbs./in./oz./sq. yd.</td>
</tr>
<tr>
<td>Tongue tear</td>
<td>0.8 lbs./oz./sq. yd.</td>
</tr>
<tr>
<td>Air porosity (permeability)</td>
<td>80 cc. per sec./sq. in./5 gm. wt.</td>
</tr>
</tbody>
</table>

Elastic modulus (extrapolated from 5% elongation) 400–900 p.s.i.
Elongation at break 97–105%

A product is made as described above in Example I except the water immersion precipitating step is omitted and the DMF solvent is removed by heating. The product has a suppleness of about 102 pounds per square inch, as measured by the cantilever test in ASTM D1388–55T, and does not have a soft drapy hand.

A 10 mil thick film is prepared from the elastomer polymer from which the non-fibrous porous matrix is prepared by casting the impregnating solution on a glass plate and then, before any appreciable amount of solvent is evaporated, the glass plate with the film thereon is immersed in water at about 24° C. for about 10 minutes to precipitate the polymer and extract the solvent. The film, after stripping from the plate, is then dried in an oven at about 120° C. The film, which is in substantially the same form as the non-fibrous porous matrix in the mat of the above described example, has a tensile stress at 5% elongation of 21 pounds per square inch.

A one mil thick film of polyethylene terephthalate is pressed onto the impregnated fibrous mat described above in the foregoing example, immediately after impregnating and before any appreciable amount of DMF is evaporated from the impregnating solution. The laminated assembly is promptly immersed in water to precipitate the polymer in the impregnating solution and extract the DMF from the impregnated mat. After drying the adhesion of the surface film to the impregnated fibrous mat is less than 25 pound per 1” strip when tested as per ASTM-D751–46T, paragraph 37–39.

When the above adhesion test is repeated and the water immersion precipitating step is omitted, the adhesion of the surface film to the impregnated fibrous mat is found to be over 20 pounds per 1” strip when tested as per ASTM-D751–46T, paragraph 37–39. These tests show the importance of the water immersion precipitating step in Example I, to produce a product having substantially no adhesion between the fibers of the non-woven mat and its non-fibrous matrix.

The product of this example has a soft and drapy hand resembling that of the better grades of soft leather suades. Smooth and uniform in appearance, the product is especially useful for making suede shoe uppers and garments as jackets, skirts and slacks. Garments made from this new suede material are durable, attractive and comfortable. Quite unexpectedly, they can be laundered repeatedly in conventional washing machines without damage. They can also be dry cleaned with the usual dry cleaning fluids, such as, e.g., perchlorethylene. The material remains supple and moisture permeable during extended use. It was surprising that such a desirable combination of properties could be attained in a polymer-treated non-woven fabric.

A further modification involves surface coating the above described sheet material with a solution of the same elastomer used to impregnate the shrunk mat to produce an upholstery material and a smooth finished shoe upper material. Pigmented and plasticized polyvinyl chloride compositions are also applied as surface coatings to the above described sheet material to produce a high grade upholstery material.

Example II

A non-woven cross-lapped mat of 1.5 denier, 1.5 inch crimped nylon staple fibers weighing about 8.5 ounces per square yard is formed on a card. The loosely formed mat is needle punched in the same manner as described in Example I. After needleling the mat has a thickness of about 0.10 inch and specific gravity about 0.08. The needleed mat is impregnated throughout with a 7.5% solution of the following meld ingredients dissolved in DMF.

<table>
<thead>
<tr>
<th>Parts by weight</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic modified copolymer of butadiene and acrylonitrile</td>
<td>100.0</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.5</td>
</tr>
<tr>
<td>Tetramethyl thiram disulfide</td>
<td>1.5</td>
</tr>
<tr>
<td>2,2’-methylene bis(4-methyl 6-tertiary butyl phenol)</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The carboxylic modified copolymer is a rubbery and somewhat tacky copolymer containing about 0.1 carboxyl equivalents of methacrylic acid or acrylic acid prepared by the aqueous copolymerization of a mixture of monomers consisting of about 55% of butadiene-1,3, about 35% acrylonitrile and about 10% of methacrylic acid.

Excess impregnant is removed by passing the impregnated mat between squeeze rolls. The impregnated mat is next immersed in cold water (about 20° C.) to precipitate the impregnant and extract the DMF. The mat is next immersed in hot water (40–100° C.) until substantially all the DMF is extracted from the impregnated mat. The cold water immersion brings about rapid precipitation of the impregnating polymer throughout the mat and prevents the impregnant from adhering to the fibers in the mat. The subsequent hot water immersion partially cures or cross-links the impregnating polymer and extracts substantially all the remaining DMF. The wet impregnated mat is dried at about 100–120° C. to remove substantially all the water and then further heated at about 150–170° C. until the precipitated impregnant is cured to the insoluble stage.

At this stage, the impregnated mat weighs about 17.0 ounces per square yard and is about 0.10 inch thick. The dried mat is next split through its thickness to form two sheets each about 0.05 inch thick. The separate sheets are buffed on each side with emery covered rolls to raise the nap which reduces the thickness to about 0.035 inch to complete the manufacturing operations.

The product is a highly air permeable, soft, drapy sheet-like sheet material having a suede finish particularly useful for wearing apparel, such as, e.g., ladies' skirts, men's jackets, shoes, and draperies. The product has the following physical properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>5.0 ounces/sq. yd.</td>
</tr>
<tr>
<td>Ratio fiber/non-fibrous matrix</td>
<td>1/1.</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.35 inch</td>
</tr>
<tr>
<td>Bending stiffness (cantilever test ASTM D–1388–55T)</td>
<td>6.1 p.s.i.</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>2.3 lbs./inch width/oz./sq.yd.</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>130%</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.16 g./cc.</td>
</tr>
</tbody>
</table>

A 10 mil thick film of the impregnating polymer is made by casting the impregnating composition on a glass plate and then before any appreciable amount of the DMF is evaporated immersing the film in water to precipitate the polymer and extract the DMF. The film was stripped from the plate and heated to dry and cure the film. The film was in substantially the same form as the non-fibrous
matrix of the foregoing Example II. The dried and cured film has a tensile stress at 5% elongation of 15 p.s.i.

A 1 mil thick nylon film is laminated to the impregnated nylon mat of Example II before any appreciable amount of the DMP solvent is evaporated as described in the adhesion test of Example I. The laminate is immersed in water before any appreciable amount of DMP is evaporated from the impregnating solution to precipitate the impregnating polymer and extract the DMP from the impregnating solution, followed by drying and curing the impregnant. When tested by the 1" strip test (ASTM D751–46T; paragraphs 37–39), there is substantially no adhesion (i.e., less than 25 lb. per 1" strip) between the surface film and the impregnated mat.

Example III

A non-woven mat of polyethylene terephthalate fibers needle punched and shrunk as described in Example I, having a thickness of 0.05 inch and a specific gravity of 0.17 is impregnated with the impregnating composition of Example II. The impregnating, precipitating, extracting, partially curing, drying and final curing steps of Example II were repeated. The product is next buffed with emery covered rolls to raise the nap which reduces the thickness to about 0.035 inch.

There is substantially no adhesion between the nonfibrous matrix (impregnated) and the fibers as determined by the adhesion test described in Example II.

The product is very soft, drapy, highly porous and has the following physical properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>6.0 ounces/sq.yd</td>
</tr>
<tr>
<td>Ratio fiber/non-fibrous matrix</td>
<td>1.0/0.45</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.35 inch</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>22 g/cc</td>
</tr>
<tr>
<td>Bending stiffness (ASTM D–1388–33T)</td>
<td>10.7 p.s.i.</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>4.3 lbs./in width/oz./sq.yd</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>70%</td>
</tr>
<tr>
<td>Tongue tear</td>
<td>0.6 lbs./oz./sq.yd</td>
</tr>
</tbody>
</table>

Example IV

A non-woven cross-lapped mat of 1.5 denier, 1.5 inch crimped high tenacity viscose rayon staple fibers weighing about 3.0 ounces/sq.yd. is formed on a card. The loosely formed mat is needle punched in the same manner as described in Example I. After needling the mat has a thickness of about 0.10 inch and a specific gravity of about 0.07. The needle mat is impregnated throughout with the impregnating composition of Example I. The precipitating, extracting, partially curing, drying, final curing, slitting and buffing steps of Example I are repeated. The product is very soft, highly porous, drapy and has essentially the same physical properties as that described in Example I.

There is substantially no adhesion between the nonfibrous porous matrices (impregnant) and the fibrous mats made in accordance with the disclosure of Examples I–IV as determined by the 1" strip adhesion test.

In place of the impregnants used in the specific examples, other resins and elastomers can be used in place thereof as long as they can be deposited throughout the fibrous mat as a continuous porous matrix having a tensile stress at 5% elongation corresponding to 5.0 to 150 p.s.i. Such elastomers and resins include plasticized polyvinyl chloride and copolymers of vinyl chloride with other ethylenically unsaturated monomers such as, e.g., vinyl acetate and vinylidene chloride; copolymers of butadiene and acrylonitrile, copolymer of butadiene and styrene, and butyl rubber.

Useful precursors for the impregnant other than water include glycol monoethyl ether, hydroxyethyl acetate, polyols such as, e.g., glycerol and ethylene glycol. The essential requirement for the precursors is that it is a non-solvent for the polymer in the impregnating composition and the fibers and be miscible with the solvent in the impregnating composition.

Especially desirable results in making flexible suede shoe uppers and garment materials are obtained with polyethylene terephthalate fibers prepared in accordance with the teachings of U.S. Patents 2,604,689 or 2,758,908. These polyester fibers have the property of retracting when heated in hot water or in hot air below the bonding temperature of the fiber. When crimped, the fibers have wool-like appearance and resilience, and are desirable interlocked in the mat. Another type of retractive filamentary material that can be used in the above example as a direct replacement for the polyethylene terephthalate fibers is regenerated cellulose of the kind described by Nicoll in U.S. Patent 2,515,834.

These fibers crimp spontaneously at room temperature in a swelling agent, such as, e.g., an aqueous alkali. Liquid ammonia will also cause retraction, by shrinkage rather than crimp formation, of ordinary viscose rayon, which also can be used in preparing the products of this invention.

Other synthetic polymeric fibers are useful in practicing this invention, including polytetrafluoroethylene, cellulose acetate, nylon, 40–60 copolymer of acrylonitrile and vinyl chloride, 30–70 copolymer of vinyl chloride and vinylidene chloride, polyethylene and polystyrene. The spontaneously expansible synthetic linear polyester fibers described in copending application S.N. 718,114, filed February 28, 1958 by Kistom and Reese may be substituted for retractive fibers of Example 1. While these other fibrous materials are not preferred over retractive polyethylene terephthalate, they can be used alone or blended with each other. The preferred retractive polyethylene terephthalate fiber can be blended with any of the aforementioned fibers.

In the case of those fibers which tend to be dissolved in the solvent for the impregnating elastomeric polymer, it is desirable to reduce the solvent action of the solvent by incorporating a non-solvent, such as, e.g., water, glycols or alcohols up to the point of incipient gelation of the elastomeric polymer and then after impregnation of the mat immediately coagulating the impregnant throughout the mat in order to remove the solvent from further contact with the fibers and prevent the formation of a bond between the fibers and the impregnant (non-fibrous matrix).

The denier of the fibers is preferably no higher than 1.5, and those having a denier of about 0.5 to 1.0 are particularly preferred. Shorter fibers are sometimes desirable in the suede type products to modify the nap characteristics. Fiber length in any case can vary from about 0.5 inch to about 3 or 4 inches, although 1.0 to 1.8 inch fibers are preferred. Shorter fibers tend to reduce the products' tensile and tear strengths and longer fibers are more difficult to handle in mat formation.

The fibers are formed into a loose mat of convenient thickness in any known manner. In most cases the initially formed mat will weigh from about 4 to about 10 ounces per square yard. Although the carding method is preferred, the mat may also be formed on a foraminous carrier from a liquid suspension of fibers, or blown or dropped from an air suspension. The technique of mat formation described by F. Wilcox in copending application S.N. 726,186, filed April 3, 1938, and now U.S. Patent 3,007,840, issued Nov. 7, 1961, is particularly useful in practicing this invention. Crosslapping the fibers into layers of dissimilar orientation within the plane of the mat provides a product having balanced stretchability. When unidirectional stretchability is preferred, of course the cross-lapping is omitted; that is, most of the fibers are laid whereby they have similar orientation in the plane of the mat.

During the needling step the loose mat is converted
into a uniformly dense and smooth felt-like structure by the barbed needles. The needles force numerous fibers, singly or in groups, into positions relatively perpendicu-
lar to the faces or plane of the mat, rendering the mat more compact and coherent. Each square inch of the mat should preferably receive at least about 1500, and not
more than about 3800 needle punches, referred to as perforation density. This is best accomplished step-
wise on alternate sides of the mat in about 8 to 20 passes through a conventional needle-loom. Too low a perfora-
tion density yields a loose mat with an excessive texture, while excessive needling tends to roughen, stiffen and weaken the mat. The needled mats before shrinking usually have a specific gravity in the range of 0.08 to 0.19, and preferably about 0.13 to 0.15.

The outstanding properties of the product of this invention are due in large part to the unique properties and physical form of the non-fibrous porous matrix for the fibrous mat. It is important that the non-fibrous porous matrix be in a form which has a tenstle stress at 5% elonga-
tion of at least 5 p.s.i. and not in excess of 150 p.s.i. The particularly preferred range of tenstle stress at 5% elongation for the non-fibrous matrix as present in the mat is 10-50 p.s.i. The particularly preferred elastomer from which the non-fibrous matrix is formed is an elastomer formed by employing a compound having 2 active hydrogen atoms bonded to amino-nitrogen atoms to chain extend the reaction product of a polyalkylene ether diisocyanate. Such an elastomer has the advantages of having high tensile strength without requiring a curing agent and not requiring a plasticizer to achieve the necessary softness, flexibility and elasticity. Furthermore, it is not deleteriously affected by most solvents, soaps, detergents and various materials used in laundering clothes. When solutions of the elastomer are deposited uniformly throughout a fibrous mat in accordance with the method of this invention, the product has a spongy microporous structure.

The especially preferred elastomers useful in carrying out this invention are the polyurethane polymers described more fully in copending application U.S. Patent 2,957,852, issued Oct. 25, 1960.

The preferred elastomer is dissolved in sufficient sol-
vent to result in a relatively low viscosity, preferably less than about 3 poises for rapid impregnation. Any good solvent for the elastomer which is completely miscible with the precipitant for the impregnant, can be used, so long as it does not seriously attack any of the fibers of the mat. While DMP is the preferred solvent for the impregnant, other useful solvents include, for example, dimethyl sulfoxide, tetrahydrofuran, tetramethyl urea, N,N-dimethyl acetamide and mixtures thereof. Acetone is useful as a diluent.

The mat is then immersed in the impregnating composition containing a low elastic modulus elastomer, or the composition is applied to the mat until the mat is substan-
tially saturated. The mat is then drained or squeezed of excess composition so that none remains on the surface. The mat contains from about 10 to about 200 parts by weight of non-volatile impregnant for each 100 parts by weight of fibers. Preferably the mat should contain about 50 to 100 parts by weight of the non-volatile impregnant per 100 parts by weight of fiber for garment uses. Excessive elastomer makes the product rubbery. Too little, on the other hand, results in a sleazy product with poor strength, poor elasticity and poor dimensional stability. Mat density, concentration and viscosity of the elastomer solution, and the extent of squeezing or draining of the loess are all factors which control the elastomer content of the mat.

The impregnated mat is preferably bathed or treated with water in any convenient manner to precipitate the impregnating elastomer uniformly through the mat, for example, by immersion or spraying. In most cases the precipitation is substantially complete within about 30 seconds of treatment, but continued treatment with water is necessary to flush all or most of the solvent from the mat. The non-fibrous porous matrix, remains after the water treatment, the product cannot be subjected to elevated drying temperatures for the drying and curing operations without destroying the suppleness of the product by caus-
ing the non-fibrous porous matrix to be adhered to the fibrous mat.

After the impregnated mat is water-bathed sufficiently to remove all or nearly all the solvent, it is force dried with the aid of heat, preferably by means which further improve its smoothness. The drying can be performed in an oven, by passing the mat over smooth heated rotating drums, or by other known web-drying methods.

When a colored product is desired, a dying step is included at any convenient stage in the process.

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.

A nap is raised 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 actually improves the suppleness of the product besides softening its surface feel.

It was surprising and unexpected that a soft downy nap of uniform appearance could be raised on a low modulus elastomer impregnated non-woven mat.

Another optional step in the process of this invention, is to treat the product with known fabric softeners, or to likewise treat the mat at any stage of the process.

It is to be understood that such steps as buffing, brushing, dyeing and pressing, while preferred in many cases, are intended to be optional, and may be included in the process at any convenient point, either prior to or after the impregnating operation.

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

The product of this invention, because of its many de-
sirable properties, is especially well-suited also for use as a substrate to be coated with any of a multitude of known coating compositions. For example, useful supple sheet materials will result from applying a flexible layer of a permeable or impermeable coatings to one or both sides of the napped or plain product. Surface coatings based on vinyl chloride polymers or copolymers are particularly useful. Moisture permeable coatings based on vinyl chloride polymers or polyurethane elastomers are of particular interest, such as, e.g., those disclosed in U.S. Patent 2,825,711 or copending application U.S. 723,669, filed March 25, 1958 by E. K. Holden, and now aban-
donned, or various synthetic rubbers, such as, e.g., neo-
prene, copolymer of butadiene and styrene or copolymer of butadiene and acrylonitrile. Soft and moisture per-
meable leather-like materials can be produced in this manner.

From the foregoing detailed description, it will be ap-
parent that the process and product of this invention have important advantages which represent an advance in the art of making sheet materials which are soft, supple and permeable. The process is practical, economical and readily adaptable to mass production. The invention provides a durable permeable sheet material of extraordinary softness and suppleness. There is also provided a napped garment material of remarkably pleasant hand. The elastic microporous suede-like sheet has unsurpassed appearance and comfort features. Obtain-
able in an unlimited array of colors, and relatively uni-
form in properties from batch to batch, the product can
be made in most any width and in any length. Long lengths are conveniently shipped and stored in roll form. Garments made from the product not only withstand repeated laundering, but are even softer to touch after such exposure. They also withstand ordinary dry cleaning. The material has good resistance to soiling and to wrinkling.

The principal use for the products of this invention, as previously indicated, is in the shoe and garment industry. Other uses for the products are as filter media, insulation, table and roll coverings, sound and vibration absorbents, liners and paddings for blankets, carpets, sleeping bags, garments and the like and as special-purpose upholstery materials. In addition, they are useful as replacements for polishing felts and chamois.

While there are above disclosed but a limited number of embodiments of the structure, process and product of the invention herein presented, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed, and it is desired therefore that only such limitations be imposed on the appended claims as are stated therein, or required by the prior art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The method of making supple moisture-permeable sheet material which comprises the following steps in sequence, forming a fibrous mat comprising synthetic fibers, impregnating said mat throughout with a solution of a synthetic polymer, extracting substantially all of the solvent from the impregnating solution by treating the impregnated mat with a liquid which is miscible with the solvent of said solution and is a non-solvent for said fibers and said synthetic polymer, and drying the impregnated mat, whereby the impregnant is deposited throughout said mat in the form of a matrix for said fibers and there is substantially no adhesion between said fibers and said matrix.

2. The method of claim 1 in which the amount of impregnating composition introduced into the mat is sufficient to deposit 10 to 200 parts by weight of non-volatile components per 100 parts by weight of fibers.

3. The method of claim 1 in which the matrix for said fibers has a tensile stress at 5% elongation of 5 to 150 pounds per square inch.

4. The method of claim 1 in which fibrous mat is shrunk prior to impregnation.

5. The method of claim 1 in which the fibers are polyethylene terephthalate.

6. The method of claim 1 in which the impregnating composition comprises an elastomer obtained by chain extending the reaction product of a polyalkylene ether glycol and an organic isocyanate with a compound having two active hydrogen atoms attached to amino-nitrogen atoms.

7. The method of claim 6 in which the impregnating composition comprises a solution of said elastomer in N,N-dimethyl formamide.

8. The method of claim 7 in which the impregnated mat is treated with water to extract the N,N-dimethyl formamide.

9. The method of claim 1 in which said fibers are polyethylene terephthalate, said solution of a synthetic polymer is an elastomer obtained by chain extending the reaction product of a polyalkylene ether glycol and an organic isocyanate with a compound having two active hydrogen atoms attached to amino-nitrogen atoms dissolved in N,N-dimethyl formamide, and said non-solvent for said fibers and said synthetic polymer is water.

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