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METHOD FOR MANUFACTURING SYNTHETIC LEATHER
Osamu Fukushima, Hiroshi Hayanami, and Kazuo Nagoshi, Kurashiki, Japan
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ABSTRACT OF THE DISCLOSURE
A method for making an air and moisture-permeable sheet material comprising impregnating a fibrous substrate, such as a mix-spun fiber, with an impregnant comprised of a high molecular weight polymeric material having rubber-like elasticity, cossagulating the impregnant, and extracting one of the polymers in the mix-spun fibers by means of a solvent which is a non-solvent for at least one other polymer in the said mix-spun fibers.

The present invention relates to a pliable, air- and moisture-permeable sheet material with a high strength and to the method of manufacturing the same. In particular, the invention is concerned with a sheet material which bears a striking resemblance to the natural leather in structure, external appearance, texture and touch, that is so-called "synthetic leather," and with the method of preparing the same.

The novel commodity, so-called "synthetic leather," has come to the object of attention in the world market in recent years, and in Japan, without exception to the rule, this has brought about a certain boom.

For a long time, the manufacture of synthetic articles having the same composition as that of the natural leather has been a dream for the skilled in a certain art. First, there has been produced the so-called "regenerated leather" by the method which comprises the two basic steps of crushing a scrap of natural leather and dissolving the resulting crushed leather, from the economical view point of utilization of scraps of natural leather rather than the view that the synthetic article should be of the same composition as that of the natural one. Next, as an attempt to provide a similar characteristic to the natural leather to the resulting article, even a camouflage has been effected by giving a similar odor to that of the natural leather to the regenerated leather. Among these attempts, there was continued to make researches on the "regenerated leather," and in a certain field the "regenerated leather" has been put into practical use in place of the natural leather and there are a number of technicians who have an expectation that the "regenerated leather" will be put into practical use in another field. In spite of such efforts, however, the first ideal has not been realized because of difficulty in synthesizing proteins which are principal constituent of the natural leather and of the fact that the obtained leather has some unfavorable characteristics, and it is not conceivable that the first ideal will be realized in the recent future and the production of the "regenerated leather" will be industrialized.

Under such conditions, as article heretofore regarded as a substitute for the natural leather, there has been the artificial leather, so-called "imitation leather." The artificial leather was made, in the early time, by coating nitrocellulose and then vinyl chloride or rubber by changing the composition of the coatings and in the external appearance by pressing grain. The physical strength of the artificial leather, however, depends only upon the fabric used.

The recent development of the plastic industry, however, has resulted in a group of worked fabrics, so-called "synthetic leather," which exceed the stage of "imitation leather" by bringing about various plastics which are not inferior to the natural leather in physical strength and chemical resisting property in the original material field, by proposing to use non-woven fabrics in place of the woven fabrics structurally in the spinning industry and by applying a method of producing microporous sponge or a wet process wherein film is formed in a liquid medium in place of a dry process in the technical field of working and processing. This so-called "synthetic leather" is competing with the natural leather in a certain field and is being used in a larger quantity than the latter in the manufacture of certain goods as it excels the natural leather in some properties and is less expensive than the latter. It seems, however, that any one of the industries is not satisfied by the synthetic leather now on the market, in Japan as well as in foreign countries, because of its unsatisfactory external appearance and characteristics. In particular, in the shoe manufacture, the synthetic leather is so inferior to the natural leather that there is an intense demand for investigations on and opportunities development in appropriate materials and constituents.

In Japan, the shoe makers first demanded a synthetic leather with an external appearance and touch similar to those of the natural leather and this demand was formable to the other industrial fields intended to use the synthetic leather, so that it has been regarded as the first requirement that the synthetic leather resembles to the natural leather in external appearance and texture and, contrarily, workability and other characteristics of the synthetic leather have been considered to be of the secondary. At the present time, however, the demand has been moved from the appearance to the qualities and there is a demand for synthetic leathers which are superior in qualities to the natural one.

The deficiencies remaining on the natural leather are the very problems also on the synthetic leather, upon estimation of the latter. Thus, it needs making clear the advantages and defects of the natural leather for exact estimation of the synthetic leathers. Briefly speaking, the novel synthetic leather should retain desirable properties of the natural leather but be free from undesirable properties of the latter.

Considering the structure of the natural leather, the dermis is the main part constituting the leather which substantially determines its qualities, the epidermis defines the external appearance, and the hypodermis, the so-called hypodermal fatty tissue, makes the characteristic back surface of the finished leather as the hide is stripped off at this part. The dermis is composed of collagen, and the characteristics of the leather attributable to the collagen are as follows:

(1) Collagen fibers, in the dermis, are intertwined with all angles to the surface of the dermis to form a firm network.

(2) The collagen fibers retain pliability even if dried completely to remove therefrom moisture and scarcely break if flexed in any direction.

(3) The collagen fibers adjacent to the papillate surface are extending in parallel to the surface of the leather and are more compact than the internal reticulating tissue and, in addition, elastic fibers spread in the interior, so that they serve for preventing the surface of the leather from cracking and for imparting to the surface of the leather a grain.

(4) Each collagen molecule has a mild linear structure, more particularly a spherical configuration, and some
molecules collect together to form, by degrees, a micelle, a fibril, a visible fiber and finally a tridimensional fiber.

The availability of the leather is not attributable to its individual properties and features but to the excellence of the combination of the individual properties. This is a remarkable feature of the leather which can not be found in the other materials and, moreover, the leather, due to a natural product, has such several specific characteristics that one can not identify. On the other hand, some defects on the leather are regarded as peculiar to the leather, therefore, scientists from the common property of the natural article. Therefore, it is essential for those skilled in the synthetic leather to surely know the advantages and defects of the natural leather, and the following items commonly may be specified as common sense. Among these, the advantages are, connected to the appropriate properties and working ability, for leather material for making shoe and the defects indicate the problems to be noticed upon design of synthetic leathers.

As the advantages may be specified the following points:

(1) The leather has a unique beauty attributable to its grain surface. Commonly the expression “leather-like” has been used, and leather-made ornaments match well both Japanese clothes and European clothes.

(2) The leather possesses great, balanced mechanical strength. The tensile strength and tear strength of the leather are greater than those of the other materials which are generally employed in the same uses as that of the leather, and there is not found any differential in the strength between the longitudinal and lateral directions as found in the other materials.

(3) The leather exhibits a unique tension-elongation curve, so to say, the leather has a greater modulus than the other materials employed in the same uses, and the differential in tensile strength and in elongation between dry state and wet state is not so great as in the other materials in spite of great differentials in the other properties.

(4) The leather is pliable, readily gets to fit and has a small specific gravity. These indicate that the leather has high flexibility in the shape and high adaptability in the working.

(5) The leather has proper moisture-absorbing property and moisture- and air-permeabilities. The development of the function combined with high molecular weight material is an essential property for raw material of products used daily, and in a highly humid environment as in Japan.

(6) The leather has temperature retaining and heat insulating properties. It is evident from its structure that in addition to the above described properties are added, and this makes it excellent heat insulating materials to be used in the winter season.

(7) The leather is capable of being formed into a product with a desired curved surface. This indicates the leather having an excellent workability, and it is said that the harmony in resiliency and creeping property is the characteristic of the component of the leather.

(8) Cutting operation is easy. Though the tissue is compact and layers having different densities are laminated, the fact that the leather possesses such properties may be attributable to the composition of various constituents.

(9) The leather is dyeable with ease. This indicates that the composition in grain surface, is compact and uniform and that the leather may be suitably used as materials for leather ornaments and wearers.

As the defects may be specified the following points:

(1) The leather is different in properties according to the race of animal and the area living the animal, and even in the same race of animal the properties of the leather are different depending upon the sex, age, feed, season and other factors, and in one piece of leather the properties differ according to portions.

(2) The leather is different in size and thickness from piece to piece, so that it has been handled manually and it is of difficulty to handle the leather by machines.

(3) The leather is, as mentioned above, restricted in size and shape combining having the same size, so that it is of difficulty to cut a patch with a desired shape from a piece of leather, and this influences highly upon the cost.

(4) For this reason the leather is not inexpensive and, in addition, the leather is not manufactured as an industrial material for the main object but it is byproduct of the meat, so that an amount of the leather supplied is influenced by the weather and the demand condition of meats and the price is varied.

(5) In conversion of hides to leathers there is needed both a long period of time and a complicated tanning technique, and the production control and quality control in the tanning industry is of difficulty because the fundamental investigation on the proteins in the raw hide and on the functions and actions in the tanning process has not yet been accomplished.

(6) It is a difficult matter to stabilize the leather against deterioration and remain damage under a high humid condition as in Japan because the leather is a natural product and is composed essentially of proteins. These defects are essential to the leather that is a natural product. Accordingly, it is supposed to be a task for one who intends to make synthetic leathers to eliminate such defects as found in the natural leather, to improve such advantages as in the natural leather without any depression in the other properties and, thereby, to improve the combined properties.

An object of the present invention is to provide a synthetic leather which retains the advantages of the natural leather and is improved fully in the defects of the latter and the method of preparing such synthetic leather.

Briefly speaking, the synthetic leather of the present invention may be obtained by forming a web or fibrous mat with a mix-spin fiber comprising at least two high molecular weight materials, incorporating the web with a solution of one or more high molecular weight materials, coating the impregnating substance in a wet or dry process and, thereafter extracting and removing at least one high molecular weight material which constitutes the mix-spin fiber by treating said web in a solution for at least one of the high molecular weight materials constituting the fiber.

The mix-spin fiber may be obtained by a wet, dry or melt spinning of a mixture of two or more high molecular weight materials, although the melt spinning process is preferable. Preferably the filament is stretched after spun.

Examples of the high molecular weight materials used are polyolefins, such as polyethylene and polypropylene; atactic and isotactic polystyrenes, alkyl or halogen substituted polystyrenes; polyamides, such as 6-nylon and 66-nylon; polyesters, such as polyethylene terephthalate; polyethylenes such as polyethylene terephthalate; polyvinyl esters such as polyvinyl acetate and polyvinyl butyrate; polyvinyl alcohol and its derivatives; polyvinyl halides such as polyvinyl chloride; polyacrylnitrile; polyvinylidene halides such as polyvinylidene chloride; cocomposites of copolymers comprising various low molecular weight condensates or polymerized materials and graft high molecular weight materials as obtained by graft polymerization of various polymerizable low molecular weight substances with the various homopolymers or cocomposites or copolymers thereof. Of course, when selecting two or more high molecular weight materials, they must be able to mix-spin. The term “be able to mix-spin” means that it is required to hold the fibrous form when spun, but does not always mean that the resulting filament must have a uniform internal structure. It is preferable that the mix ratio of these mix-spin fiber is 20% or more of one high molecular weight material with respect to the other material. The high molecular weight
material to be removed and extracted in the mix-spun fiber preferably is swollen with or dissolved in the solvent in the solution of the high molecular weight material to be impregnated in the mat and, in this case, there is obtainable a satisfactorily compact synthetic leather due to a press effect during the cochanging step. Then a web or fibrous mat in a wet or dry process from the resulting mix-spun fiber. The web or fibrous mat thus formed is too coarse and when desiring to obtain a final product with a high strength, the web or fibrous mat may be tightened in a suitable manner. This process preferably is carried out a web sliver. The fiber is cut into a staple, which is formed into a random web by means of a random webber. The random web is then tightened and three dimensionalized by means of a needle punch. When the tightening is insufficient, the web is further tightened by compression. It is preferable to heat the web during the compression. The tightening also may be effected by application of shrink to the fibers. The demand to obtain a final product with a high strength may be attained by stretching the sheet material without allowing any shrinkage.

The present invention has a distinctive feature in the process of manufacture of dimensionalized non-woven fabric. In the manufacturer of a good synthetic leather from a three-dimensionalized non-woven fabric, it is a fundamental condition that the mat is pliant and supple. To obtain a pliant and supple mat, it is preferred to use a fiber with a fine denier less than 1 denier, preferably less than 0.5 denier. It is, however, difficult to form a random web by passing such fine fiber through a card sliver and to form a three-dimensionalized non-woven fabric therefrom by means of a needle punch because of a poor spinnability of such fine fibers.

Contrary to these facts, in the present invention there may be used a spinnable fine fiber of from 1.5 to 3.0 denier to form a mat. A thick fiber with a denier as large as from 1.5 to 3.0 denier is far superior in spinnability to a fine fiber with a denier as small as 0.5 denier or less. A mat which has been made from a large fiber with a denier of as large as from 1.5 to 3.0 denier is in general not pliant, but at least one high molecular weight material within the fiber is extruded and removed in a subsequent extraction process, whereby it is possible to obtain a mat having the same pliability that as of that made from a fine fiber with a denier of about 0.5 denier.

In the present invention a fibrous material made from a mix-spun fiber composed of two components, one being soluble and another being insoluble in the subsequent step. This brings about an additional advantage. To say, when manufacturing a mat from a fiber obtained alone one high molecular weight material, if the fiber is poor in spinnability, so that it is difficult to manufacture a mat, to said high molecular weight material and the mixture is spun to obtain a mix-spun fiber having a good spinnability, from which a mat is manufactured. For instance, a fiber formed of a 6-nylon alone has a poor spinnability due to its low Young's modulus and to its unsuitable dry-to-wet ratio in Young's modulus. As mentioned above 6-nylon fiber having a fiber denier as small as 0.5 denier is very difficult in the spinnability. On the contrary, a mix-spun fiber formed of a mixture of 6-nylon and a polyethylene having an improved Young's modulus and wet-to-dry ratio in Young's modulus as shown in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Mix ratio</th>
<th>Polyethylene</th>
<th>0 0 10 20 30 40 50 60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's modulus</td>
<td>Dry (g/cm³)</td>
<td>8 16 24 32 40 48 56 64</td>
</tr>
<tr>
<td>Wet (g/cm³)</td>
<td>10 20 30 40 50 60 70 80</td>
<td></td>
</tr>
</tbody>
</table>

As shown from the above table, the mix-spun fiber comprising 6-nylon and polyethylene is improved clearly in Young's modulus and the wet-to-dry ratio is also improved highly. Thus, the use of the mix-spun fiber with a fineness of 1.5-3.0 denier in place of a fiber with a fine density of about 0.5 denier makes possible to form a three-dimensional non-woven fabric without any difficulty, by employing conventional equipments and under conventional processing conditions, because of a remarkable improvement in spinnability and of an improved separability from carding step.

The web or sheet material so formed in the above steps is impregnated with a solution of a high molecular weight material. The high molecular weight material includes: (1) one or more high molecular weight material having rubber-like elasticity and (2) mixtures of one or more high molecular weight material having rubber-like elasticity with one or more high molecular weight material having no rubber-like elasticity. The solution need not be a true solution, but may be an emulsion as far as it is possible to impregnate the web therewith. To the solution there may be added salts, dyes, pigments, fillers, various surface active agents and other additives.

As those materials are used any of such ones which are insoluble in the solvent to be used in extraction of an extractable high molecular weight material in the mix-spun fiber. Examples are polyurethane-type elastic high molecular weight materials, acrylics, synthetic rubbers, copolymerized polyethylene and polyolefin derivatives, internally plasticized high molecular weight materials and other elastic high molecular weight materials having a rubbery elasticity.

As the high molecular weight material having no rubbery elasticity, use may be made of various polymerized material, i.e., condensated high molecular weight materials such as polyvinyl chloride, polyacrylonitrile, polystyrene, polyvinyl alcohol or acetalized product thereof, polyvinyl acetal, polyamides, modified polyamides, polypropylene, polylethylene, polyurethanes, polyeureas, polysters, poly-carbonates or cocondensated or copolymerized materials thereof, or graft polymerized high molecular weight materials.

After impregnation of the web with the high molecular weight material, the impregnated material is coagulated in a wet and/or dry process. It is preferred to press or hot press the impregnated sheet material either before, during or after the coagulating process.

The sheet material is then treated with a solvent to extract therefrom at least one of the high molecular weight materials which are components of the mix-spun fiber forming the sheet material. It is preferable to remove, during or after the coagulating step, a part of the impregnated high molecular weight materials capable of extracting and removing and a portion of a coating film which has been applied to a grain surface as hereafter described.

The solvent to be used in the invention for extraction of at least one of the high molecular weight materials which constitute the mix-spun fiber should be solvent for at least one high molecular weight material (soluble component) but non-solvent for the remainder (insoluble component) of the high molecular weight materials forming the mix-spun fiber. Although the solvent suitably used in the extraction varies with the nature of the mix-spun fiber as a raw material of the artificial leather of the invention, there may be used water, organic solvents, such as aromatic compounds, cyclic ethers, aliphatic hydrocarbons, ketones, cyclic ketones and the like; various salt solutions, such as methanol solutions of calcium chloride, titanium tetrachloride, lithium chloride and the like; and mixtures thereof.

The synthetic leather of the invention thus obtained is composed of a layer of fiber which retains a complete fibrous structure as in the natural leather, and the synthetic leather of the present invention is similar in external appearance, texture, touch and other characteristics to the natural leather. The synthetic leather of the present invention accomplishes to the problems for synthetic leathers as fully described at the head of this specification.
The fact that the synthetic leather of the invention is comparable with or surpasses the natural leather in all aspects is based on the integral structure and the characteristics of the structure will be mentioned hereinafter.

As causes for this result may be stated: that the fiber itself is made more pliant by the micro-pores therein formed and that the soluble component of the fiber exposed to the surface of the fiber is extracted to form a number of spaces between the impregnated materials and the fiber and whereby the fiber separates the high molecular weight materials having rubbing elasticity to become movable each other. The micro-pores and spaces result in essential improvements in air permeability, moisture permeability and air-retaining property and in the natural leather-like texture.

A large number of micro-pores of the shaped article of the invention is not only based on spaces formed between the fibers each other composed of the shaped article, but also on hollows of the fiber itself composed of the shaped article. Porosity of the fiber depends upon the proportions of two or more high molecular weight materials in the initial fiber to be used in making the shaped article. This will be illustrated by the following example.

Chips prepared by blending a 6-nylon and a polystyrene at various mix ratio are extruded through a nozzle having 100 holes each of 0.2 mm. diameter to form fibers having different mix ratios, which are stretched 300% at 175°C and then 50% at 200°C (the total stretch ratio of 500%). The stretched fibers are extracted with benzene at 65°C to remove therefrom polystyrene. The properties of the porous fibers are as follows:

<table>
<thead>
<tr>
<th>Mixture ratio of polystyrene (percent)</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Fineness (d.))</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>2.1</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>(Strength (g.d./d.))</td>
<td>2.8</td>
<td>2.6</td>
<td>2.4</td>
<td>2.2</td>
<td>2.0</td>
<td>1.8</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>(Elongation (percent))</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>(Porosity (percent))</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

Note.—A—Cross-sectional area of the fiber after extractions of polystyrene; B—Cross-sectional area of the fiber before extractions of polystyrene.

(in the above table, the porosity indicates value obtained by dividing the deniers of the fiber after extraction of polystyrene by the deniers of the fiber composed of insoluble components only having the same sectional area as that of the former.)

As evident from the above table, the fiber, which constitutes the shaped product of the present invention, has a porosity of up to about 70%.

Furthermore, the remarkable pliability is the characteristic of the synthetic leather of the invention.

Generally speaking, in order to form a pliable mat it is desirable to use a fiber having a fine denier because a mat which has been formed of a fiber having a large fineness results in losing the pliability of the fiber, however, has a defect of having a poor spinnability. On the other hand, in the invention there may be used fiber having a relatively large fineness with a good spinnability in the step of forming the mat and there may be obtained by using such a fiber a synthetic leather having the same pliability of one obtained by using a fiber having a small fineness, because of depression in Young's modulus caused by extraction and removal of at least one high molecular weight material which constitutes the fiber.

And, by buffing the back surface of the obtained synthetic leather the fiber is fibrilized at the buffed part to a very fine denier, and this imparts to the synthetic leather an excellent leather-like texture.

The method of preparing synthetic leathers according to the invention will be further illustrated by the following example which is illustrative rather than limitative of the invention.

A chip consisting of a blend of 40 parts of a 6-nylon and 60 parts of a polystyrene is extruded by means of a screw-type extruder through a spinneret with 300 holes each of 0.2 mm. in diameter at spinning temperature of 300°C into a draughting zone cooled to a temperature of 120°C by air blast and is wound up at a rate of 400 m/min. The mixed fiber thus spun is formed crimps of 24/in. and cut to a length of 3 cm. and then formed into a three-dimensional web of 330 g/m.² by means of a random webber and a needle puncher. The web is lightly compressed by means of hot rollers at 100°C. The so formed web is immersed in a 13% solution in dimethylformamide of a polyurethane type elastic high molecular weight material obtained by reaction of polyol of adipic acid and ethylene glycol and diphenylmethane disiocyanate and glycol and coagulated in water and then dried, and treated with toluene to extract the remaining solvent and polystyrene in the fiber. The web thus treated is improved remarkably in pliability and texture as compared with the web prior to the extraction and has fundamental characteristics as leathers, such as air-retaining property, air-permeability, moisture-permeability and others. As causes for these results may be stated: that the fiber itself is made more pliant by including continuous and random micro-pores therein as a result of extraction of the polystyrene, that in the surface of the fiber the part removed polystyrene is indented and space is formed between the impregnated high molecular weight material and the fiber to become movable readily each other, and that air-permeability, moisture-permeability and air-re-

The high molecular weight material suitably used as coating material includes: (1) one or more high molecular weight materials having rubber elasticity, and (2) mixtures of one or more high molecular weight materials having rubber elasticity and one or more high molecular weight materials having rubber elasticity.
weight materials having no rubbery elasticity. The term "high molecular weight material having rubbery elasticity" and "high molecular weight material having no rubbery elasticity" have the same meanings as mentioned hereinbefore and, as also mentioned above, the "solution" of high molecular weight material means not only "true solution" but also "emulsion".

To the solution there may be added salts, dyes, pigments, fillers, various surface active agents and other additives.

For spontaneous removal and extraction of portion of the high molecular weight material in the impregnating material and of portion of the high molecular weight material in the grain surface with removal of at least the high molecular weight material in the fiber, it is preferable that these three high molecular weight materials are of the same. This, however, is not of necessity.

The removal of portion of the high molecular weight material in the impregnating material and of portion of the high molecular weight material coated as grain surface accompanying to the removal of a high molecular weight material in the fiber imparts to the resulting synthetic leather more improved characteristics, such as satisfactory pliability and air- and moisture-permeability. To provide a grain surface, another preferred embodiment of the invention is as follows. A proper amount of a high molecular weight material is applied to the surface of the web or the sheet material in any stage of preparation of the synthetic leather and is thereafter coagulated in a dry or wet process; specified examples of the modified processes are as follows:

(1) A web of mix-spin fiber is impregnated with a solution of high molecular weight material and the impregnating material is partly or entirely, coagulated in dry and/or wet processes, thereafter a solution of high molecular weight material is applied thereto by coating or spraying to form a grain surface and is then coagulated in dry and/or wet processes. Then the web is soaked in a solvent for at least one high molecular weight material in the mix-spin fiber to extract therefrom the said high molecular weight material, and washed and dried.

(2) A web of mix-spin fiber is impregnated with a solution of high molecular weight material and, thereafter, a solution of high molecular weight material is applied thereto by coating or spraying to form a grain surface.

Then the both high molecular weight materials are coagulated in wet processes. At least one high molecular weight material in the mix-spin fiber is extracted therefrom and the so treated web is washed and dried.

(3) A web of mix-spin fiber is impregnated with a solution of high molecular weight material and the high molecular weight material is coagulated in a wet process. The web is then washed and dried and, thereafter, a solution of high molecular weight material is applied thereto by coating or spraying to form a grain surface.

Then at least one high molecular weight material in the mix-spin fiber is extracted therefrom and the so treated web is washed and dried.

Even if a solution of high molecular weight material is applied relatively thick on formation of the grain surface by coating or spraying of the high molecular weight material, the resulting synthetic leather has satisfactory air- and moisture-permeability, such properties being important characteristics of leathers, because portion of the applied high molecular weight material is removed by extraction in a subsequent step of the process, and the removal of portion of the high molecular weight material results in formation of a moderate indention which makes the resulting synthetic leather very similar in external appearance to the natural leather.

The grain surface may also be obtained by forming a web with a mix-spin fiber made from a blend of high molecular weight material having rubbery elasticity and a high molecular weight material having no rubbery elasticity, laminating the said web on a synthetic leather of the invention as already mentioned above and, thereafter, completely or almost completely dissolving said high molecular weight materials in said web and, thereby, bonding said web to said synthetic leather.

In the manufacture of the synthetic leather of the invention, there may be added, if desired, a step of partially dissolving the unextractable high molecular weight materials in the mix-spin fiber to adhere the fibers to other fibers.

Furthermore, the mix-spin fiber of a raw material for the synthetic leather of the invention may be used in admixture with a proportion of various fibers comprising monopolymer or natural fibers. In the manufacture of the synthetic leather or like shaped articles of the invention, a woven fabric composed of a synthetic fiber consisting of monopolymer, or natural fiber may be used as a core layer or substratum.

According to the invention, the two steps of "coagulation" and of "extraction" may be conducted simultaneously.

The present invention will be illustrated by the following examples which are by no means limitative.

EXAMPLE 1

A stretched and cramped nylon-polystyrene 40:60 mix-spin filament of 2 denier was cut into a staple fiber of 5.0 cm. length and the staple fiber was formed by random webbing and subsequent needle punching into a non-woven mat of a weight of 220 g./m². The non-woven mat thus formed was immersed in an impregnating solution prepared by adding 0.4% of cellulose octadecylurethane as softener to a 8% solution in dimethylformamide of a polyurethane ester obtained by reaction of a polyethylene propylene adipate of a molecular weight of 1,500 (mole ratio of ethylene glycol units to propylene glycol units of 0.7:0.3), p,p'-diphenylmethane dianisoyl and ethylene glycol in the mole ratio of 1:2.5:1.5, and then squeezed by means of doctor blades at each side of the mat to adjust the amount of the solution taken up by the mat to about eight times the weight of the mat. A 10% solution of said polyurethane in dimethylformamide, in the amount of four times the weight of the fibrous mat, was coated to surface of the so impregnated mat. The mat was then immersed in a 30% aqueous solution of dimethylformamide at 30°C. for a period of 15 minutes and squeezed while coagulating the impregnating and coated materials, and then washed with water for a short period of time, after which it was passed through hot press rollers and then extracted and removed at least 95% of polystyrene in the nylon-polystyrene mix-spin fiber by toulene at 70°C.

The sheet material thus obtained was extremely pliant due to poor adhesion between nylon fibers and polyurethane ester and presence of random micro-ports which had been formed in the nylon fibers as a result of extraction of polystyrene, and possessed a smooth texture. The grain surface of the sheet material was extremely rough due to presence of fibers and was fine-grained and pliant, and possessed a texture similar to that of natural leather, especially those for wear uses. The properties of the sheet material were similar to those of sheep skin as shown in the following table.

<table>
<thead>
<tr>
<th>Weight (g./m²)</th>
<th>213</th>
<th>299</th>
<th>218</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microscope (mm)</td>
<td>0.68</td>
<td>0.33</td>
<td>0.44</td>
</tr>
<tr>
<td>Apparent specific gravity (g/cm³)</td>
<td>0.45</td>
<td>0.51</td>
<td>0.34</td>
</tr>
<tr>
<td>Tensile strength (kg. /cm²)</td>
<td>7.50</td>
<td>8.80</td>
<td>8.00</td>
</tr>
<tr>
<td>Elongation (per cent)</td>
<td>110%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Surface area (m²)</td>
<td>110</td>
<td>120</td>
<td>110</td>
</tr>
<tr>
<td>Total weight (g.)</td>
<td>1,900</td>
<td>1,900</td>
<td>1,900</td>
</tr>
<tr>
<td>Air permeability (m³)</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Moisture permeability (g/cm²/day)</td>
<td>8,400</td>
<td>8,200</td>
<td>7,300</td>
</tr>
</tbody>
</table>

1Longitudinal/latitudinal.
EXAMPLE 2
A non-woven mat of a weight of 330 g./m.², composed of a nylon-polystyrene 40:60 mix-spin fiber of 5.0 cm. length and of 3.0 denier, was impregnated in a immersing liquid prepared by adding to a 13% solution of a polyurethane elastomer as in Example 1 in dimethylformamide 2.5% of sorbitin monostearate and 3% of each carbon black and titanium dioxide, and squeezed at both sides by means of doctor blades to adjust the amount of the liquid impregnated to from ten to eleven times the weight of the fibrous mat. A 20% solution of a polyurethane elastomer in dimethylformamide, in the amount 2.5 times the weight of the fibrous mat, was coated to the surface of the so impregnated mat. The mat was then immersed in a 30% aqueous solution of dimethylformamide for 20 minutes to coagulate and, thereafter, extracted impregnate in the fiber by toluene at 65-70°C. The sheet material thus obtained was of an apparent specific gravity of 0.5-0.6 and possessed a compact texture. In addition, the sheet material possessed a moderate pliability due to poor adhesion between resin and fibers and presence in fibers of random micro-pores resulting from the extraction, and exhibited a texture similar to that of the natural leather for shoe upper use. The properties of the sheet material were as shown in the following table.

<table>
<thead>
<tr>
<th>Weight (g/m²)</th>
<th>Thickness (mm.)</th>
<th>Specific gravity (g/cm³)</th>
<th>Tensile strength (g/cm²)</th>
<th>Elongation (percent)</th>
<th>Remaining strain (5% strain) (percent)</th>
<th>Tear strength (g/cm²)</th>
<th>Rigidity resistance (48 hours) (percent)</th>
<th>Air permeability (ml/m²/24 hours)</th>
<th>Moisture permeability (g/m²/24 hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>890</td>
<td>0.63</td>
<td>0.61</td>
<td>1.88</td>
<td>2.0</td>
<td>2.0</td>
<td>11.9</td>
<td>6.5</td>
<td>90</td>
<td>1,280</td>
</tr>
</tbody>
</table>

1 Longitudinal X-tal.
2 More than 5.000.
3 More than 3 hours.

The sheet materials as shown in the above examples may be dyed, or applied a smooth surface by known method such as dyeing, spraying, coating or laminating a solution or emulsion of a high molecular weight material or embossing or otherwise finishing.

EXAMPLE 3
A blend of 50 parts of a 6-nitro and 50 parts of a polystyrene was melt spun by means of extruder into filaments and stretched by 6 times to obtain a mix-spin fiber of 1.5 denier, which was wound and crimped to 18/in., cut into 50 mm. length and, thereafter, passed through a random webber and a needle loom to form a web with a three-dimensional network structure. The web was impregnated with a 6% solution of a polyurethane prepared by reacting a polyester derived from adipic acid and ethylene glycol with diethylene glycol disuccinate to form a prepolymer and subsequently reacting the prepolymer with a diol, and was then immersed in water to coagulate the polyurethane. After dried, the shaped article thus formed was immersed in toluene at 90°C. For one hour to extract polystyrene, then washed with methanol and dried. The finished shaped article of the invention was a pliable leather-like product with a high elasticity.

EXAMPLE 4
Single surface of the pliable shaped article, as obtained in Example 3, was burned and the shaped article was then hot pressed. There 7% solution of a polyurethane type high molecular weight material as used in Example 1 in dimethylformamide was applied by spraying to the burnt surface of the shaped article to form a very thin coating film. Thus, there was obtained a synthetic leather just like natural leather.

EXAMPLE 5
A blend of 50 parts of polyethylene terephthalate and 50 parts of polystyrene was melt spun by means of an extruder into filaments, and hot drawn by 5 times to obtain a 2 denier filament. The filament was formed into a web with a three-dimensional network structure by the same manner as in Example 3. The web was impregnated with a 6% solution obtained by dissolving a mixture of 60 parts of a polyurethane-type high molecular weight material as in Example 1 and 40 parts of a polyethylene terephthalate in dimethylformamide and, thereafter, a 5% solution obtained by dissolving a mixture of 40 parts of a polyurethane type high molecular weight material, 30 parts of a polyvinyl chloride and 30 parts of polystyrene in dimethylformamide was again sprayed to grain surface of the impregnated web. The web was then coagulated by water and treated in toluene at 80°C to completely extract polystyrene in the resulting shaped article which was then washed with methanol and dried.

EXAMPLE 6
A mix-spin filament formed of a blend of 50 parts of a polyacrylonitrile and 50 parts of a polyvinyl alcohol (1.5 denier) was formed crimps of 18/in. and cut into a staple fiber of 25 mm. length, from which a web of 200 g./m.² was obtained by means of a random webber and a needle puncher. The web was, after hot pressed by means of hot rollers, impregnated with a 6% solution of a polystyrene in toluene and squeezed by means of rubber rollers to adjust the amount of the solution taken up by the web to 600% by weight of the web. The solution was, thereafter, sprayed again to the surface and the web was coagulated, while squeezing, in water at 40°C and then extracted with alcohol by standing the web in water at 90°C and, subsequently washed sufficiently with water and methanol. The synthetic leather of the invention thus obtained was similar in external appearance, texture and other properties to those of natural leather.

EXAMPLE 7
A mix-spin filament (1.5 denier) formed of a blend of 50 parts of a polystyrene and 50 parts of a polyethylene terephthalate was formed crimps of 20/in., and cut into 3 cm. length. The staple fibers thus obtained was formed, in the same manner as in Example 6, into a three-dimensioned random web with a weight of 250 g./m.². The web was impregnated with a 6% solution in dimethylformamide-acetone (1:1) of a polyurethane type high molecular weight material prepared by reacting a polyethylene diamine with diphenylmethane disuccinate to form a prepolymer and reacting the prepolymer with a diol and, thereafter, the web was squeezed by means of rubber rollers so as to adjust the amount of the solution taken up by the web to 600% by weight of the web. The solution was 5% applied again to the surface of the web and the web was, after stood still for a short period of time, coagulated by 30% aqueous dimethylformamide solution, while squeezing. The shaped article thus formed was immersed in toluene at 80°C for 60 minutes to effect complete extraction of polystyrene in the mix-spin
fiber, and then washed and dried. The artificial leather thus obtained possessed the same external appearance, texture and other properties as that of natural leathers.

**EXAMPLE 8**

A mix-spin filament composed of a blend of 40 parts of a 6-nylon and 60 parts of a polyvinyl alcohol was stretched by 6 times at 200° C. to obtain a fiber of 1.5 denier. The filament was formed crimps of 18/in., and cut into 50 mm. length and, thereafter, passed through a random webber and a needle loom to form a web with a three-dimensional net-work structure. The web was impregnated with a 6% solution in dimethylformamide of a polyurethane prepared by reacting polyester obtained from ethylene glycol and adipic acid with a diphenylmethane disiocyanate and a diol and then immersed in water so as to effect coagulation of polyurethane and at the same time extraction of polyvinyl alcohol contained in the mix-spin fiber and was, thereafter, washed again with water and dried. The shaped article of the invention thus obtained was an extremely pliant leather-like product with a high elasticity.

**EXAMPLE 9**

A mix-spin filament of 2 denier obtained by melt spinning a blend of 45 parts of a polyester derived from terephthalic acid and ethylene glycol and 55 parts of a poly- 

styrene by an extruder and hot drawing by 5 times. The fiber was formed into a web with a three-dimen-

sional network structure in a manner as in Example 8 and the web was impregnated with a 6% solution of a blend of 60 parts of a polyurethane type high molecular weight material as in Example 1 and 40 parts of a poly-

styrene in dimethylformamide. Then a 5% solution of a blend of 40 parts of a polyurethane type high molecular weight material, 30 parts of a polyvinyl chloride and 30 parts of poly styrene in dimethylformamide was sprayed to the grain surface and, thereafter, the web was treated in cyclohexane at 50° C. to remove completely poly-

styrene and coagulate polyurethane in the shaped article and then was washed with methanol and dried.

What we claim is:

1. A method for the manufacture of pliant, supple, air-

and moisture-permeable sheet material, comprising:

(a) impregnating a fibrous substrate with a solution of high molecular weight material selected from the group consisting of:

(i) at least one polymeric substance having rubber-like elasticity, and

(ii) a mixture of at least one polymeric substance having rubber-like elasticity with at least one polymeric substance not having rubber-like elasticity,

said fibrous substrate being comprised of mix-spin fibers shaped from polymers comprising at least two high molecular weight materials selected from the group consisting of polyamide, linear condensation polyester, polyetheramide, polyvinyl ester, poly-

vinyl alcohol, derivatives of polyvinyl alcohol, poly-

olefin, atactic and isotactic polystyrene, alkyl-sub-

stituted polystyrene, halogen-substituted polystyrene, polynyl halide, polycrionitrile, and polynyl-

idene halide;

(b) coagulating the impregnant;

(c) hence extracting at least one of the polymers contained in the mix-spin fibers for means of a solvent therefor which is a non-solvent for at least one other polymer in the said mix-spin fibers; and

(d) there being initially present in the said mix-spin fibers from about 10 percent to about 60 percent by weight of the polymeric material extracted according to step (c).

2. The method as defined by claim 1, wherein the high molecular weight material (i) is at least one member selected from the group consisting of elastomeric seg-

mented polyurethane, polyacrylate, synthetic rubber, chlorinated polylefin and chlorinated polyethylene, and further wherein the high molecular weight material (ii) is a mixture of the above high molecular weight material (i) with at least one member selected from the group consisting of polyvinyl chloride, polycrionitrile, polystyrene, polyvinyl alcohol, acetylated polyvinyl alcohol, polyvinyl acetate, polyamide, polypropylene, polylethylene, nonelastic polyurethane, polyyurea, linear condensation polyester and polycarbonate.

3. The method as defined by claim 2, further comprising providing a grain surface characteristic of leather on the sheet material by applying thereto a coating of a high molecular weight material selected from the group consisting of:

(i) at least one polymeric substance having rubber- like elasticity, and

(ii) a mixture of at least one polymeric substance having rubber-like elasticity with at least one poly-

meric substance not having rubber-like elasticity.

4. The method as defined by claim 2, wherein the mix-

spin fibers are bi-component.

5. The method as defined by claim 2, wherein the coagu-

lation and extraction are effected simultaneously.

6. The method as defined by claim 2, wherein the im-

pregnant is itself extracted to some extent by the solvent employed in step (c).

7. The method as defined by claim 2, wherein the solu-

vent of step (c) is selected from the group consisting of:

water, an aromatic hydrocarbon, a cyclic ether, an all-

phatic hydrocarbon, an aliphatic ketone, a cyclic ketone, and a methanol solution of calcium chloride, titanium tetrachloride and lithium chloride, and mixtures thereof.

8. The method as defined by claim 2, wherein the solution of step (a) is a true solution.

9. The method as defined by claim 2, wherein the solu-

tion of step (a) is an emulsion.

10. The method as defined by claim 2, wherein the fibrous substrate is a non-woven batt.

11. The method as defined by claim 2, wherein the fibrous substrate has been mechanically compressed.

12. The method as defined by claim 2, wherein the mix-

spin fibers of the fibrous substrate have been shrunk.

13. The method as defined by claim 2, wherein the fibrous substrate is formed from mix-spin fibers obtained by mixed spinning of at least two polymers.

14. The method as defined by claim 2, wherein the im-

pregnated sheet material is pressed prior to coagulation.

15. The method as defined by claim 2, wherein the im-

pregnated sheet material is pressed during coagulation.

16. The method as defined by claim 2, wherein the im-

pregnated sheet material is pressed subsequent to coagulation.

17. The method as defined by claim 3, wherein the high molecular weight material (i) is at least one member selected from the group consisting of elastomeric seg-

mented polyurethane, polyacrylate, synthetic rubber, chlorinated polylefin and chlorinated polyethylene, and further wherein the high molecular weight material (ii) is a mixture of the above high molecular weight material (i) with at least one member selected from the group consisting of polyvinyl chloride, polycrionitrile, polystyrene, polyvinyl alcohol, acetylated polyvinyl alcohol, polyvinyl acetate, polyamide, polypropylene, polylethylene, nonelastic polyurethane, polyyurea, linear condensation polyester and polycarbonate.

18. The method as defined by claim 3, wherein the high molecular weight material used for the coating is of the same type used as the impregnant.

19. The method as defined by claim 3, wherein the im-

pregnant and the surface coating are themselves extracted to some extent by the solvent employed in step (c).

20. The method as defined by claim 4, wherein the mix-

spin fibers are composed of poly-(e-caprolactam) and polystyrene.
21. The method as defined by claim 4 wherein the denier of the mix-spun fibers ranges from between about 1.5 and 3.0, and further wherein such fibers are composed of poly(ε-caprolactam) and polystyrene.

22. The method as defined by claim 11, wherein the fibrous substrate has been heated during compression.

23. The method as defined by claim 17, wherein the grain surface is provided by applying to a surface of the sheet material, subsequent to the extraction step (c), a solution of the high molecular weight material and thence coagulating such coating.

24. The method as defined by claim 17, wherein the grain surface is provided by applying to a surface of the sheet material, prior to the extraction step (c), a solution of the high molecular weight material and thence coagulating such coating.

25. The method as defined by claim 17, wherein the grain surface is provided by applying to a surface of the sheet material, prior to coagulation step (b), a solution of the high molecular weight material and thence simultaneously coagulating such coating and the impregnant.

26. The method as defined by claim 19, wherein the three high molecular weight materials are the same.

27. The method as defined by claim 21, wherein the impregnation of step (a) is with a solution of an elastomeric segmented polyurethane in dimethylformamide.

28. The method as defined by claim 27, wherein the polystyrene is extracted according to step (c) with toluene.

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WILLIAM D. MARTIN, Primary Examiner.
THEODORE G. DAVIS, Assistant Examiner.
U.S. Cl. X.R.

117—63, 135.5, 138.8, 140