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IMPREGNATED FIBROUS MATERIALS AND PROCESS OF MAKING THE SAME

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ABSTRACT OF THE DISCLOSURE

An impregnated fibrous material particularly suitable for use as a synthetic leather which is comprised of a compressively shrunk nonwoven web of textile length synthetic fibers impregnated with an elastomeric binder. The web is preferably needled.

This application is a continuation of Ser. No. 451,342 filed Apr. 27, 1965 and now abandoned.

This invention relates to a synthetic leather or coating base material characterized by a leather-like feel, resilience, and texture.

A number of substitutes for leather have come into general use. Such materials include plastic films, coated fabrics, and coated or uncoated papers. Such materials are usually stronger, more abrasion resistant, more waterproof, and more resistant to flexing than leather and are also generally more uniform in properties. Synthetic leathers are utilized for shoe uppers, leather coats, gaskets, gloves, slippers, luggage, brief cases, camera cases, handbags, and the like.

It has now been found that a novel synthetic leather structure characterized by improved flexibility, internal bonding strength, resilience, and reduced piping can be prepared which comprises an extensibilized, preferably a biaxially-extensibilized, nonwoven web of snythetic fibers which has been impregnated with a polymeric binder material.

Extensibilizing or compressive shrinking of webs is known to the art. U.S. Pats. Nos. 2,624,245; 3,122,469; and 3,055,496 are directed to cellulosic webs which have been compressively shrunk and to apparatus for accomplishing the shrinkage. It has now been found that a superior product can be prepared by compressively shrinking a nonwoven web of textile length snythetic fibers.

The compressive shrinking of the web is carried out prior to impregnation, after impregnation but while there is still moisture in the fiber, e.g., about 20 to 30%), or on the dried, impregnated web. Preferably, the compressive shrinking is accomplished after the impregnation of the nonwoven web while the web has a moisture content of about 25%. However, improvements in flexibility, piping, and delamination resistance over comparable impregnated webs which have not been compressively shrunk are noted regardless of when the compressive shinking is accomplished.

Fibers suitable for use in the present invention are synthetic fibers. As examples of such synthetic fibers, mention may be made of polyamide (nylon), acrylic, rayon, polyethylene, polypropylene, cellulose acetate, cellulose triacetate, polyvinyl alcohol, polyester (Dacron), saran (vinyidene chloride polymer), vinyl chloride/acrylonitrile copolymer (Dynel), acrylonitrile (Orlon), polytetrafluoroethylene, and modacrylic fibers. The fibers are ¼ to 3 inches in length, preferably ½ to 1½ inches. The

denier ranges from 0.5 to 15 denier per filament, preferably 1 to 6.

The nonwoven web may be prepared by methods known to the art, for example, by air laying equipment or by normal paper-making equipment such as Rotoformer or Fourdrinier machines. The nonwoven webs are employed in the form they come off the web-making equipment, or alternatively, they are pressed to increase the density. The weight of the nonwoven webs ranges from 1 to 20 ounces per square yard, preferably 6 to 10 ounces per square yard. If drying of the webs is desired, conventional methods are employed.

After the formation of the nonwoven web, it is preferably needled with barbed needles in order to lock the fibers together and substantially increase the internal bonding strength of the web. More preferably, the nonwoven web is needled on both sides. The degree of needling is determined by the internal bonding strength desired in the web; the greater the degree of needling, the greater the internal bonding of the web. Preferably, about 15 passes on each side of the web is carried out with conventional needling devices. It should be understood that while the needling step is a preferred embodiment, the nonwoven web may be further processed without needling.

The nonwoven webs are provided with additional internal bonding strength by means of polymeric binder materials known to the art. The preferred binders are polymeric elastomers having high adhesion to the fiber, a minimum elongation of 400%, a minimum tensile strength of 50 p.s.i., and a maximum modulus of elasticity of 1000 p.s.i. Particularly preferred binders are carboxylic butadiene-containing copolymers. In a preferred embodiment a small amount, e.g., 5% or less, of a wet strength resin such as phenol formaldehyde or melamine formaldehyde was also employed. The level of impregnation of the polymer on the fiber ranges between 50 and 150% by weight based on the weight of the fiber.

As examples of suitable impregnating binders, mention may be made of natural and synthetic rubbers such as butadiene/styrene, copolymers, butadiene/acrylonitrile copolymers, neoprene, and the like. Other saturants are described in the following United States patents: 2,410,078; 2,416,232; 2,438,195; 2,441,523; 2,692,253; 2,760,884; 2,799,596; 2,848,105; 2,848,344; 2,899,353; 2,905,584; and 2,837,109.

The impregnating compositions may also employ antioxidants, fillers, thickeners, curing agents, and the like. The impregnating materials are employed in both the cured and uncured state. Preferably, the polymeric materials are employed as latices or water dispersions. Solvent solutions and melts may also be used.

The nonwoven web may be impregnated by conventional means. If the web is formed by air laying methods or other dry methods, it may be impregnated in the dry state. If it is formed by wet, paper-making techniques, it may be saturated wet as it comes off the paper-making machine or first dried and then saturated. Preferably, the web is formed by air-laying methods, and the dry web is saturated.

The compressive shrinking is accomplished by compacting and rearranging the fibers through compression of the web between two complementary surfaces. One of the surfaces at the time of contacting the web is an expanded elastic adherent surface and the other is a stable nonadherent surface such as a steel bar or roll. After being gripped between the two surfaces, the elastic surface is caused to contract which results in shrinkage of the web. This shrinkage is best carried out at a web temperature in the range of 210 to 300° F. and under sufficient compression perpendicular to the surfaces of the web to pre-

vent more than a 5 percent increase in the thickness of the impregnated web.

The webs are compressively shrunk in a single direction by one pass through the compressive shrinking machine in one direction, or the webs may be compressively shrunk in two directions, the machine direction (MD) and in the direction perpendicular to the machine direction, i.e., the cross-direction (CD). Shrinkage in two directions is accomplished by passing the web through the apparatus described in U.S. Pat. No. 2,624,245 in one direction, turning the web 90° and again passing it through the apparatus or by a single pass through the device described in U.S. Pat. No. 3,122,469 which compressively shrinks the webs in both the machine and cross-direction at the same time. The disclosures of U.S. Pats. Nos. 2,624,245; 3,055,496; and 3,122,469 are incorporated herein to the extent applicable.

After the nonwoven web has been impregnated and compressively shrunk, it may be employed in that form as synthetic leather. In a preferred embodiment, however, the material is laminated to a fabric, preferably a woven fabric, to provide dimensional stability. The impregnated, compacted material is also preferably coated with a polymeric material to simulate the finish of leather. Preferably, the coating is of a flexible type such as a polyurethane, plasticized polyvinyl chloride, or a carboxylic butadiene-acrylonitrile copolymer to provide a material with a scuff resistance greater than leather, high water resistance, and a moisture vapor permeability of greater than 1000 grams per 100 square meters per hour.

Table 1 illustrates synthetic leather constructions within the scope of the present invention and the properties of such materials. In the following nonlimiting examples, the needled webs were processed on a needle loom manufactured by the James Hunter Machine Company using Torrington needles 15 x 18 x 36 x 3½ CB. Fifteen passes on the needle loom were made on both sides of the web in the following manner:

No. of passes	Advance of web per needle penetration (inches)	Depth of needle penetration (inches)
5	¼	¼
5	¼	⅜
5	3/16	½

In all cases the fibers used were 1 9/16 inches in length and 6 denier/filament. In Examples 1 to 29 the web weight was 5 ounches per square yard and the impregnant was a 67/33 butadiene/acrylonitrile copolymer latex. In Examples 31 to 37 the impregnating composition comprised 98% carboxylicbutadiene-medium nitrile copolymer and 2% phenol formaldehyde resin. In Examples 30, 31, and 32 the web weight prior to impregnation was 9 ounces per square yard. In Examples 33, 34, and 35 the web weight prior to impregnation was 7 ounces per square yard. In Examples 36 and 37 the web weight prior to impregnation was 14 ounces per square yard.

In all the examples impregnation was carried out on the dry web prior to compressive shrinking. The impregnation level is weight percent of impregnant based on the weight of fiber (solids on solids). The thickness is reported on the compressively shrunk material.

In the following table "Semi-dry" refers to an impregnated web which has been dried to a moisture level of about 25%. "Re-wet" refers to an impregnated web which was dried to a level of less than 5% and then rewet to a level of about 25% prior to compressive shrinking. "Dry" refers to impregnated webs which have a moisture content of about 5% or less.

Control samples, i.e., materials which were not subjected to the compressive shrinking operation, are also included for comparative purposes.

Piping is the development of wrinkles in the specimen when it is pressed around a mandrel. The figure reported is the smallest mandrel radius around which the specimen can be bent without wrinkling.

Delamination resistance is the force, expressed in units of ounces per inch of width, required to continue the splitting of the specimen into approximately two equal plies. Two specimens 10 in. x 1 in., two strips of rug binding tape 9 in. in length, are placed so that approximately 0.5 in. of paper extends beyond each end of the tape. The specimens are pressed for 30 seconds at 275° F. and 5 p.s.i. with about 0.5 in. of tape extending beyond the edge of the press. The two free ends of the tape are pulled until the specimen starts to separate into two approximately equal plies. The two free ends of the tape are then placed in the jaws of an Instron Tester, and the machine was run at 10 inches/minute.

Gurley Stiffness is a measure of the force required to bend a specimen through a certain angle. Stiffness was determined on a Gurley R. D. Stiffness Tester.

TABLE I

Ex. No.	Fiber	Needled	Impregnation (percent)	Percent shrink, MD×CD	Compressive shrinking: Semi-dry	Compressive shrinking: Re-wet	Compressive shrinking: Dry	Thickness (mils)	Piping (in.) MD×CD	Gurley Stiffness mgms., MD×CD	Delamination resistance
1	100% dacron	Yes	55	0						555×1,116	
2	do	Yes	55	6×5		X		23	0×0	374×636	
3	do	Yes	55	1×1	X			27	¼×0	449×725	
4	do	Yes	70						¾×¼	935×1,303	
5	do	Yes	80	5×3		X		20	¼×0	447×427	
6	do	Yes	80	11×3	X			27	½×0	466×846	
7	do	Yes	113					38	½×¼	1,057×2,325	
8	do	Yes	112	7×5		X		29	0×0	730×766	
9	do	Yes	130	5×3	X			32	½×0	605×890	
10	do	No	39					41	½×1	1,467×1,378	
11	do	No	62	16×15		X		27	0×0	399×570	
12	do	No	52	15×15	X			30	0×0	534×542	
13	do	No	61					40	½×½	837×1,467	
14	do	No	68	18×25		X		25	0×0	795×534	
15	do	No	57	11×14	X			27	0×0	438×445	
16	do	No	104					50	1×¾	1,673×2,083	
17	do	No	113	40×18		X		22	0×0	570×1,004	
18	do	No	92	13×12	X			30	0×0	539×445	
19	50% dacron; 50% rayon	Yes	79					32	¼×0	534×844	
20	do	Yes	77	16×15		X		19	0×0	285×256	
21	do	Yes	99	20×13	X			21	0×0	338×306	
22	do	Yes	99					28	¼×½	751×648	
23	do	Yes	109	23×16		X		24	0×0	427×402	
24	do	Yes	124	16×18	X			22	0×0	452×310	
25	100% nylon	Yes	57					39	¼×¼	951×676	
26	do	Yes	64	3×2			X	35	0×0	612×506	
27	do	Yes	60	11×9		X		26	0×0	516×338	
28	do	Yes	67	4×6	X			33	0×0	534×538	
29	do	Yes	77	2×5				41	¼×¼	1,283×783	
30	100% rayon	Yes	66	24×16		X		44	0×0	1,210×1,121	160+
31	do	Yes	68	16×14			X	49	0×0	880×972	160+
32	do	Yes	79					80	1×¾	3,072×3,355	103
33	100% rayon viscose	Yes	71	25×31		X		34	0×0	622×854	160+
34	do	Yes	54	19×16			X	30	0×0	384×420	113
35	do	Yes	54					41	¼×¼	623×683	82
36	do	Yes	57	23×25	X			55	0×0	3,378×3,845	126
37	do	Yes	82					146	3×3	12,278×15,824	90

It will be noted from the data in Table 1 that the impregnated webs which have been compressively shrunk have superior delamination resistance, less piping, and better flexibility than corresponding impregnated webs which have not undergone the compressive shrinking. It will also be noted that improvements in flexibility, piping, and delamiantion resistance are achieved in nonwoven webs which have not been needled prior to compressive shrinking. However, as stated above, the preferred materials are needled to provide higher internal bonding strength.

The materials of the present invention also possess reduced resilience as compared with materials which are not compressively shrunk. Lack of resilience is especially desirable in materials used for shoe uppers. This property can be measured by folding the material back on itself and observing how quickly the material recovers to the unbent position. Materials of the present inveniton possess substantially less recovery than prior art materials.

By means of the compressive shrinking operation, the web is reduced in thickness and the density is increased to some degree. A higher internal bonding strength is achieved in the materials of the present invention with the use of less elastomeric binder. The less binder in the web, the more porous the material will be and the more absorbent the fibers will be. These two factors result in a more comfortable shoe upper material. These advantages are gained without the loss of internal bonding strength occasioned by the decreased amount of binder in the web.

It is claimed:

1. An impregnated fibrous material particularly suited for use as synthetic leather consisting of a compressively shrunk nonwoven web of synthetic fibers having a length of from ½ to 3 inches, said web having a moisture content of about 25% prior to compressive shrinking, and being impregnated with an elastomeric binder material at a level of between 50 and 150% by weight based on the weight of said fibers.

2. The process for preparing a fibrous impregnated material particularly suited for use as synthetic leather which consists of impregnating a nonwoven web of synthetic fibers which have a length of from ½ to 3 inches with an elastomeric binder to a level of about 50–150% by weight based on the weight of the fibers and compressively shrinking the impregnated web, the web having a moisture content of about 25% prior to compressive shrinking.

References Cited

UNITED STATES PATENTS

2,881,505	4/1959	Hoffman	28—72.2
3,245,863	4/1966	Sonnichsen et al.	161—72
3,317,335	5/1967	Marrinan et al.	28—72.2 X

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