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SYNTHETIC LEATHER MATERIALS

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U.S. Cl. 161—82 12 Claims

ABSTRACT OF THE DISCLOSURE

A cellulosic web which has been impregnated with a polymeric binder and a compound which can be a glycol, polyoxyethylene lanolin, silicone oil or an alkyl ester of a fatty acid, is compressively shrunk to produce a smoother-surfaced product improved with respect to the properties of flexibility and stiffness. The impregnated web may be secured to a dimentionally stabilizing fabric.

This application is a continuation-in-part of application Ser. No. 482,921 filed Aug. 26, 1965, and now abandoned.

This invention relates to a synthetic leather or coating base material characterized by leatherlike 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 and are usually stronger, more abrasion resistant, more waterproof, and generally more uniform in properties than leather. Synthetic leathers are utilized for shoe uppers, leather coats, gaskets, gloves, slippers, luggage, brief cases, camera cases, bags, and the like.

It has now been found that a novel synthetic leather structure characterized by improved internal bonding strength, resilience, reduced piping, and particularly improved flex life can be prepared which comprises an extensibilized, preferably biaxially extensibilized, nonwoven web of cellulosic fibers which have been impregnated with a composition containing a polymeric binder material and a specified additive.

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 having a significantly improved flex life can be prepared by compressively shrinking a nonwoven cellulosic web which has been impregnated with a polymeric binder and a specified additive, described below. The compressive shrinking of the web is carried out 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 still has moisture content of about 25%. However, improvement in the properties of the product, particularly with regard to flex life over comparable impregnated webs which have not been impregnated with a composition containing the additive of the invention or which have not been compressively shrunk are noted regardless of when the compressive shrinking is accomplished. The webs of the present invention are preferably shrunk 1 to 35% in one direction, and more preferably, 1 to 35% in both the machine- and cross-direction.

The term "cellulosic web" refers to a web made by conventional techniques, and particularly by wet-method paper-making techniques from conventional cellulosic pulps wherein there is some hydration bonding of the relatively short fibers in the web. 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 60 lbs./3000 sq. ft. to 200 lbs./3000 sq. ft., preferably 100 lbs. to 150 lbs. per 3000 sq. ft. If drying of the webs is desired, conventional methods are employed.

The additives employed in the present invention are glycols, polyoxyethylene lanolin, silicone oil, dioctyl phthalate and alkyl esters of fatty acids, e.g., butyl oleate. A particularly preferred class of additives are the glycols, especially polyglycols, e.g., ethylene glycol and polypropylene glycol. The additives are preferably employed at a level of about 5 to 30% by weight based on the weight of the fibers and more preferably 15 to 20%.

The additive of the invention is preferably introduced into the nonwoven web as a component of the impregnating composition. However, the additive may be applied, e.g. by spraying or dipping the web into a bath of the additive before or after the impregnation step.

Polymeric binder materials known to the art are employed in the impregnating composition. 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 polymers. In a preferred embodiment a small amount, e.g., 5% or less of a wet strength resin such as phenol formaldehyde or melamine formaldehyde, is also employed. The level of impregnation of the polymer on the fiber generally ranges between 50 and 150% by weight based on the weight of the fiber. Preferably, an impregnation level of about 100% is employed.

As example of suitable impregnating binders, mention may be made of natural and synthetic rubbers such as butadiene-styrene coploymers, butadiene-acrylonitrile copolymers, neoprene and the like. Other saturants are described in the following U.S. Pats. 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.

Impregnating compositions may also contain antioxidants, fillers, thickeners, curing agents, and the like. Impregating materials in the web are employed in both cured and uncured state. Preferably, the polymeric materials are employed as latices or water dispersions. Solids solutions and melts may also be employed.

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 prevent more than a 5% increase in the thickness of the impregnated web.

The webs are compressively shrunk in a single direction

by passing through the compressive shrinking machine in one direction or the webs may be compressively shrunk in two directions, i.e., the machine-direction (MD) and in the direction perpendicular to the machine-direction or the cross-direction (CD). Shrinkage in two directions is accomplished by passing the web through the apparatus described in U.S. Pat. No. 2,625,254, in one direction, turning the web 90° and again passing it through the apparatus. Shrinkage in two directions may also be accomplished 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-direction and the 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 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 a greater degree of dimensional stability. The impregnant-compacted material is also preferably coated with a polymeric material to simulate the finish of leather. As examples of a suitable coating, mention may be made of flexible materials such as a polyurethane, a plasticized polyvinyl chloride or carboxylic butadiene-acrylonitrile copolymer which 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.

The following nonlimiting examples illustrate the novel products of the present invention.

EXAMPLE 1

(Control)

A cellulosic web having a ream weight of 139 pounds was impregnated to a level of 100% by weight based on the weight of the fiber of the following composition:

	Percent
SBR latex (76% butadiene, 23% styrene, 1% carboxylic comonomer)	97.5
Phenol formaldehyde resin	2.0
Sodium salt of ethylene diamine tetracetic acid	0.5

The levels of materials are on a weight-solids basis. The impregnating composition had a total solids of 35%. After impregnation and squeezing out the excess saturant with squeeze rolls, the web was dried at room temperature to equilibrium moisture content at 50% relative humidity. The samples were then wet with water to a moisture content of about 30% of the fiber and compressively shrunk wherein the temperature in the nip of the compacting machine was 200° F. and a compression of 18% of belt thickness was employed. Compressive shrinking was carried out in both the machine-direction of the paper as well as the cross-direction. The webs were then dried to a moisture content of about 5% by weight based on the weight of the fiber and then cured 1 minute at 375° F. Some of the samples were tested at this point for Gurley stiffness, flex life, and delamination resistance. Others were laminated to a slack mercerized fabric by means of a neoprene solvent adhesive. After the adhesive dried, two plies were pressed together to a compression of 5 mils at a temperature of 225° F. for three minutes. The laminates were then subjected to the same tests as the unlaminated webs. The results of these tests are set forth in Table 1.

EXAMPLE 2

An impregnated web was prepared and processed using the same procedure as in Example 1 except that 17.5 weight percent (solids basis) of latex was replaced with polyoxyethylene lanolin.

Table 1 shows the results of physical tests carried out on the above materials. Flex life was determined on a device that bent the sample in a 90° angle 90 times per minute.

TABLE 1

	Example 1	Example 2
Caliper (mils)	31	30
Percent shrink (MD x CD)	16 x 17	12 x 18
Gurley stiffness, mgms	1,004 x 1,045	1,045 x 995
Flex life, hours (MD x CD)	108 x 47	289 x 185

In Table 2 the results of physical tests carried out on the laminates are reported.

TABLE 2

	Example 1	Example 2
Caliper (mils)	59	59
Gurley stiffness, mgms	3,112 x 2,249	3,088 x 2,054
Flex life, hours (MD x CD)	43x43	262 x 538

From the results of Table 1 it can be seen that the product which contained the polyoxyethylene lanolin additive possessed a significantly greater flex life than the control, 3 to 4 times as much, even at essentially the same stiffness level as the control, and therefore is more supple and more like natural leather. It should be further noted that the control has been subjected to a greater degree of shrinkage than the web of Example 2, but that the improvement in flex life is still noted.

In Table 2 even greater improvement in flex life is reported; about 6 times in the MD flex life and about 11 times in the CD flex life.

In Examples 3 to 10 impregnated webs were prepared and laminated using the same procedure and materials as in Example 1 except for the additive. The impregnating composition was as follows:

	Percent
SBR latex (70% butadiene, 23% styrene, 1% carboxylic comonomer)	80.0
Fiber lubricant	17.5
Phenol formaldehyde resin	2.0
Sodium salt of ethylene diamine tetracetic acid	0.5

The specific additive was as follows:

Example 3—Control
Example 4—Sorbitol
Example 5—Polyethylene glycol
Example 6—Polypropylene glycol
Example 7—Polypropylene glycol
Example 8—Butyl oleate
Example 9—Dioctyl phthalate
Example 10—Silicone oil

TABLE 3

Example No.	Percent impregnation	Percent shrinkage MD x CD	Caliper (mils)	Ream weight	Gurley stiffness	Delamination resistance (oz./in. width)	Flex life (hours) MD x CD
3	103	17 x 19	32.0	104	1,602 x 1,157	51	87 x 87
4	101	15 x 12	37.5	110	1,155 x 979	37	15 x 351
5	101	13 x 14	30.0	94.5	889 x 711	48	400 x 400
6	99	10 x 10	29.0	100	800 x 711	57	500 x 496
7	100	11 x 12	29.0	100	889 x 711	58	500 x 500
8	100	14 x 14	27.0	100	979 x 712	34	136 x 351
9	100	12 x 12	28.0	100	712 x 712	44	15 x 351
10	94	15 x 16	32.0	94	1,068 x 889	26	424 x 136

The results of Table 3 show the significant improvement in flex life by the employment of the additives of the invention. Examples 5, 6 and 7 wherein the preferred additive of the invention was employed exhibited significant improvement in flex life in both the MD and the

CD direction as well as significantly decreased stiffness.

In order to evaluate the effect of the compressive shrinking operation on the properties of the materials, physical testing was carried out on materials in all respects identical to the materials described in Examples 3 to 10 except that they did not undergo compressive shrinking.

TABLE 4

Example No.	Percent impregnation	Caliper, mils	Ream weight, lbs.	Gurley stiffness, mgms.	Delamination resistance (oz./in. width)	Flex life (hours) MD×CD
3	102	30	105	2,667 x 1,869	44	87 x 160
4	101	32	103	3,293 x 2,047	37	15 x 135
5	100	32	100	2,848 x 1,869	44	15 x 400
6	95	32	98	3,026 x 1,869	44	136 x 15
7	100	32	101	3,293 x 2,314	40	15 x 15
8	98	30	98	1,778 x 779	25	15 x 15
9	100	28	100	1,869 x 1,315	39	87 x 15
10	93	30	93	2,667 x 1,503	37	207 x 87

The results of Table 4 show that both compressive shrinking and the additive of the invention provide greater improvements in flex life. In general there is less flexibility when the sample has not been shrunk, and in most cases the flex life results are poorer than the control (Example 4) which contained no additive.

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. On two specimens 10 inches x 1 inch, two strips of rug binding tape 9 inches in length, are placed so that approximately 0.5 inch 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 inch 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 Instrom 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 stiffness tester.

The addition of the additive of the invention to the web provides a web surface substantially devoid of fissures and smoother than has been attainable heretofore. There is also an improvement in the property of stiffness of the webs providing a more leatherlike feel to the product.

I claim:

1. An impregnated fibrous material particularly suited for use as synthetic leather comprising a compressively shrunk, cellulosic, fibrous web impregnated between about 50 and 150% based on the weight of the fiber with an elastomeric binder material and between about 5 and 30% based on the weight of the fiber of a compound selected from the group consisting of glycols, polyoxyethylene lanolin, silicone oil, dioctyl phthalate and alkyl esters of fatty acids.

2. The product as defined in claim 1 wherein said compound is present at a level of 15 to 20%.

3. The product of claim 1 wherein said elastomeric binder material additionally contains a minor amount of a wet strength resin.

4. The product as defined in claim 1 wherein said web is compressively shrunk 1 to 35% in the machine-direction and 1 to 35% in the cross-direction.

5. An impregnated fibrous material particularly suited for use as synthetic leather comprising a compressively shrunk, cellulosic, fibrous web impregnated between about 50 and 150% based on the weight of the fiber with an elastomeric binder material and between about 5 and 30% based on the weight of the fiber with a glycol.

6. The product of claim 4 wherein said glycol is a polyglycol.

7. An impregnated, fibrous material particularly suited for use as synthetic leather comprising a compressively shrunk, cellulosic, fibrous web impregnated between about 50 and 150% based on the weight of the fiber with an elastomeric binder material and between about 5 and 30% based on the weight of the fiber of a compound selected from the group consisting of glycols, polyoxyethylene lanolin, silicone oil, dioctyl phthalate and alkyl esters of fatty acids, and, secured to said impregnated fibrous web, a dimensionally stabilizing fabric.

8. The product of claim 7 wherein said dimensionally stabilizing fabric is a woven fabric.

9. The product of claim 7 wherein the impregnated fibrous web is coated with a polymeric material.

10. The product of claim 7 wherein said compound is a polyglycol.

11. An impregnated fibrous material particularly suited for use as a synthetic leather comprising a compressively shrunk, cellulosic, fibrous web impregnated between about 50 and 150% based on the weight of the fiber with an elastomeric binder and between about 5 to 30%, based on the weight of the fiber, of a compound selected from the group consisting of glycols, polyoxyethylene lanolin, silicone oil, dioctyl phthalate and alkyl esters of fatty acids, said impregnated fibrous web being adhesively secured to a dimensionally stabilizing fabric and having a surface coating of a polymeric material.

12. The material of claim 11 wherein said dimensionally stabilizing fabric is a woven fabric and said polymeric material is selected from the group consisting of polyurethane, plasticized polyvinyl chloride and a carboxylic butadiene-acrylonitrile copolymer.

References Cited

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