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3,537,871

IMITATION LEATHER

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FIG. 1

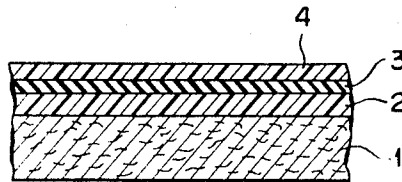


FIG. 2

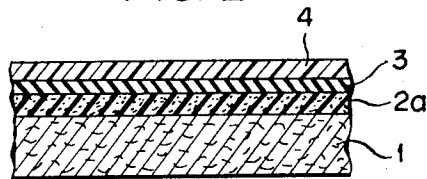
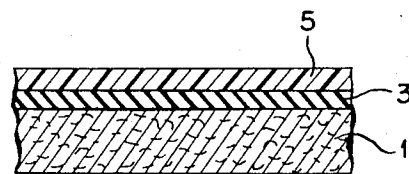


FIG. 3



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IMITATION LEATHER

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13 Claims

ABSTRACT OF THE DISCLOSURE

The imitation leather is composed of a non-woven base fabric of a mixture of collagen fiber and natural or synthetic fiber, and a coating film of amino acid resin adhering to the base fabric by means of an intermediate layer of resin binder.

BACKGROUND OF INVENTION

This invention relates to an imitation leather having as a base material, a non-woven fabric composed of a mixture of collagen fibers obtained from natural leather and natural or synthetic fibers.

Hitherto, as is well known in the art, various proposals and investigations have been made for the purpose of providing artificial leathers having the many excellent characteristics of natural leathers.

However, known artificial leathers and imitation leathers are substantially inferior to natural leather in one and frequently more than one respect. Thus, known artificial and imitation leathers are for the most part deficient in cold resistance, heat resistance, air permeability, moisture regain and touch or texture.

In the past, artificial leather has usually been prepared by applying a coating film of vinyl chloride resin, polyurethane resin, nylon resin or the like resinous material to an ordinary non-woven fabric or napped woven or knit fabric, and its characteristics are then determined by the nature of the base material employed.

SUMMARY OF INVENTION

A new artificial leather has been discovered which has many characteristics resembling those of natural leather and which is comparable to natural leathers especially with respect to moisture regain and air permeability. According to the invention, the new artificial leather is comprised of a non-woven base fabric of a mixture of collagen fiber of natural leather and fiber selected from the group consisting of natural fiber and synthetic fiber, said fibers having an entangled structure, at least one layer of resin binder adhering to at least one surface of said base fabric, and a coating film of amino acid resin adhering to said resin binder. The coating film of amino acid resin corresponds to the grain layer of natural leather.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1, FIG. 2 and FIG. 3 are each enlarged cross-sectional views of artificial leathers of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The base material used for the new artificial leather of the present invention is a non-woven fabric composed of a mixture of about 20 to 50% of a natural or a synthetic fiber such as cotton, nylon, polyester, or the like and 50 to 80% of a fibrous collagen obtained from a natural skin or hide. The collagen fibers are obtained from the corium layer of the skin or hide, usually from

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chromed split hide, in fiber lengths of about 0.5 to 16 cm. The natural or synthetic fiber and the collagen fiber is formed into the non-woven base fabric by matting or entangling the two types of fibers to form a compact mass, an appropriate binder is also usually employed. Preferably for this use the resulting material has a thickness of about 0.3 to 2.0 mm.

The poly(amino carboxylic acid) resin which in accordance with this invention is used to form the surface coating of at least one side of the base material may be for example an N-carboxyglutamic acid amide resin or an N-carboxyaspartic acid amide resin. Such a resin may be obtained by polymerizing about 5 to 10 parts of a lower alkyl glutamate or aspartate such as the methyl, ethyl or butyl derivative, in about 10 to 95 parts of a liquid medium such as ethylene dichloride and/or dioxane. The poly(amino acid) are dopes which are clear viscous liquids, not viscous enough to be drawn into filaments. The average degree of polymerization of such a resin is of the order of 5,000.

The poly(amino acid) resin is ordinarily diluted with a solvent such as dioxane to a suitable viscosity before being applied to the base fabric. The resin is applied in a convenient manner such as in a casting or a roll-coater process and is then dried usually at a slightly elevated temperature, to form a resinous film. Preferably a temperature of the order of 100° C. is used to effect complete drying, although higher or lower temperatures, i.e., about 40 to 130° C. may be used if desired.

Since the poly(amino acid) resin does not bind well with the base fabric a binder is employed to cause the film of poly(amino acid) resin to adhere to the base fabric. Binders which have been found to be particularly effective for this purpose include polyurethane resin and acrylic resin. These materials may be used alone or in combination, and a particularly effective binder consists of a layer of polyurethane resin and a layer of acrylic resin. A layer of acrylic resin is applied particularly where there is a need for high bonding strength between the base fabric and the surface film of poly(amino acid). The binder, dissolved in an appropriate solvent is applied directly to the base fabric. The poly(amino acid) resin is then applied to the binder-coated base fabric and the product is heat dried to form the imitation leather of the invention.

In one aspect of the invention, a porous layer, rather than a solid layer of binder is used to form the imitation leather of the invention.

The invention will be further described with reference to the figures. In FIG. 1, the non-woven base fabric 1, containing a mixture of collagen fiber and synthetic or natural fibers is coated with a layer of binder 2, which in this case is a layer of about 0.01 to 1 mm. thick of polyurethane resin. An anchoring layer 3 which is acrylic layer is coated on the binder 2 and the final layer 4 of poly(amino acid) is anchored and bound to the base fabric 1 by the intervening resin layers 2 and 3. In FIG. 2, the non-woven base fabric 1 is coated with a porous layer of binder 2a which is polyurethane resin. The anchoring layer 3 which is acrylic layer coats the porous binder layer and anchors the film of poly(amino acid) 4. In FIG. 3, the base fiber 1 is coated with a binder layer 3 which is acrylic resin; the film 5 of which is a copolymer of an amino acid resin such as of an amino carboxylic acid-polyurethane resin or an amino carboxylic acid-acrylic resin is bound to the non-woven base fabric 1 by layer 3.

The following examples further illustrate the best methods contemplated for preparing the imitation leather of the invention, but these examples must not be interpreted as limiting or restricting the invention in any manner whatsoever.

(a) Example 1—Preparation of the chromed collagen fiber

A chromed split is soaked in about 5 parts by volume of a warm aqueous solution containing a nonionic surface active agent at temperature of 50–60° C. for 16 hours is then washed with water for one hour. The thus treated split is neutralized by tumbling in a rotary drum with about 2 parts by volume of a warm 1% aqueous solution of sodium bicarbonate at a temperature of 40° C. for 1 hour and is subsequently washed with water for 30 minutes. The neutralized split is then oiled by tumbling in a rotary drum with about 2 parts by volume of warm water at 60° C. containing dissolved therein 2.5% by weight, based on the weight of the split, of a sulfated olive oil for 30 minutes; the oiled split is dehydrated by means of a centrifugal separator and dried with hot air at temperatures of at most 50° C. to have a moisture content of about 35–45%. The dried split is then beaten by means of a stamp mill for 30 minutes, and is disintegrated by pressing it on a scratch roll of a diameter of about 60 cm. having on its peripheral surface a number of saw-toothed flukes and revolving at 1300 r.p.m.

The chromed collagen fiber thus produced has an average diameter of 0.05 mm. and fiber lengths of 0.5–5 cm. of which about 75% of individual fibers are of lengths of about 3.2 cm. The fibrous mass is soft and has the appearance of cotton or wool lint.

Example 2—Preparation of non-woven base material

Chromed collagen fiber (2–4 cm. in length) containing 40% by weight of Tetron fiber mixed therewith (about 4 cm. in length) was formed into non-orientated web by treatment successively with a land feeder or land webber. Then the web was punched with a fiber rocker to give about 200 punchings per square centimeter. The punched web was impregnated with a binder emulsion, squeezed to remove the excess emulsion. The resultant sheet was first dried at 120° C. for 15 minutes with infrared ray then at 130° C. for additional 20 minutes. In this instant, fibers of the chromed collagen intertwined with each other by thermal shrinkage to form a state favorable for preparing into non-woven fabrics. The impregnated and heated fiber sheet was then subjected to curing at 110° C. for 60 seconds to produce non-woven fabric cloth.

The strength in both lengthwise and lateral directions of the non-woven cloth thus obtained is given in Table 1.

TABLE 1

Tearing strength, kg./3 cm.	(Lengthwise...)	6.0
	(Lateral.....)	6.0
Tensile strength, kg.	(Lengthwise...)	12.8
	(Lateral.....)	20.9
Elongation, percent	(Lengthwise...)	64.6
	(Lateral.....)	70.2

It is obvious from the above Table 1 that the non-woven cloth has a tearing strength ratio towards lengthwise to lateral directions of 1:1, a tensile strength of 0.75:1 and an elongation of 0.93:1. From this result, the cloth was found to be substantially free from orientative difference.

The properties of the web or non-woven fabrics of the chromed collagen fiber may be varied by suitably setting the ratio and length of the material fibers.

Example 3—Preparation of imitation leather

A non-woven fabric of 60 parts of a chromed collagen fiber of lengths of about 2.7 mm. and an average fiber diameter of about 0.05 mm. 40 parts of a polyethylene terephthalate fiber of 6 d./f. and 3.5 cm. in length and 50 parts of an acrylic resin binder (as solid), was prepared as described in Example 1.

To a single surface of this web of non-woven fabric which was about 1.2 mm. thick was applied a solution of

a polyurethane resin in ethyl acetate by a transfer coating process. The web of non-woven fabric so coated was immediately introduced into a dryer and heated therein at a temperature of 100–150° C. for about 3–5 minutes and it was then wound up into a roll which was allowed to stand for 2–4 days to cure and effect a crosslinking reaction.

The web of non-woven fabric was then coated with a solution of a copolymer of 80 parts of butyl acrylate with 20 parts of a mixture of acrylonitrile and acrylamide in toluene by means of a doctor blade and subsequently heat dried at 50–60° C. for 3–5 minutes. The web was then coated with a solution of as an amino acid resin, a poly (N-carboxy-glutamate) in ethylene dichloride and subsequently heated at 120–130° C. for 3–5 minutes. Although the product thus obtained had, as hereinbefore mentioned, various properties closely resemble to those of natural leathers, it was subjected to embossing to improve the external appearance thereof.

This process was carried out using the same base fabric and the same materials described above except that a solution of polyurethane resin in a mixture of ethyl acetate and toluene was applied to the base fabric using a doctor coating process. After drying and then standing to effect crosslinking, a solution of the butyl acetate acrylonitrile, acrylamide copolymer in ethyl acetate was applied on top of the first coating on the base fabric, by a reverse roll coater. This was dried as already described; and then a solution of amino acid resin in dioxane was applied to the thus coated base fabric. The product was substantially the same as that described above.

Example 4—Preparation of imitation leather

A web of non-woven fabric was coated with a solution of a polyurethane resin in dimethylformamide and then soaked in water to extract the solvent, thereby forming a porous layer of polyurethane resin. The fabric so coated was then heated, cured, coated with copolymer dried and coated with poly(amino acid) as described in the first two paragraphs of Example 3.

The product thus obtained has the air permeability and moisture regain of natural leathers as shown in Table 2 below. In addition, the non-woven fabric used as base material had the capacity of retaining 16–17% by weight, based on the weight of the base fabric of moisture, so that the product could “breathe” and retained its leather-like touch when used for shoes and other apparel without causing chapping and overheating.

Example 5—Preparation of imitation leather

To a surface of a non-woven fabric of 1.8 mm. thickness formed of 70 parts of a chromed collagen fiber (average fiber diameter of 0.05 mm. and fiber length of about 2.0 cm.), 30 parts of a nylon and 55 parts of a binder consisting essentially of a nitrile butadiene rubber (N.B.R.), there was applied in the thickness of 0.01 mm. an acrylic resin binder and thereover in the thickness, of 0.02 mm. a copolymer obtained by polymerizing 5 parts of monomeric N-carboxyglutamic amide and 0.5 part of a monomeric urethane in a mixture of 90 parts of ethylene dichloride and 4.5 parts of dioxane. The coated fabric was then passed through a drying oven (the temperature within the oven about 110° C.), at a rate as to afford a dwell time of 3–5 minutes to form a top layer of a resinous film. The coated fabric thus obtained exhibited a moisture regain as indicated in the Table 2 below and had the feel and texture of natural leather.

Example 6—Method of determining water vapor absorption

A specimen disk of 70 mm. ϕ is obtained. The specimen is put in an atmosphere of 20° C. x 65% R.H. for a long period of time and weighed. The specimen is then put in a chamber maintained at 40° C. x 95% R.H. for

24 hours, exposed to an atmosphere of 20° C. x 65% R.H. for 10 minutes and weighed. The percent increase in weight is indicated as water vapor absorption.

The results of comparative tests of water vapor absorption or moisture regain are given in Table 2.

Specimens	Thickness, mm.	Water vapor absorption, percent
Oxhide.....	1.5	8.78
Sheepskin.....	1.5	4.97
Product of Ex. 3.....	1.9	6.03
Product of Ex. 1.....	1.0	4.15
Product of Ex. 2.....	1.0	3.80
"Corfam" (brown) (sold by Du Pont Co.)..	1.1	0.20

The data in Table 2 indicates that the water vapor absorption of the product of the present invention varies depending on the amount of the chromed collagen fiber and of the binder in the non-woven fabric.

The water vapor absorption decreases with increase in the proportion of the natural or synthetic fibers. While this invention is not limited by or dependent on a particular theory, it is believed that the high water and moisture absorptions of the chromed collagen fiber are attributable to the face that the chromed collagen fiber is a hydrophilic protein containing numerous amino, carboxyl and hydroxyl groups.

The poly(amino acid) film itself has an external appearance of natural leather and a high strength and a low extensibility so that it retains an elegant luster and an embossment which has been imposed thereon, for a long period of time. Thus it retains leather-like qualities for a long period of time. Further, because it has moisture regain or hygroscopicity it retains a warm, soft and dry touch through all seasons. The properties of the artificial leather surface coating of the present invention cooperating with the properties of the base material, result in a product of excellent properties comparable to those of natural leather including weathering resistance. As pointed out above, the moisture or water vapor absorption of the product of the present invention can be varied. The product has a good processability and can be sewed and ironed without any difficulty and, if so processed, it does not lose the embossment given thereto. This means that the artificial leather of the present invention can be handled or treated like ordinary textile fabric, and that it can be conveniently sewed into final products at low cost. Air and moisture do not pass through the product of the present invention, readily, but the chromed collagen fiber in the non-woven fabric absorbs and liberates moisture and, therefore, the product of the present invention behaves as if it had air permeability.

What I claim and desire to secure by Letters Patent is:

1. Imitation leather comprising a non-woven base fabric comprised of a mixture of 80 to 50% by weight collagen fiber of natural leather and in an amount of 20-50% by weight based on the weight of the mixture a fiber selected from the group consisting of natural fiber and synthetic fiber, said fibers having an entangled structure, at least one layer of resin binder adhering to at least one surface of said base fabric, and a coating film of amino acid resin adhering to said resin binder

said amino acid resin being selected from a member of the group consisting of N-carboxyglutamic acid amide resin and N-carboxyaspartic acid amide resin.

2. Imitation leather according to claim 1 wherein said coating film is poly(N-carboxyglutamate).

3. Imitation leather according to claim 1 wherein said resin binder is selected from at least one member of the group consisting of polyurethane resin and acrylic resin.

4. Imitation leather according to claim 1 wherein said resin binder is comprised of polyurethane.

5. Imitation leather according to claim 1 wherein said layer of resin binder is comprised of a porous layer of polyurethane.

6. Imitation leather according to claim 1 wherein said resin binder is comprised of polyacrylic resin.

7. Imitation leather according to claim 1 wherein said coating film is embossed with a leather-like grain.

8. Imitation leather according to claim 1 in which said collagen fiber is in fiber lengths of about 0.5 to 16 cm..

9. Imitation leather according to claim 1 in which said collagen fiber is obtained from corium layers of a chromed split hide in fiber lengths of about 0.5 to 16 cm..

10. Imitation leather according to claim 1 in which said base fabric comprises a binder.

11. Imitation leather according to claim 1 in which a plurality of layers of resin binder are used and in which said binding layers are comprised of at least one layer of acrylic resin and at least one layer of polyurethane resin.

12. Imitation leather according to claim 1 in which said coating film is a copolymer of N-carboxyglutamic acid amide and urethane, the proportion by weight of acid amide to urethane being about 10 to 1.

13. A method for preparing imitation leather which comprises forming a web of base fabric from about 80-50% by weight of chromed collagen fiber in lengths of about 0.5 cm. to 16 cm. and about 50-20% by weight of fiber selected from the group which consists of natural fiber and synthetic fiber, applying at least one layer of binder to the base fabric and applying over said binder a coating of an amino acid resin selected from a member of the group consisting of N-carboxyglutamic acid amide resin and N-carboxyaspartic acid amide resin.

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