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[54] **PROCESS FOR PRODUCTION OF SYNTHETIC
LEATHER**
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ABSTRACT: A synthetic leather is produced by impregnating a fiber web with a binder solution, coating one surface of the said web with a solution of a synthetic resin having a viscosity higher than that of the said binder solution before the said binder is coagulated, and thereafter coagulating the said binder and the synthetic resin simultaneously. In another embodiment, it is produced by impregnating a fiber web with a binder solution, applying to one surface of the said web at least one kind of binder solution having a viscosity higher than that of the first-mentioned binder solution in the order of a lower viscosity before the already applied binders are coagulated, applying to the said surface a solution of a synthetic resin having a viscosity of 50–10,000 poises, and thereafter coagulating the said binders and the synthetic resin simultaneously.

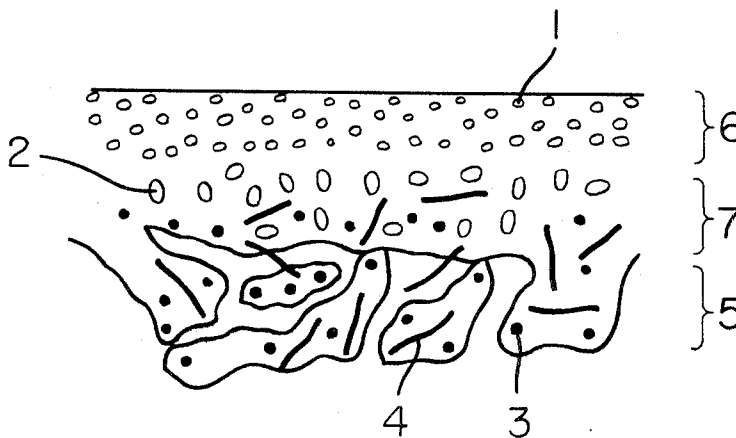
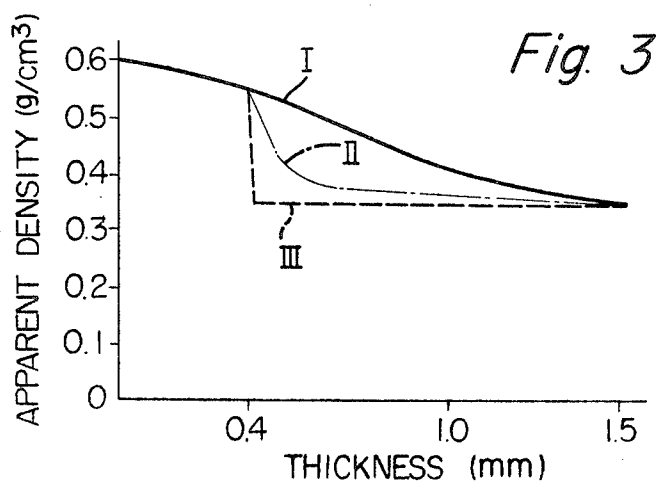
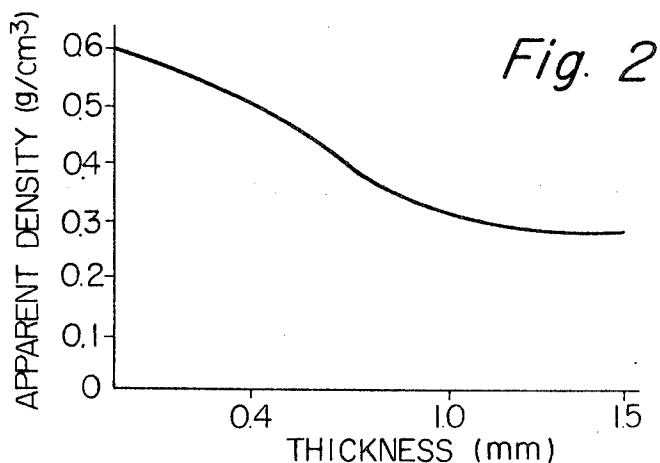
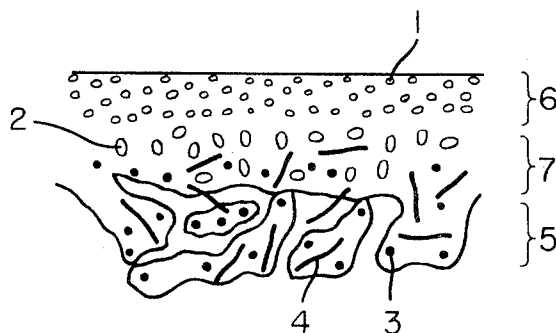


Fig. 1



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PROCESS FOR PRODUCTION OF SYNTHETIC LEATHER

This invention relates to a process for the production of a synthetic leather comprising a fiber web as a substrate and a synthetic resin as a surface layer. More particularly, the invention relates to a process for the production of a synthetic leather by impregnating a fiber web with a binder solution, coating the web with a solution of a synthetic resin having a viscosity higher than that of the said binder solution before the binder is coagulated, and thereafter coagulating the said binder and synthetic resin simultaneously.

Methods of producing a synthetic leather having a surface layer of a synthetic resin are already known and some examples are as follows:

1. A method by which the surface of a woven or knitted article is coated with a synthetic resin;
2. A method by which the surface of a nonwoven fabric is coated with a synthetic resin; and,
3. A method by which a nonwoven fabric is caused to adhere to the under surface of a woven article coated with a synthetic resin.

None of these methods, however, give an interior structure having a continuous density gradient like that of a natural leather, and the resulting product disadvantageously does not look like leather in respect of its behavior towards flexural deformation or ability of forming a bended surface. Synthetic leathers obtained by methods 1 and 3 are not characterized by the absence of orientation as seen in a natural leather because the orientation of the woven article as substrate appears in them as their own orientation, and therefore they are restricted in their use as leather. Furthermore, the synthetic leather obtained by method (1) encounters a great difficulty when processed at its back surface, for instance, in a shoe-making process, especially a side-buffing operation because its properties relating to strength mostly depend on the woven article. According to method 2, a synthetic resin is coated on a dried nonwoven fabric as a surface layer. It is impossible therefore for this method to obtain an integrated area consisting of the resinous surface layer and the binder, and to give a synthetic leather satisfactory in respect of density gradient and cohesion between layers.

Some of the known methods of giving a density gradient to a nonwoven fabric are as follows; that is, a method by which a binder is applied to a laminate consisting of a plurality of fiber webs each having a different denier or the laminate is punched; a method by which a laminate consisting of a plurality of fiber webs each having a different shrinkage is punched, and then subjected to a shrinkage treatment; a method by which the depth of a needle penetration into the laminate is controlled; and a method of imparting a density gradient by applying a binder or paste to a nonwoven fabric, and pressing it thereinto from the side on which it is applied or sucking it from the opposite side. But all of these methods are complicated in respect of operation and apparatus. In addition, all of the products obtained necessitate the coating of a resin on a nonwoven fabric to obtain a leatherlike glossy surface, and also it is difficult in such products to integrate the surface resinous layer and the nonwoven fabric layer, which results in a tendency of the layers to separate from each other.

An object of this invention is to remove the above-mentioned defects, and to provide a synthetic leather having a structure and an outer appearance like those of a natural leather in which an interface of a binder for a nonwoven fabric and that of a resin in a surface layer are integrated whereby a high strength is retained against the separation of the surface resinous layer from the nonwoven fabric.

Another object of this invention is to provide a synthetic leather having an interior structure with a density gradient.

Other objects of the invention will become apparent from the description which follows.

A synthetic leather which conforms to these objects of the invention can be obtained by impregnating a fiber web with a binder solution, coating one surface of the said web with a solution of a synthetic resin having a viscosity higher than that

of the said binder solution before the binder is coagulated, and thereafter simultaneously coagulating the binder impregnated among the fibers of the web and the resin coated on the surface of the web thereby to integrate them.

In the accompanying drawings:

FIG. 1 is a cross-sectional view of the synthetic leather according to this invention; and

FIGS. 2 and 3 are graphs showing a density gradient.

As the fiber to constitute the fiber web of this invention, a natural fiber such as cotton, flax, silk and wool, a regenerated fiber such as rayon, and a synthetic fiber such as polyamide, polyester, polyacrylonitrile and polyolefine are used either singly or in combination. These fibers may be modified by an ordinarily known method such as composite-spinning, copolymerization and grafting. And these fibers may have a denier of 0.5 to 10, but from the standpoint of tactile hand as synthetic leather, the denier of 1.5 to 4 is most preferable. The fiber length is preferably in the range of 10 mm. to 100 mm., especially preferred being a length of 38 mm. to 76 mm. in view of the tactile hand and operability as synthetic leather.

The fiber web as a substrate of the synthetic leather of this invention is prepared from such fiber by a customary method and apparatus such as card, garnett and random webber. A preferable fiber web has a weight per unit area of 100-1,000 g./m.², especially 200-300 g./m.². If necessary, the intertwining of the individual fibers with each other can be enhanced by needle-punching such web. The conditions for punching may be determined depending on the denier of the fiber to be used, the fiber length, the type of the fiber to be used, the weight of the web per unit area and the properties required of a final product. Under the ordinarily used conditions, punching is carried out by using needles (No. 32-42, Standard of The Torrington Co., U.S.A.) with the number of penetration of 200-800, particularly 300-500, per square centimeter and a needle penetration depth of 6-12 mm. The web can also be set by compression with a hot roll instead of punching.

The binder to be impregnated into the fiber web and the synthetic resin to be applied on its surface preferably have a chemical composition of the same series as they are coagulated simultaneously. Preferable resins to be used as the binder and the surface layer-forming synthetic resin are thermoplastic resins such as polyamides, polyesters, poly(vinyl chloride), polyacrylonitrile and polyurethane. They may be used in combinations of two or more. These resins are applied to the fiber web in the form of a solution in a solvent which is nonsolvent for the fibers that make up the fiber web. The solution of the synthetic resin for forming a surface layer should have a viscosity higher than the binder solution does. The viscosity of the solution of the surface layer resin is in the range of 20 to 10,000 poises, and that of the binder solution is chosen within the range of 0.1 to 100 poises. If desired, a filler such as wood powder and calcium carbonate, a pigment such as carbon black, an antifoaming agent or an antioxidant can be incorporated into a solution of the synthetic resin.

In impregnating the fiber web with the binder solution, it is preferable to press the binder uniformly into the interior layer of the web by using a squeezing device such as screen and mangle. Subsequent to this operation, the synthetic resin for the surface layer is coated all over one surface of the web by means of a reverse roll coater or knife coater before the binder is coagulated. In this manner, the surface layer-forming resin is applied before the binder is coagulated and a liquid-liquid mixing is effected at the interfaces. Consequently, when the surface layer of the synthetic resin and the binder are simultaneously coagulated, the web and surface layer are integrated to an extent such that they may not be separated from each other.

The coagulation of the binder and the surface layer-forming resin is carried out by two ways, one of which is a wet method wherein the solvent is extracted in a liquid such as water which is compatible with the solvent, and the other of which is a dry method wherein the solvent extraction is carried out by such operation as heating. In consideration of the state of the resin

after coagulation and the shape of the cell, the wet method is desirable to get a synthetic leather. As a porous structure is formed on the surface layer by solvent extraction in a coagulating step, the intended synthetic leather akin to a natural leather can be obtained by water-washing and drying after the coagulating step. To enhance the smoothness of the surface layer, the resulting leather is pressed while heating at a temperature below the melting point of the fiber of the web and above the softening point of the resin.

The synthetic leather obtained in this manner may be subjected to an embossing apparatus. For the purpose of enhancing the gloss and hue of the surface, a paint such as nitrocellulose lacquer may be applied to the leather by spraying, coating or printing.

According to a modification of the process described above, the density gradient of the structure can be made more resembling to that of a natural leather by changing the method of applying a binder solution to a fiber web. Namely, according to a specific embodiment of this invention, a synthetic leather having such density gradient can be obtained by impregnating a fiber web with a binder solution, applying at least one kind of binder solution having a viscosity higher than that of the first-mentioned binder solution to one surface of the said web in the order of a lower viscosity before the already applied binders are coagulated, coating the said surface with a solution of a synthetic resin having a viscosity preferably higher than that of the last-applied binder solution before these binders are coagulated, and thereafter coagulating the said binders and the synthetic resin simultaneously. Thus, a density gradient changing continuously from the surface layer to the back layer is formed. The binder is present in the web in concentration higher towards the surface owing to the difference in the amount of the binder to be penetrated into the web which is caused by the difference in viscosity of the binder solutions applied in sequence.

Hence, the structure of the synthetic leather obtained according to this embodiment of the invention is not a simple laminated structure as seen in the conventional synthetic leather, but looks almost like that of a natural leather. The behavior of this synthetic leather towards bending deformation is almost the same as that of a natural leather, too.

Of course, the same kind of a substrate web, binder and synthetic resin of the surface layer can be used in this embodiment, and the same method is also used in coagulation.

Since in this embodiment, the difference in viscosity of the binder solutions gives a density gradient changing continuously from the surface layer to the back layer of the web, the density gradient is more gentle as more kinds of binder solution of different viscosity are used, with the result that the structure is more like that of a natural leather. It is however desirable to restrict the number of binder applying procedures to two to three times because of disadvantages in productivity and cost of production.

In fact, a synthetic leather satisfactory for practical purposes can be obtained by impregnating a web with a binder solution, applying a binder solution having a viscosity higher than that of the first-mentioned binder solution to one surface of the web, further coating the said surface with a solution of a synthetic resin for a surface layer having a viscosity preferably higher than that of the said binder solution, and thereafter coagulating the said binders and the synthetic resin. In this method, the binder solution to be impregnated into the web has a viscosity of 0.1-100 poises, and the second-applied binder solution and the finally coated synthetic resin solution both have a viscosity in the range of 50 to 10,000 poises.

The binder first impregnated into the web is primarily intended to bond individual fibers of the web at intersecting points, and the next-applied binder is intended to bring about a density gradient by utilizing its smaller amount of penetration (distance of penetration from the surface on which the binder is applied) than the first-applied binder which is penetrated throughout the section of the web, and also to set the individual fibers of the web at the surface layer. The

synthetic resin finally coated on the web surface is for the purpose of enhancing the outer appearance of the product as a leather, and to improve such mechanical properties as resistance to scuffing and to flexural fatigue.

FIG. 1 of the accompanying drawings is an enlarged sectional view of the synthetic leather obtained by the above-mentioned embodiment of this invention. The reference numeral 1 represents a microcell structure, 2 a macrocell structure, 3 and 4, a nylon 6 fiber that makes up the web, 5, a binder impregnated into the web at the outset and a filler, 6, a microporous film composed of a filler and a synthetic resin for forming a surface layer which is coated in the last place, and 7, a structure having a density gradient formed of the first-impregnated binder solution and the next-applied binder solution having a higher viscosity. In the synthetic leather of this invention obtained in the above-mentioned manner, the binders in the web and the surface layer-forming resin are simultaneously coagulated and integrated at their interface, and so it has a high cohesion between layers. Also, because of the penetration of the surface resin into the interior of the web, a density gradient is provided from the surface to the back surface by the surface layer resin and the binders. It is therefore possible for the method of this invention to provide a structure having a density gradient continuous from the flesh side to the grain surface side and a structure wherein the flesh side and the grain side are integrated. Furthermore, because of a complete setting by the resin of individual fibers near the surface layer, the traces of punching do not appear on the surface of the synthetic leather of this invention in a processing procedure in which the leather is processed in an elongated state, for instance in toe-lasting step of shoemaking. In other words, the surface of the synthetic leather is not roughened.

Now, the invention will be described by way of working examples.

EXAMPLE 1

A web having a weight per unit area of 300 g/m.² was produced by means of a random webber from nylon 6 staples having a denier of 4, a fiber length of 51 mm., a titanium oxide content of 0.2 percent, and a number of crimps of 15 turns/25 mm.

This web was needle punched by means of a needle-loom (James Hunter Co., U.S.A.). The needles used were regular barbs (standard No. 42 of The Torrington Co., U.S.A.). The number of needle penetration per square centimeter was 500, and the needle penetration depth was 8 mm. The resulting punched web was immersed in a 15 percent solution (with a viscosity of 20 poises) in dimethylformamide of a polyester polyurethane prepared by chain-extending with butanediol a prepolymer form polyethylene adipate having a molecular weight of about 2,000 and diphenylmethane-4,4'-diisocyanate (MDI), compressed until the takeup reached 20 parts by weight as against 100 parts of the fiber, and then immediately coated on its one surface with a 20 percent solution (with a viscosity of 128 poises) in dimethylformamide of the same polyester polyurethane as mentioned above by using a blade with a clearance of 2.0 mm. The so treated web was deprived of the solvent by pouring it into water (coagulation bath) at 20° C. The time needed for the solvent extraction was 20 minutes. After complete coagulation, it was washed with water, and dried. There was obtained a synthetic leather having a total thickness of 1.5 mm. which is composed of an about 1.1 mm. thick interior structure having a continuous density gradient provided by the binders and the resin on the surface layer and an about 0.4 mm. thick porous film of the resin of the surface layer. The density gradient of this synthetic leather is shown in FIG. 2.

The same punched web was impregnated with the same 15 percent binder solution in the same amount, and after coagulating, water washing and drying the so impregnated binder solution, the said 20 percent resin solution was applied to one surface of the web and then coagulated. The resulting

synthetic leather was designated as control synthetic leather (corresponding to the conventional article obtained by method 2 mentioned at the outset of this specification). A comparison of this control leather with the synthetic leather obtained by this example reveals, as shown in table 1, that the synthetic leather according to the method of this invention is remarkably superior to the control product in respect of pliability and water permeability, and no separation between the surface resin layer and the nonwoven fabric is seen.

TABLE 1

	Thickness (mm.)	Apparent density (g./cm. ³)	Tensile strength (kg./cm.)	Elongation at break (percent)	Gurey's stiffness (mg.)	Water per- meability (g./m. ² /24 hr.)	Cohesion between layers (kg./2 cm.)
Synthetic leather of this invention.....	1.50	0.56	18.0	120	2,350	1,750	Inseparable
Control synthetic leather.....	1.50	0.55	15.1	90	3,500	1,003	2.0

EXAMPLE 2

One mole of poly (ε-caprolactone) having a molecular weight of 1850 and an acid value of 0.11 was reacted with 2 moles of diphenylmethane-4,4'-diisocyanate to form a prepolymer having a molecular weight of 2530. One mole of the resulting prepolymer and 0.985 mole of ethylene diamine are chain-extended in dimethylformamide to give a 25 percent polyurethane solution having a viscosity of 1,250 poises. This solution was diluted to 15 percent with dimethylformamide to make a solution having a viscosity of 13 poises. In this solution, the same punches web as used in example 1 was immersed, and squeezed by a mangle until the takeup of the solid polyurethane content reached 50 parts as against 100 parts of the fiber of the web. A resin solution having a viscosity of 2,000 poises and a solid content concentration of 30 percent was applied to one surface of the web by means of a reverse roll coater. This resin solution had been prepared by incorporating into the polyurethane solution 35 parts of poly (vinyl chloride) and 20 parts of a plasticizer (DOP), all amounts being based on 100 parts of the solid polyurethane, and adjusting its concentration to 30 percent with the use of dimethylformamide.

The coagulating, water-washing, and drying treatments of the so treated web under the same conditions as in example 1 gave a synthetic leather having a good tactile hand.

EXAMPLE 3

A polyurethane prepolymer was prepared by reacting 2 moles of polytetrahydrofuran having a molecular weight of 2,080 with 3.2 moles of a mixture of 2,4-tolylenediisocyanate with 2,6-tolylenediisocyanate. This prepolymer was reacted with an equimolar amount of hydraxine hydrate in dimethylformamide to form a polyurethane solution. A copolymer of 65 mole butadiene and 35 mole acrylonitrile in an amount same as that of the polyurethane solid content was dissolved into the resulting polyurethane solution, and diluted with dimethylformamide to give a solution having a viscosity of 5 poises and a solid concentration of 10 percent.

With the use of the resulting solution as a binder solution, the same procedure as that of example 2 was followed except that a knife coater was used instead of the reverse roll coater. The obtained product was serviceable as a synthetic leather as it had a strong cohesion between layers and a density gradient owing to the penetration of the surface layer resin solution into the interior of the web.

EXAMPLE 4

A prepolymer was prepared by reacting poly (1,4-butylene adipate) having a molecular weight of 2,000 and an acid value of 4.6 with diphenylmethane-4,4'-diisocyanate. The resulting prepolymer was reacted with butanediol in dimethylformamide to effect chain extension to form a polyurethane solution having a viscosity of 520 poises and a concentration of 35 percent. This polyurethane solution was diluted to 20 percent

with dimethylformamide to make a solution having a viscosity of 20 poises. In this solution the same punched web as used in example 1 was immersed, and squeezed until the takeup of the solid content reached 60 parts as against 100 parts of the fiber of the web. Immediately thereafter, a resin solution for forming a surface layer was applied to one surface of the so treated web by means of a knife coater. This resin solution had been prepared by adding 5 parts, based on 100 parts of the solid polyurethane, of carbon black to the said polyurethane solu-

tion having a concentration of 35 percent and a viscosity of 520 poises, and adjusting the concentration and the viscosity to 36.7 percent and 560 poises respectively.

The same coagulating, water-washing and drying treatments as those of 1 1 gave a synthetic leather having a good tactile hand.

EXAMPLE 5

A web having a weight per unit area of 200 g./m.² was produced from nylon 6 staples having a denier of 1.5, a fiber length of 38 mm., a number of crimps of 15 turns/inch, and a titanium oxide content of 0.2 percent by means of a random webber. The web was passed through a pair of hot rolls heated to 160° C., compressed and set. The same treatment as that of example 1 gave a synthetic leather having a good tactile hand.

EXAMPLE 6

A web having a weight per unit area of 250 g./m.² was produced from a polyester fiber having a denier of 1.5, a fiber length of 38 mm., and a number of crimps of 15 turns/inch by means of a cross lapper. The web was punched by a needle loom (James-Hunter Co., U.S.A.) with the number of needle penetration of 1,000/cm², and the needle penetration depth of 6 mm. The so treated web was passed through a pair of hot rolls heated to 160° C., and the thickness after hot-pressing was adjusted to 1.0 mm.

A copolymer of 65 mole butadiene and 35 mole acrylonitrile was dissolved in dimethylformamide to a concentration of 15 percent to make a solution having a viscosity of 6 poises. The web was immersed in this solution, and squeezed by a mangle until the takeup of the solid copolymer content reached 50 parts as against 100 parts of the fiber of the web. Immediately thereafter, a resin solution for forming a surface layer was applied to one surface of the web by means of a reverse roll coater. This resin solution had been prepared by adding to the said copolymer solution 20 parts of cellulose powder having an average particle size of 20 microns and 5 parts of carbon black, all amounts being based on 100 parts of the copolymer and adjusting the concentration and the viscosity of the solution to 30 percent and 230 poises respectively with the use of dimethylformamide.

The same coagulating, water-washing and drying treatments of the web gave a synthetic leather conforming to the objects of this invention.

EXAMPLE 7

One hundred parts of a copolymer composed of 35 moles of vinyl acetate and 65 moles of vinyl chloride, 20 parts of carbon black, 50 parts of a plasticizer (DOP) and 35 parts of calcium carbonate were dissolved in dimethylformamide to make a solution having a concentration of 30 percent and a viscosity of 100 poises. With the use of the resulting solution as a resin solution for forming a surface layer, the same procedure as that of example 6 was followed, and a synthetic leather conforming to the objects of this invention was obtained.

EXAMPLE 8

A web having a weight per unit area of 250 g./m.² was produced from nylon 6 staples having a denier of 3.5, a fiber length of 51 mm., a titanium oxide content of 0.2 percent and a number of crimps of 15 turns/25 mm. by means of a random webber. The web was punched by means of a needle loom (James-Hunter Co., U.S.A.). The used needles were standard No. 42 regular barbs of The Torrington Co., U.S.A. The number of needle penetration was 500/cm², and the needle penetration depth was 10 mm.

A prepolymer was prepared from polyethylene adipate having a molecular weight of about 2,000 and MDI, and chain extended with butanediol to form polyester polyurethane. A mixture composed of 80 parts of this polyurethane, 20 parts of carbon black and 60 parts of pulp was dissolved into dimethylformamide to form three solutions having a solid content concentration of 15 percent (solution I), 30 percent (solution II), and 40 percent (solution III), respectively. The viscosity of the solution was 19 poises (for solution I), 100 poises (for solution II), and 1,000 poises (for solution III). As mentioned hereinbelow, these solutions were applied to the said web in the order of a lower viscosity.

The web was dip coated with solution I until the takeup of the solid content reached 40 parts by weight as against 100 parts by weight of the web. Immediately thereafter, without any solvent extraction procedure, solution II was applied to the same surface to which the solution I had been applied by means of a reverse roll coater until the takeup of the solid content reached 54 parts by weight as against 100 parts by weight of the web. Finally, solution III was applied to the same surface until the takeup of the solid content reached 48 parts by weight as against 100 parts by weight of the fiber.

The so treated web was then conducted to a water vessel at 20° C., and immersed in it for 18 minutes to effect solvent extraction and coagulation of the resin. To remove the solvent completely, the web was immersed for 20 minutes in an open soaper at 80° C. after coagulation of the resin, washed with water, and dried. The obtained synthetic leather was good in tactile hand, and consisted of about 1.1 mm. of a thick substrate layer and about 0.4 mm. of a thick surface layer with a continuous gentle density gradient caused by the resin and the filler.

Now, the synthetic leather of this invention will be compared with the synthetic leathers obtained by the conventional method and the commercially available synthetic leathers with respect to various properties. The results are shown in table 2 and FIG. 3.

FIG. 3 is a plot of thickness against apparent density for three leathers, of which curve I is for the synthetic leather of the present invention, curve II is for comparison sample A and curve III is for comparison sample B.

Sample A was obtained by the following procedure. The punched web was dip coated with the said solution I under the same conditions, immersed in water at 20° C. for 30 minutes to coagulate the resin, and dried for 10 minutes in a hot air dryer at 120° C. One surface of the web was then coated with solution II by means of a reverse roll coater until the takeup of the solid content reached 54 parts by weights as against 100

parts by weight of the fiber of the web. Immediately thereafter, without coagulating the solution, solution III was applied to the same surface by means of a knife coater until the takeup of the solid content reached 48 parts by weight as against 100 parts by weight of the fiber of the web. The so treated web was immersed in water at 20° C. for 15 minutes to coagulate the solution, immersed in an open soaping at 80° C. for 20 minutes, washed with water, and dried.

Sample B was obtained by impregnating the needle-punched web with the said solution I, coagulating it, applying solution II to one surface of it, coagulating it in water in the like manner, and drying it.

Commercially available sample A is a synthetic leather wherein a woven fabric is disposed between the substrate and the surface coat, and commercially available sample B is a synthetic leather wherein a woven fabric is not disposed between them.

EXAMPLE 9

A prepolymer having a molecular weight of 2,530 was prepared by reacting 1 mole of poly (ϵ -caprolactone) having a molecular weight of 1,850 and an acid value of 0.11 with 2 moles of diphenylmethane-4,4'-diisocyanate. One mole of this prepolymer was reacted with 0.985 mole of ethylenediamine in dimethyl sulfoxide to form a 25 percent polyurethane solution having a viscosity of 1,250 poises. From this solution, three kinds of resin solutions were prepared in the same manner as in example 8, that is, a solution having a concentration of 10 percent and a viscosity of 4 poises, a solution having a concentration of 18 percent and a viscosity of 80 poises prepared by adding 5 parts, based on 100 parts by weight of the solid polyurethane, of carbon black to the original solution, and diluting it with dimethyl sulfoxide to a concentration of 18 percent, and a resin solution having a viscosity of 270 poises prepared by adding carbon black to the original solution and diluting it with dimethyl sulfoxide to a concentration of 20 percent. Synthetic leathers were produced by using these three kinds of solution having a different viscosity and impregnating, coating, coagulating, water washing and drying according to the same procedures as in example 8. These synthetic leathers had a continuous density gradient and a strong cohesion between layers. Excellent shoes could be made from these synthetic leathers without surface roughening in the toe-lasting of a shoe-making process.

EXAMPLE 10

In the same manner as in example 8, three kinds of resin solution were prepared. Namely, we provided a solution having a viscosity of 1 poise prepared by dissolving a copolymer of 35 mole acrylonitrile and 65 mole butadiene in dimethylformamide to a concentration of 10 percent, and two solutions having a viscosity of 200 poises and 850 poises respectively prepared by adding to the said solution 5 parts by weight of carbon black and 20 parts by weight of cellulose powder having an average particle size of 20 microns, all amounts being based on 100 parts by weight of the said solid copolymer content, and diluting the solution with dimethylformamide to a concentration of 20 percent and 25 percent respectively.

TABLE 2

	Thickness (mm.)	Tensile strength (kg./cm.)	Resistance to 10% elongation (kg./cm.)	Density gradient	Bending characteristic	Smoothness	Cohesion between layers (kg./2 cm.)
Product of this invention.....	1.50	18.5	3.50	Like natural leather. ¹	Like natural leather. ⁴	Good.....	Inseparable.
Sample A.....	1.60	16.2	2.80	Some ²	Somewhat rubber-like.....	Ordinary.....	2.2.
Sample B.....	1.60	15.0	2.02	Absent ³	Rubber-like.....	Poor.....	2.0.
Commercially available product A.....	1.60	18.5	6.2	do.....	do.....	Good.....	0.8.
Commercially available product B.....	1.50	16.0	2.7	do. ³	do.....	Ordinary.....	2.2.

¹ See curve I in Fig. 3.

² See curve II in Fig. 3.

³ See curve III in Fig. 3.

⁴ The "like natural leather" means that in a bending test of a synthetic leather at the radius of curvature of 0.5-1.0 cm., a bending resistance B₁ measured when the leather is bent with the surface (grain side) directed outwardly and a bending resistance B₂ measured when the leather is bent with the said surface directed inwardly satisfy the following relation: B₁ > B₂.

The needle-punched web of example 8 was coated with the three solutions in the order of a lower viscosity to give a synthetic leather excellent in cohesion between layers and smoothness which had a continuous density gradient.

EXAMPLE 11

One surface of the web of example 8 containing solution I was coated with a resin solution having a concentration of 30 percent and a viscosity of 2,000 poises obtained by adding 20 parts of poly(vinyl chloride), 10 parts of plasticizer (DOP) and 50 parts of cellulose powder having an average particle size of 20 microns, all amounts being based on 100 parts of the solid polyurethane content, to the polyurethane solution used in example 8 and diluting the solution with dimethylformamide, and further with a resin solution having a concentration of 36 percent and a viscosity of 1,300 poises prepared by adding 10 parts of a plasticizer (DOP) and 30 parts of calcium carbonate, all amounts based on 100 parts of the solid polyurethane content, to the said polyurethane solution, and diluting it with dimethylformamide. The subsequent treatment in the same manner as in example 8 gave a synthetic leather excellent in smoothness and cohesion between layers having a continuous density gradient.

EXAMPLE 12

A web having a weight per unit area of 250 g/m² was produced by means of a random webber from nylon 6 staples having a denier of 3, a fiber length of 51 mm., a number of crimps of 25 turns/inch, and a titanium oxide content of 0.2 percent. The resulting web was passed through a pair of hot rolls heated to 160° C., and set to a thickness of 1.0 mm. The same treatment as in example 9 of this web gave a similar synthetic leather.

We claim:

1. A process for manufacturing synthetic leather, which comprises impregnating a fiber web with a solution of a binder and solvent, coating one surface of the web prior to coagulation of the binder, with a solution of a synthetic resin and solvent having a viscosity higher than that of the binder solution, and simultaneously coagulating the binder and synthetic resin by a wet method wherein the solvents are extracted in a liquid which is compatible with the solvents.

2. The process according to claim 1, wherein the binder and synthetic resin are the same type of polymer.

3. A process for manufacturing synthetic leather, which comprises impregnating a fiber web with a solution of a binder and solvent, applying to one surface of the web prior to coagulation of the said binder, and in the order of increasing viscosities, a plurality of binder solutions exhibiting viscosities differing each from the others, each binder solution having a viscosity higher than the binder solution initially impregnated into the web, coating this same surface of the web prior to

coagulation of the binder solutions, with a solution of a synthetic resin and solvent having a viscosity higher than the last-applied binder solution and within the range of 50-10,000 poises, and simultaneously coagulating the binders and synthetic resin by a wet method wherein the solvents are extracted in a liquid which is compatible with the solvents.

4. The process according to claim 3, wherein each of the binders and the synthetic resin are the same type of polymer.

5. A process for manufacturing synthetic leather, which comprises

a. forming a fiber web of a weight per unit area of 100-1,000 g./cm.²,

b. needle punching the web utilizing a needle penetration depth of 6-12 mm.,

c. impregnating the needle punched web with a solution of a binder and solvent having a viscosity of 0.1-100 poises,

d. coating one surface of the web prior to coagulation of the binder, with a solution of a synthetic resin and solvent having a viscosity higher than that of the binder solution and within the range of 50-10,000 poises whereby liquid-liquid mixing between the binder solution and synthetic resin solution is effected at the interface of the respective solutions,

e. simultaneously coagulating the binder and synthetic resin with water, and

f. drying the resultant product.

6. A process for manufacturing synthetic leather, which comprises

a. forming a fiber web of a weight per unit area of 100-1,000 g./cm.²,

b. needle punching the web utilizing a needle penetration depth of 6-12 mm.,

c. impregnating the needle-punched web with a solution of a binder and solvent having a viscosity of 0.1-100 poises, applying to one surface of the web prior to coagulation of the said binder, and in the order of increasing viscosities, a plurality of binder solutions exhibiting viscosities differing each from the others, each binder solution having a viscosity higher than the binder solution initially impregnated into the web,

d. coating this same surface of the web prior to coagulation of the binder solutions, with a solution of a synthetic resin and solvent having a viscosity higher than the last-applied binder solution and within the range of 50-10,000 poises whereby liquid-liquid mixing among the binder solutions and synthetic resin solution is effected at the interfaces of the the solutions in the order in which they were applied,

e. simultaneously coagulating the binder solutions and synthetic resin solution with water, and

f. drying the resultant product.