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3,483,283 PROCESS FOR PRODUCTION OF SHEET MATERIALS

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7 Claims

ABSTRACT OF THE DISCLOSURE

A napless and surface smooth high density flexible sheet material adapted for use as a leather substitute is prepared by impregnating a needle-punched unwoven mat of synthetic fibers with a temporary binder solution of a polymer which is extractable from the mat with a solvent which has no action on the mat, drying said mat, pressing and/or buffing the surface of said mat, impregnating the binder polymer-impregnated mat throughout with a solution of an elastomeric polymer which is inert to said solvent, coagulating said elastomeric polymer with a liquid which is a non-solvent for said mat and said elastomeric polymer, then removing said binder polymer from the mat with a solvent which has no action on the mat and the elastomeric polymer and drying said mat.

The present invention relates to a process for the production of a sheet material of high density by impregnating an unwoven fibrous sheet or a three-dimensional random web (substance A) composed of fibres with a solution of a polymer (substance B) having a rubbery elasticity and then coagulating the solution by wet process, in which the unwoven fibrous sheet or the web is temporarily set by a binder (substance C) soluble in a specific solvent by means of press before the impregnation procedure, and then impregnated with the solution of the substance B (the polymer having a rubbery elasticity), after which the impregnated solution is coagulated, and thereafter the substance C is extracted and removed with a solvent capable of dissolving only the substance C without dissolving the substances A and B.

The object of the invention is a process for production of flexible sheet material having a high density.

According to the method of the invention, by the use of a temporary binding agent, substance C, it is possible to control the impregnation rate of the solution of the substance B to a desired value, and to prevent deformation of the form in the directions of length, width and thickness in the impregnation and coagulation steps and the deformation of the form of fibre itself, so that naps are not formed and when a coating solution of the substance B is coated on the uncoagulated surface of the impregnated sheet material, a thin and smooth coating layer can be formed. Furthermore, the sheet which is hardened owing to setting by the substance C recovers the original flexibility by extracting and removing the binder (substance C) after coagulating the substance B.

Other process for producing a sheet material of high density has been known wherein a non-compressed sheet material is impregnated with a solution of the substance B and then the sheet material is compressed in a semi-coagulated state of said solution, but in this manner it is difficult to select and control a suitable semi-coagulated state of the solution, so that said known process is not a desirable one as compared with the process according to the invention.

According to the present invention, such a compressing step in the semi-coagulated state is not necessary, which is an important advantage in industry.

When a solution of polymer (substance B) having a high concentration is impregnated in the fibrous sheet followed by coagulation to produce a sheet material, the resulting sheet material has a dense structure, so that even if the binder (substance C) is extracted and removed to remove the adhesion between fibres, the sheet is liable to show still a hard texture. However, if various softening agents which make the substance B porous and flexible when coagulating the substance B by wet process are added in the solution of the substance B, a sheet material of a natural leather like texture which has a denseness due to impregnation of the solution having a high concentration but is not hard, that is flexible, and resilient, can be obtained. Of course, it is possible to produce the sheet materials having various textures and flexibilities depending upon the use purposes of the sheet materials by suitably selecting the conditions, such as, the kinds of the substances A, B and C; the rate of the substance A set by the substance C; the concentration of the substance B; the amount of softening agents added; the density of the layer coated on the surface; the coagulating condition and the like. Further, since the fibres are set according to the process of the invention, thus obtained sheet material has few naps, and an extremely smooth surface. Accordingly such a sheet is useful, when forming a coating layer on a surface of the fibrous sheet, but if the compressed and set unwoven fibrous sheet is subjected to a surface finishing such as buffing, the smoothness is further improved and a very thin (for example 0.2 to 0.3 mm.) and smooth coating layer can be formed.

The fibers for the three-dimensional unwoven fibrous sheet (substance A) in the present invention may be composed of synthetic polymers such as polyamide, polyester, polyacrylonitrile, polyvinyl chloride and polyester and fibers made by spinning mixtures thereof, graft fibers, natural fibers and mixtures thereof.

As the substance B, mention may be made of polymers having rubbery elasticity, such as polyurethane elastomer, N-methoxymethylpolyamide, acrylonitrile-butadiene copolymer, ethylene-vinyl acetate copolymer, various synthetic rubbers, natural rubbers, and the like.

As the substance C use may be made of any binder capable of adhering and setting the substance A, such as polyvinyl alcohol, derivatives thereof, water-soluble starch, carboxymethylcellulose, partially saponified acrylates, polyacrylamide, cellulose acetate, polyvinyl acetate, polyvinyl chloride, and the like, but they must be extracted and removed by a solvent (for example water) which does not dissolve the substances A and B, after impregnating the substance A with the substance B followed by coagulation. In the process of the invention, a sufficient amount of the substance C is used to attain the setting effect and said substance is removed by extraction after coagulating the substance B. This point is also different from the method producing a conventional unwoven fabric in which a small amount of binder is used so as not to injure the texture of the fabric.

The process of the invention will further describe with reference to the following examples, in which parts and percentages are parts by weight and percentages by weight respectively.

EXAMPLE 1

Drawn and crimped nylon-6 staple fibres (5.0 cm.) of 2.0 deniers were formed into a random web, which was subjected to needle punching to provide an unwoven fibrous mat of 300 g./m.² in weight. Thus obtained mat was immersed in 4.5% of an aqueous solution of polyvinyl alcohol and then squeezed to such an extent that

an amount of the solution impregnated was about 150 to 200% of weight of the mat. Thereafter, the mat was dried by hot air to an amount of the solution impregnated of 50 to 80% and then subjected to hot rolling pressing at 120° C., after which the mat was completely dried. By the above process, the original fibrous sheet having about 2.5 mm. in thickness was compressed and set to a thickness of 2.1 mm. and then the resulting sheet was subjected to surface buffing to 1.7 to 1.8 mm. in thickness to improve the smoothness of the surface. A 20% solution of polyurethane elastomer having a molecular weight of 1,500, which consists of polyethylene-propylene-(0.7:0.3 mol)-adipate-glycol, P,P'-diphenylmethane diisocyanate, and ethylene glycol (mol ratio 1:25:1.5) in dimethylformamide was mixed with 6% of sorbitan monostearate and 8% of stearyl alcohol, based on elastomer weight and the resulting impregnating solution was impregnated in the above processed unwoven mat in an amount of about 6 times based on weight of the mat. Thereafter, a coating solution composed of a 22% solution of the same polyurethane elastomer in dimethylformamide was applied on a surface of the mat by slit or reverse coating to such an extent that an amount of the polyurethane elastomer coated was 150 g./m.² (amount of solution: 680 g./m.²) and the impregnated and coated solution was coagulated for 30 min. with a 40% aqueous solution of dimethylformamide controlled at 45° C. The mat was then immersed for 2 hours in hot water at 50 to 60° C. to dissolve off sufficiently the solvent and further squeezed and immersed in hot water at 80° C. repeatedly 6 times for one hour to remove polyvinyl alcohol and then dried by hot air at 80° C. The weight and the thickness of the mat after drying were 770 g./m.² and about 1.8 mm. respectively. After reduced the thickness of the mat to 1.5 to 1.6 mm. The surface of the mat was subjected to colour spraying and emboss finishing to provide a sheet material having a leather like appearance and texture. The properties of thus obtained sheet material are shown in the following table.

TABLE 1

	Product of the invention	Box calf
Weight (g./m. ²)	660	870
Thickness (mm.)	1.50	1.32
Specific gravity (g./cc.)	0.44	0.66
Breaking load (kg./3 cm.)	65	100
Tensile strength (kg./mm. ²)	1.45	2.53
Elongation (percent)	52	57
Young's Modulus (kg./mm. ²)	2.50	2.1
Tear strength (kg.)	4.2	7.9
Moisture permeability ¹ (g./liter/24 hours)	3,620	4,390
Water resistance ²	(3)	(4)

¹ JIS Z-0208.² JIS L-1006-1961.³ 100 cm. 5 min.⁴ 100 above 10 min.

EXAMPLE 2

Drawn and crimped nylon staple fibres (5.0 cm.) having 1.0 denier were formed into a random web, which was subjected to needle punching to obtain an unwoven fibrous mat of 160 g./m.² and the mat was immersed in a 45% aqueous solution of polyvinyl alcohol. After squeezing by pressing to a solution content of 150 to 180%, the mat was dried by hot air at 65° C. to a solution content of 50 to 80% and then dried gradually by means of a cylindrical dryer having a temperature gradient of 70° C. to 120° C. to set the unwoven fibrous mat of 2.5 to 2.7 mm. in thickness to a thickness of 1.2 to 1.4 mm. The surface of the mat was subjected to buff finishing to the thickness of 1.1 mm. Thus prepared mat was impregnated with a 14% solution of a polyurethane elastomer having a molecular weight of 2,000 which consists of polyethylene propylene adipate glycol, P,P'-diphenylmethane diisocyanate and ethylene glycol (mol ratio 1:6:5) in dimethylformamide added with 6% of sorbitan monostearate and 3% of stearyl alcohol based on elastomer weight in an amount of 7 times of weight of the

mat. The surface of the mat was squeezed to remove the excess solution. A coating solution of a 12% solution of the above mentioned polyurethane elastomer in dimethylformamide was coated on the surface of the mat to such an extent that an amount of the polyurethane elastomer coated was 40 g./m.² (amount of solution: 335 g./m.²). Thereafter, the impregnated and coated solution was coagulated for 20 min. with a 30% aqueous solution of dimethylformamide adjusted to 40° C. and the mat was washed with hot water at 50 to 60° C. for 1 hour to remove the solvent. Then after removed polyvinyl alcohol by squeezing and immersing repeatedly in hot water at 80° C. 6 times for 1 hour, the mat was dried by hot air at 80° C. After drying, the weight and the thickness of the sheet were 290 g./m.² and 1.1 mm. respectively. The back face was cut out by 0.2 to 0.3 mm. to obtain the thickness of about 0.8 mm. The sheet was then dyed and treated by a softening agent (lubricating agent), and then subjected to emboss treatment and spray finishing to provide the leather like sheet material as shown in Table 2.

TABLE 2

	Product of the invention	Sheepskin
Weight (g./m. ²)	240	260
Thickness (mm.)	0.8	0.59
Specific gravity (g./cc.)	0.30	0.44
Breaking load (kg./3 cm.)	19.0	21.4
Tensile strength (kg./mm. ²)	0.80	1.21
Elongation (percent)	62	45.0
Young's Modulus (kg./mm. ²)	1.31	1.47
Tear strength (kg.)	3.2	1.40
Moisture permeability (g./m. ² /24 hours)	3,560	6,895
Water resistance (hour)	(1)	(2)

¹ 3.5 centimeters.² 10 centimeters, 8 seconds.

EXAMPLE 3

A web consisting of polyacrylonitrile fibres of 2 deniers and 60 cm. in length was subjected to needle punching to provide an unwoven fibrous sheet having a specific gravity of 0.09 and 300 g./m.² and a three-dimensional structure. The unwoven fibrous sheet was immersed in a 10% solution of polyvinyl acetate in methanol and then was squeezed to such an extent that an amount of said resin impregnated was 20% based on weight of the unwoven sheet, after which methanol was evaporated. The unwoven fibrous sheet was heat pressed to reduce the thickness and increase the specific gravity of 0.25. That is, the fibre density of the unwoven fibrous sheet was increased about 2.2 times by the treatment with the binder. Thus pressed and set unwoven fibrous sheet was immersed in a synthetic rubber latex comprising acrylonitrile-butadiene and the unwoven fibrous sheet was squeezed to such an extent that an amount of the latex impregnated was 3 times based on the weight of the unwoven fibrous sheet, and dried. The polyvinyl acetate set the unwoven fibrous sheet was extracted and removed by methanol and further, the sheet was washed with water and dried by hot air at 70° C. Thus obtained sheet was flexible and strong. The resulting sheet can be used conveniently for mounting materials for furnitures and house decoration as leather like sheet materials by applying a suitable film or coating or spraying a polymer solution on the surface thereof.

What we claim is:

1. A process for the manufacture of a flexible leather-like sheet material which comprises the steps of (1) providing a non-woven mat of needle-punched fibers, (2) impregnating said mat with a solution of an adhesive first polymer selected from the group consisting of polyvinyl alcohol, polyvinyl acetate, polyvinyl chloride, polyacrylamide, partially saponified acrylates, cellulose acetate, carboxymethylcellulose and water-soluble starch as a temporary binder for the fibers thereof, (3) setting said first polymer by heat and pressure thereby binding fibers thereof and forming a sheet of a predetermined thickness, (4) impregnating said sheet with a

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solution of an elastomeric second polymer from the group consisting of polyurethane, N-methoxy polyamide, acrylonitrile-butadiene copolymer, ethylene-vinyl acetate copolymer, synthetic rubber and natural rubber and a softening agent therefor, (5) coagulating and setting said second polymer, and (6) then removing said adhesive first polymer from the resulting sheet by extraction thereof with a solvent for said first polymer which solvent is inert to said fibers and to said second polymer, thereby producing a flexible, moisture-permeable leather-like sheet.

2. A process for the manufacture of a flexible leather-like sheet material which comprises the steps of (1) providing a non-woven mat of needle-punched fibers, (2) impregnating said mat with a solution of an adhesive first polymer selected from the group consisting of polyvinyl alcohol, polyvinyl acetate, polyvinyl chloride, polyacrylamide, partially saponified acrylates, cellulose acetate, carboxymethylcellulose and water-soluble starch as a temporary binder for the fibers thereof, (3) setting said first polymer by heat and pressure thereby binding fibers thereof and forming a sheet of a predetermined thickness, (4) impregnating said sheet with a dilute solution of an elastomeric second polymer from the group consisting of polyurethane, N-methoxy polyamide, acrylonitrile-butadiene copolymer, ethylene-vinyl acetate copolymer, synthetic rubber and natural rubber, (5) coagulating and setting said second polymer, and (6) then removing said adhesive first polymer from the resulting sheet by extraction thereof with a solvent for said first polymer which solvent is inert to said fibers and to said

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second polymer, thereby producing a flexible, moisture-permeable leather-like sheet.

3. A process according to claim 2 wherein the fibers are selected from the group consisting of polyamide fibers and polyamide-polystyrene fibers.

4. A process according to claim 2 wherein the elastomeric polymer is polyurethane.

5. A process according to claim 4 wherein the fibers are polyamide and the adhesive polymer is polyvinyl alcohol.

6. A process according to claim 2 wherein an elastomeric polymer is applied to and coagulated on at least one surface of the impregnated sheet.

7. A process according to claim 2 wherein the adhesive first polymer is polyvinyl acetate and the extracting solvent is methanol.

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