(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 134 899 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
15.12.2010 Bulletin 2010/50

(21) Application number: **07736695.3**

(22) Date of filing: **16.03.2007**

(51) Int Cl.:
D06N 3/14 *(2006.01)* ***D06N 3/00*** *(2006.01)*

(86) International application number:
PCT/IT2007/000190

(87) International publication number:
WO 2008/114284 (25.09.2008 Gazette 2008/39)

(54) **PROCESS FOR THE PREPARATION OF A SEMIFINISHED MATERIAL TO BE USED TO PRODUCE LEATHER- LIKE ARTICLES OR COATED FABRICS AND MATERIAL THEREOF**

VERFAHREN ZUR HERSTELLUNG EINES HALBZEUGS ZUR HERSTELLUNG LEDERARTIGER ERZEUGNISSE ODER BESCHICHTETER GEWEBE UND MATERIAL DARAUS

PROCÉDÉ DE PRÉPARATION D'UN MATÉRIAU SEMI-FINI À UTILISER POUR PRODUIRE DES ARTICLES EN SIMILICUIR OU DES TISSUS ENDUITS ET MATÉRIAU ASSOCIÉ

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR

(43) Date of publication of application:
23.12.2009 Bulletin 2009/52

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Description

FIELD OF THE INVENTION

[0001] . The present invention relates to a process for preparing a semifinished material to be used for manufacturing leather-like or coated fabric items and a semifinished product that can be obtained by means of said process. Particularly, this invention relates to a Process allowing to obtain a semifinished product provided with excellent tactile, visual and mechanical characteristics suitable to make it advantageously exploitable in a number of fields of leather-like or coated fabric items such as, for example, shoes, bags, sofas.

BACKGROUND OF THE INVENTION

[0002] . Semifinished materials that can be used in the leather-like or coated fabrics fields have been known for some time. These materials generally consist of a woven or nonwoven backing which is treated with polymeric substances such as to give characteristics of elasticity, resistance and touch as much similar as possible to natural hide and leather.

[0003] . These characteristics are usually obtained by subjecting the substrate to a conventional coagulation treatment in which a polymeric resin in the liquid state is deposited on said backing, coated and treated by means of suitable equipment such as to obtain the coagulation of the resin on the surface thereof. A polyurethane coating layer is described in JP 04 308280, JP 63 085185 and JP 05 163683.

[0004] . At the same time, a liquid polymeric layer is prepared on paper and then cured. This step has the function of preparing the visible part of the semifinished material according to patterns or designs as desired.

[0005] . The polymeric layer on paper is then coated, on the polymer side, with an adhesive substance, also of polymeric nature, on which is placed said backing that has been subjected to coagulation and the whole is treated such as to obtain an individual sheet of multilayer material, which is used for manufacturing items such as shoes, bags, upholstery for sofas.

[0006] . The materials resulting from the Process described above is provided with such tactile, resistance, abrasion, ageing, lightfastness characteristics as to be suitable to be used as a substitute for hide or natural leather in the manufacture of said items.

[0007] . While the prior art semifinished material is successfully traded, it however has important limitations mainly in terms of scratch resistance, abrasion resistance, flex life, lightfastness.

[0008] . In other words, the performance of the material is limited, such that a need is felt in the field to find a material with improved characteristics, which allows a more convenient use or even novel characteristics.

SUMMARY OF THE INVENTION

[0009] . The technical problem addressed by the present invention is thus to provide a semifinished material to be used in the manufacture of leather-like or coated fabric items which is capable of having typical characteristics of said materials that are considerably improved as compared with the currently marketed materials, as well as novel characteristics.

[0010] . This problem is solved by a process for manufacturing a semifinished material that is capable of giving said characteristics thus making the final product not only substantially identical to hide and natural leather, but also provides improved physical-mechanical characteristics as compared with known materials.

[0011] . A first object of the present invention is, accordingly, a process for preparing a semifinished product to be used in the manufacture of leather-like or coated fabric items.

[0012] . A second object of the invention is a semifinished material that can be obtained in accordance with said process.

DETAILED DESCRIPTION OF THE INVENTION

[0013] . As extensive testing has proved, it has been surprisingly found that when a suitable backing is treated with a particular selection of polymeric substances, a semifinished material can be obtained, which is provided with unexpectedly improved characteristics as compared with the currently marketed materials.

[0014] . In accordance with the present invention, the process for preparing a semifinished material for manufacturing leather-like or coated fabric items, thus comprises the steps of:

- providing a woven or nonwoven substrate;
- providing a liquid coagulation mixture comprising an aliphatic or aromatic polycarbonate-base polyurethane polymer, an organic solvent, and optionally water;
- depositing at least one layer of said liquid mixture on said substrate;
- coagulating said mixture on said substrate.

[0015] . Preferably, the woven or nonwoven substrate can be selected from polyester and/or cotton fabrics, polyester microfiber, polyester elastomer, polyamide, polyamide elastomer, mono or multilayer spunlace and/or spunbonded and/or carded nonwoven, needled polyester viscose, polyamide polyester, viscose polyamide nonwovens. More preferably, the substrate is a woven fabric, polyester and cotton twill weave cloth, thickness of 0.3 to 0.6 mm, weft linear density Ne 6 $\pm$ 1, 100% cotton, 14 beat-up $\pm$ 1, warp linear density Ne 16 $\pm$ 1, 25 polyester threads (65%) cotton (35%) or nonwoven 100% polyester, 150 gr/m^2 Spunlace, linear density 1.950 dtex, thickness 0.3/0.6 mm.

[0016] . The coagulation liquid mixture comprises an aliphatic or aromatic polycarbonate-base polyurethane polymer. More preferably, it is an aliphatic polycarbonate-base polyurethane polymer. Still more preferably, the polymer is in liquid form and is characterised by a solid content of 29% to 31% by weight upon the weight of the liquid dissolved in DMF (dimethylformamide) of 71% to 69% by weight upon the weight of the liquid, by a viscosity of 800-1200 DPA.S (calculated by means of a Brookfield viscometer according to the manufacturer's procedure) at 25°C under dynamic rotation, by 350% elongation rate, by 100% modulus (MPa) of 3.5 and 300% modulus (MPa) of 18. Particularly, a polymer provided with said characteristics is for example the product sold by DAINIPPON under the trade name of CRISVON™ SPM 12.

[0017] . The organic solvent can be any of the organic solvents commonly used for diluting polymer resins such as, for example, a polar solvent such as methoxy propanol methyl acetate and dimethylformamide. This solvent is added at amounts ranging between 60% and 50% by weight upon the weight of the coagulation mixture such that the final polymer amount in this mixture ranges between 11.6% and 15.5%. Preferably, this solvent is dimethylformamide (DMF). Dimethylformamide can be used at such amounts as to dilute the polymeric moiety of the mixture to 40-50% by weight upon the mixture total weight.

[0018] . Furthermore, said mixture can preferably also comprise cellulose fiber ranging between 1% and 25% by weight upon the mixture total weight.

[0019] . The coagulation mixture can further comprise a flame retardant preferably phosphates and chlorides-based at a ratio between 1% and 20% by weight upon the mixture total weight. This flame retardant can be selected from conventional organic derivate halogens.

[0020] . Said first mixture is prepared by first mixing the dimethylformamide (DMF) with the optional flame retardants and the optional cellulose fiber and then adding the polyurethane resin and the colouring agents at said amounts under stirring.

[0021] . The step of depositing the mixture on the substrate can be preferably carried out based on a type of technique known in the field.

[0022] . This technique provides coating the mixture. The coating is carried out by continuously depositing the liquid mixture on a rotating smooth roller upon which and at a predetermined distance from the surface thereof is positioned a blade having the function of controlling and keeping a constant and uniform layer of mixture applied to the substrate.

[0023] . In any case, independently of the technique used, the deposit is carried out such as to release one or more layers of said coagulation mixture on the substrate, having a thickness of 0.1 to 2 mm, preferably of 0.5 to 1.5 mm.

[0024] . The coagulation is carried out by dipping the substrate with the respective mixture being applied thereto into a water-containing tank at a temperature ranging between 10° and 50°C, preferably between 20° and 40°C, for a time ranging between 8 minutes and 10 minutes. Preferably, the tank comprises water and dimethylformamide at a ratio of 95% water and 5% dimethylformamide to 5% water and 95% dimethylformamide upon total weight.

[0025] . Subsequently, the coagulation is ended with washing and drying steps. The washing is carried out by passing the substrate into more washing tanks where water at a temperature ranging between 15° and 50°C, preferably between 20° and 40°C, flows countercurrently relative to the feeding direction of the substrate. The drying can be carried out in a conventional oven at a temperature ranging between 100° and 150°C, preferably between 120° and 130°C for a time ranging between 5 minutes and 8 minutes, according to the type of substrate being treated.

[0026] . Preferably, furthermore, the process according to the invention can comprise a step of wetting said substrate with water optionally admixed to an organic solvent prior to the application of the coagulation mixture layer. This step has the purpose of preventing the coagulation mixture from passing through the entire thickness of the substrate and thus maintaining, after the mixture polymer has been coagulated, a higher level of softness of the substrate mainly when the final material must meet particular requirements just in terms of touch.

[0027] . The step of wetting said woven or nonwoven substrate before applying the liquid coagulation mixture can be carried out by dipping the substrate in a water-containing tank or in a water/organic solvent wetting solution in which 2% to 60% organic solvent is provided upon the total weight of the wetting solution. Particularly, the organic solvent can be any conventional organic solvent. For example, the dimethylformamide can be used in solution with water.

[0028] . Said wetting step can be followed by a drying step. Particularly, the drying step can comprise a twisting step, for example by passing through a pair of rollers, and a heating step into a conventional oven at a temperature ranging between 30° and 100°C for a time ranging between 5 minutes and 8 minutes according to the type of substrate being used.

[0029] . It should be noted that said liquid coagulation mixture can further comprise conventional inorganic and/or organic pigment-based colouring agents such as to give colours to the semifinished material suitable to the final purpose, i.e. providing items such as those illustrated above.

[0030] . In addition, the material resulting from the process described above can be subjected to further peculiar processing steps of the textile/tanning finishing operations, aiming at changing the appearance and touch according to particular requirements or preferences also dictated by the type of the desired final product to be manufactured. Examples of conventional processing can be mechanical processing in a dry/humid environment, optionally additioned with silicone softeners, such as

drumming, creasing, ageing processing, pleating, tumbler working, perching.

[0031] . In accordance with a variant embodiment, the process for preparing a semifinished material for manufacturing leather-like or coated fabric items can comprise the further steps of:

- providing a "skin" liquid mixture, comprising a polymer of polyurethanes, polyesters, both aromatic and aliphatic polyesters or polycarbonates, in solution with a mixture of at least two organic solvents;
- depositing at least one layer of said mixture on said layer of coagulated mixture of said woven or nonwoven substrate;
- hardening said at least one layer.

[0032] . The step of depositing the skin mixture can be carried out by means of two types of techniques. The first technique provides depositing the mixture on the substrate and then passing the substrate through a pair of rollers of which at least one is provided with a surface carrying drawings or patterns suitable to model the mixture prior to hardening, according to the desired final appearance to be obtained for the material.

[0033] . The second type is substantially identical to the coating step described above with reference to the treatment of the woven or nonwoven substrate with the coagulation mixture with the difference that the coating or deposit is carried out on a paper backing (release paper) which is then joined to the woven or nonwoven substrate.

[0034] . Particularly, the second type comprises:

- depositing at least one layer of said "skin" mixture on a paper backing;
- hardening said at least one layer of "skin" mixture on said paper backing;
- providing an liquid adhesion mixture comprising a polymer such as set forth with reference to the coagulation mixture and organic solvents;
- depositing said adhesion mixture on said at least one layer of said "skin" mixture;
- placing said coagulated backing on said adhesion mixture layer such that the coagulated layer of the substrate mixture is contacted with said adhesion mixture;
- curing said adhesion mixture such as to obtain the adhesion between said substrate and said paper backing to form the semifinished material.

[0035] . The polymers that can be used for the "skin" mixture preferably comprise a polymer of polyurethanes, polyesters, both aromatic and aliphatic polyesters or polycarbonates at amounts ranging between 1,9% and 18.9% by weight upon the mixture total weight, More preferably, the polymer is polycarbonate base aliphatic polyurethane. Still more preferably, the polymer is in liquid form and is characterised by a solid content of 19% to 21% by weight, by a viscosity ranging between 300 and 600 DPA.S (calculated by means of a Brookfield viscometer according to the manufacturer's procedure) at 25°C under dynamic rotation, by an elongation rate of 330%, by a 100% modulus (MPa) of 20 and 300% modulus (MPa) of 46.5. Particularly, a polymer provided with said characteristics is for example the product sold by DAINIPPON under the trade name of CRISVON™ NY 324D.

[0036] . The organic solvents used for diluting the "skin" mixture polymer are preferably prepared in a mixture of at least two selected from toluene, isobutyl methyl ketone, methoxy propanol methyl acetate, cyclohexanone, acetone, methyl ethyl ketone and dimethylformamide. Particularly, the solvents are used at amounts ranging between 10% and 90% by weight upon the total weight of the "skin" mixture. More preferably, the solvent mixture consists of DMF and MEK (methyl ethyl ketone) used at amounts of 28% and 7% by weight upon the total weight of "skin" mixture, respectively.

[0037] . The "skin" mixture can further comprise 0.05% to 5% by weight upon the total weight of the silicone oil mixture. Preferably, the silicone oils are selected from touch modifiers or low-migration flow additives, which are well known in the field, for example the product sold by Cytec under the trade name of Ucecoat™ stm.

[0038] . Furthermore, the mixture can comprise inorganic and/or organic colouring agents, for example in the form of pastes with high weathering and chemical resistance at amounts of 10% to 20% by weight upon the mixture weight and can be selected from the series of Poliplast™ LA products sold by Irsea S.p.a.

[0039] The step of hardening said mixture on a paper backing is carried out by means of heating at a temperature ranging between 60° and 150°C for a period of time ranging between 3 minutes and 5 minutes according to the type of backing. Particularly, the mixture is coated on the paper backing by means of conventional equipment (for flexographic printing) such as to create a thickness ranging between 0.50 mm and 1.05 mm.

[0040] . The liquid adhesion mixture comprises a polymer identical to the polymer described above with reference to the coagulation mixture.

[0041] . Particularly, the adhesion mixture differs from the coagulation mixture in that the polymer is diluted with an organic solvent mixture comprising at least two solvents that are preferably selected from toluene, methyl isobutyl ketone, methoxy propanol methyl acetate, cyclohexanone, acetone, methyl ethyl ketone and dimethylformamide. Particularly, the solvents are provided in the adhesion mixture at amounts ranging between 15% and 40% by weight such as to obtain a polymer amount of 2.9% to 12.4% by weight upon the mixture total weight. More preferably, the mixture consists of 14% DMF and 20% MEK (methyl ethyl ketone) upon the total weight of the adhesion mixture.

[0042] . The step of depositing the adhesion mixture on: the backing is substantially carried out in the same manner in which the "skin" mixture is deposited, again,

on the paper backing. Preferably, a layer of said mixture is deposited with a thickness ranging between 0.5 to 1.00 mm.

[0043] . The step of curing the adhesion mixture is carried out after the coagulated substrate has been deposited on the hardened backing and covered with the adhesion mixture still in the liquid state, such that the corresponding faces that have been treated with the mixtures come in contact with each other. This curing is preferably carried out by heating in oven at temperatures ranging between 60° and 150°C for a time ranging between 2 and 5 minutes.

[0044] . The advantage offered by this variant embodiment is that the semifinished material can be provided with aesthetic characteristics of various nature according to the requirements or preferences. In fact, both the use of embossed rolls and paper backing act as a negative impression for forming predetermined aesthetic designs.

[0045] . The final product obtained is a semifinished material comprising a woven or nonwoven layer having a thickness of 0.3 mm to 0.6 mm and a polymeric layer having a thickness of 0.1 mm to 4.05 mm, preferably the latter ranges from 0.5 to 1.5 mm.

[0046] . Particularly, said material is characterized by having the following features:

- softness identical to or higher than that typical of natural leather;
- abrasion resistance according to EN 13520 Martindale test higher than 30,000 dry cycles, preferably 1 million cycles and higher than 6,000 wet cycles, preferably 300,000 cycles;
- flex life according to EN 13512 Bally test at ambient temperature higher than 150,000, preferably 400,000 and at a temperature of -10°C higher than 30,000, preferably 100,000;
- lightfastness according to UNI 9427 Xenotest with 1500 watt lamp higher than 72 h, preferably 150H (8 blue scale) ;
- fastness to ageing, according to EN 12749 hydrolysis test, 8 week duration, does not exhibit any physical-mechanical deterioration.

[0047] . A further object of the present invention is a leather-like or coated fabric item comprising a semifinished material as described above. Particularly, items that can comprise the subject material can be typical items of the shoe industry, bags and suitcases, briefcases, wallets, key rings, belts, furnishing items such as pieces of furniture, sofas, armchairs (also in the nautical field), sanitary coverings, and various furnishing accessories.

[0048] . An embodiment given by way of non-limiting example of the invention is given herein below.

PREPARATION OF THE COAGULATED SUBSTRATE

[0049] . A fabric roll, polyester and cotton twill weave cloth, thickness of 0.4 to 0.6 mm, weft linear density Ne 6 ± 1, 100% cotton, 14 beat-up ±1, warp linear density Ne 16 ±1, 25 polyester threads (65%) cotton (35%) or nonwoven, 100% polyester, 150 gr/m^2 Spunlace, linear density 1.950 dtex, thickness 0.4/0.6 mm is unwound and passed through a conventional coagulation equipment where it is dipped into a tank containing water such as to obtain the complete wetting of the same. Subsequently, the woven or nonwoven fabric is passed through a pair of rollers to carry out twisting and eliminating most of the water. The woven or nonwoven fabric is then passed into a heated oven at a temperature of 60°C for 3 minutes to be dried. After it has been dried, it is sent to the coating station where the coagulation mixture is applied, which consists of CRISVON™ SPM 12 sold by DAINIPPON diluted with 55% DMF. Particularly, a tube positioned above the woven or nonwoven fabric roll deposits, continuously and with a back and forth movement along the roll axis, the mixture in the liquid form during the unwinding rotation of said roll. Simultaneously, both adjacent and downstream of the tube, a blade ensures that the proper amount of mixture is evenly coated all over the surface of the woven or nonwoven fabric.

[0050] . Thereafter, the coated woven or nonwoven fabric enters a coagulation station embodied by a tank containing a solution of 10% DMF and 90% water at a temperature of 30°C and is left there for 10 minutes.

[0051] . The woven or nonwoven fabric exiting the coagulation tank is sent to six different washing tanks where countercurrent water flows in order to take up the solvent.

PREPARATION OF THE PAPER BAKING (RELEASE PAPER)

[0052] . A roll of plasticized release paper having a desired pattern is unwound within a conventional release paper-treating equipment. In this equipment, during said unwinding, a blade for flexographic printing continuously deposits a first mixture consisting of the CRISVON™ NY 324D liquid polymer sold by DAINIPPON diluted with 27% DMF and 7% MEK and additioned with 1% silicone oils and 15% conventional colouring pastes in the same manner as described above with reference to the deposit of the coagulation mixture. After the deposit has been carried out, the backing is continuously passed into a heated oven at a temperature of 100°C and resides there for a time of 5 minutes, thereby ensuring the hardening of the same.

[0053] . At this stage, an adhesion mixture consisting of CRISVON™ SPM 12 diluted with 13% DMF and 20% MEK and 15% conventional colouring pastes is deposited in an entirely similar manner to what has been described above on the hardened layer of the first mixture.

COMPOSITION OF THE SEMIFINISHED MATERIAL

[0054] . By means of a conventional equipment, the coagulated substrate roll is unwound and the woven or nonwoven fabric is placed with the coagulated side there-

of on the substrate on which the adhesion mixture has been just deposited. At this stage, the coagulated woven or nonwoven substrate and coated release paper backing, thus overlapped, are passed into a heated oven at 100°C for a time of 5 minutes during which the adhesion mixture is cured, such as to join the substrate to the backing. Finally, the material exiting from the oven is cooled on water-cooled cylinders and the release paper is removed therefrom. The thus-obtained semifinished material has been subjected to some testing and has exhibited surprising characteristics. Particularly, said material is characterised in that it has the following characteristics:

- abrasion resistance according to EN 13520 Martindale test, 1 million dry cycles and 300,000 wet cycles;
- flex life according to the EN 13512 Bally test, at ambient temperature of 400,000 and at -10°C temperature of 100,000;
- lightfastness according to UNI 9427 Xenotest with 1500 watt lamp of 150H (8 blue scale);
- fastness to ageing, according to the EN 12749 hydrolysis test, 8 week-ageing, it does not exhibit any physical-mechanical deterioration.

[0055] . Now, it should be understood that the material in accordance with the invention allows meeting the requirements as set forth in the introductory part of the present description.

[0056] . Particularly, the characteristics found during the testing have surprisingly evidenced incredibly improved values as compared with conventional materials produced in accordance with known techniques. Furthermore, the appearance and touch sensation have proved to be very similar to, and in some cases, better than natural hide and leather.

[0057] . Further variant embodiments of the process and material can be conceived and carried out by those skilled in the art while remaining within the scope of protection of the invention such as defined in the annexed claims herein below.

Claims

1. A process for preparing a semifinished material for manufacturing leather-like or coated fabric items comprises the steps of:

   - providing a woven or nonwoven substrate;
   - providing a liquid coagulation mixture comprising a polymer of aliphatic or aromatic polycarbonate base polyurethane, an organic solvent, and optionally water;
   - depositing at least one layer of said liquid mixture on said substrate;
   - coagulating said mixture on said substrate;

   characterised in that said substrate is wetted with water optionally admixed to an organic solvent before depositing the coagulation mixture.

2. The process according to claim 1, wherein the woven or nonwoven substrate is selected from polyester and/or cotton fabrics, polyester microfiber, polyester elastomer, polyamide, polyamide elastomer, mono or multilayer spunlace and/or spunbonded and/or carded nonwoven, needled polyester viscose, polyamide polyester, viscose polyamide nonwovens.

3. The process according to claim 1 or 2, wherein the substrate is a woven fabric, polyester and cotton twill weave cloth, thickness of 0.4 to 0.6 mm, weft linear density Ne 6 ± 1, 100% cotton, 14 beat-up ± -1, warp linear density Ne 16 ± -1, 25 polyester threads (65%) cotton (35%) or 100% polyester nonwoven, 150 gr/m^2 Spunlace, 1,950 dtex linear density, thickness 0.4/0.6 mm.

4. The process according to any claim 1 to 3, wherein said polymer is provided at amounts of 11.6% to 15.5% by weight upon the total weight of the coagulation mixture.

5. The process according to any claim 1 to 4, wherein said coagulation mixture comprises a liquid polymeric portion wherein the polymer is **characterized by** a solid content of 29% to 31% by weight upon the weight of the liquid dissolved in organic solvent, viscosity ranging between 800 and 1200 DPA.S at 25°C under dynamic rotation, elongation rate of 350%, 100% module (MPa) of 3,5 and 300% module (MPa) of 18.

6. The process according to any claim 1 to 5, wherein said organic solvent is a polar solvent such as methoxy propanol methyl acetate and dimethylformamide provided at amounts ranging between 50% and 60% by weight upon the total weight of the coagulation mixture.

7. The process according to claim 6, wherein said organic solvent is dimethylformamide used at amounts of 50-60% by weight upon the total weight of the mixture.

8. The process according to any claim 1 to 7, wherein said coagulation mixture comprises cellulose fiber at amounts ranging between 1% and 25% by weight upon the mixture total weight.

9. The process according to any claim 1 to 8, wherein said first mixture comprises a flame retardant at amounts ranging between 1% and 20% by weight upon the mixture weight.

10. The process according to any claim 1 to 9, wherein the deposit of one or more layers of said coagulation

mixture is carried out such as to form a thickness ranging between 0.1 and 2 mm.

11. The process according to any claim 1 to 10, comprising the further steps of:

- providing a "skin" liquid mixture, comprising a polymer of polyurethanes, polyesters, both aromatic and aliphatic polyesters or polycarbonates, in solution with a mixture of organic solvents;
- depositing at least one layer of said mixture on said layer of coagulated mixture of said woven or nonwoven substrate on the coagulated side;
- hardening said at least one "skin" mixture layer.

12. The process according to claim 11, wherein the depositing step comprises depositing the "skin" mixture on said substrate and subsequently passing the substrate through a pair of rolls of which at least one is provided with a surface carrying drawings or patterns.

13. The process according to claim 11, wherein the depositing step comprises:

- depositing at least one layer of said "skin" mixture on a paper backing;
- hardening said at least one layer on said paper backing;
- providing a liquid adhesion mixture, comprising a polymer of polyurethanes, polyesters, both aromatic and aliphatic polyesters or polycarbonates, in solution with at least two organic solvents;
- depositing said adhesion mixture on said at least one layer of said "skin" mixture;
- placing said coagulated backing on said adhesion mixture layer such that the coagulated layer of the substrate mixture is contacted with said adhesion mixture;
- curing said adhesion mixture such as to obtain the adhesion between said substrate and said paper backing to form the semifinished material.

14. The process according to claim 13, wherein said polymer of said "skin" mixture is provided at amounts ranging between 1.9% and 18.9% by weight upon the mixture total weight and said at least two organic solvents are provided at amounts between 10% and 90% by weight upon the weight of said "skin" mixture.

15. The Process according to claim 14, wherein said at least two organic solvents are selected from toluene, methyl isobutyl ketone, methoxy propanol methyl acetate, cyclohexanone, acetone, methyl ethyl ketone and dimethylformamide.

16. The process according to any claim 11 to 15, wherein said "skin" mixture comprises a liquid polymeric portion wherein the polymer is **characterized by** a solid content of 19% to 21% by weight upon the mixture weight, by a viscosity ranging between 300 and 600 DPA.S at 25°C under dynamic rotation, elongation rate of 330%, 100% module (MPa) of 20 and 300% module (MPa) of 46.5.

17. The process according to any claim 11 to 15, wherein said "skin" mixture comprises 28% DMF and 7% MEK (methyl ethyl ketone) upon the total weight of said mixture, as the organic solvents.

18. The process according to any claim 11 to 17, wherein said "skin" mixture comprises silicone oils at amounts ranging between 0.05% and 5% by weight upon the mixture weight.

19. The process according to any claim 13 to 18, wherein the step of hardening said skin mixture on a paper backing takes place such as to create a thickness ranging between 0.50 mm and 1.05 mm.

20. The process according to any claim 13 to 19, wherein the adhesion mixture comprises a polymer identical to that used for the coagulation mixture, diluted with a mixture of at least two organic solvents selected from toluene, methyl isobutyl ketone, methoxy propanol methyl acetate, cyclohexanone, acetone, methyl ethyl ketone and dimethylformamide.

21. The process according to any claim 13 to 20, wherein the polymer of said adhesion mixture is provided at amounts of 2.9% to 12.4% by weight upon the total weight of the mixture.

22. The process according to any claim 13 to 21, wherein the solvents are DMF and MEK (methyl ethyl ketone) at amounts of 14% and 20% upon the mixture weight, respectively.

23. The process according to any claim 13 to 22, wherein a layer of said adhesion mixture is applied with a thickness ranging between 0.5 and 1 mm.

Patentansprüche

1. Verfahren zum Herstellen eines Halbzeugs zur Produktion von lederartigen Gegenständen oder Gegenständen aus beschichtetem Gewebe, umfassend die Schritte:

- Bereitstellen eines gewebten oder nichtgewebten Substrats;
- Bereitstellen einer flüssigen Koagulationsmischung umfassend ein Polymer aus Polyu-

rethan basierend auf aliphatischem oder aromatischem Polycarbonat, ein organisches Lösungsmittel und gegebenenfalls Wasser;
- Abscheiden von wenigstens einer Schicht der flüssigen Mischung auf dem Substrat;
- Koagulieren der Mischung auf dem Substrat;
dadurch gekennzeichnet, dass das Substrat vor dem Abscheiden der Koagulationsmischung mit Wasser, das gegebenenfalls mit einem organischen Lösungsmittel vermischt ist, angefeuchtet wird.

2. Verfahren nach Anspruch 1, wobei das gewebte oder nichtgewebte Substrat ausgewählt ist aus Polyester- und/oder Baumwollgeweben, Polyester-Mikrofaser, Polyester-Elastomer, Polyamid, Polyamid-Elastomer, Mono- oder Mehrschichten-Spunlace und/oder Spinnvlies und/oder kardiertem Faservlies, genadelter Polyester-Viskose, Polyamid-Polyester, Viskose-Polyamid-Faservliesen.

3. Verfahren nach Anspruch 1 oder 2, wobei das Substrat ein Gewebe, Polyester- und Baumwollköpergewebe, Dicke 0,4 bis 0,6 mm, längenbezogene Masse des Schussfadens (weft linear density) Ne 6 $\pm$ 1, 100 % Baumwolle, 14 Schussanschlag (beat-up) $\pm$ -1, längenbezogene Masse des Kettfadens (warp linear density) Ne 16 $\pm$ -1, 25 Polyesterfäden (65 %) Baumwolle (35 %) oder 100 % Polyester-Faservlies, 150 g/m^2 Spunlace, 1950 dtex längenbezogene Masse, Dicke 0,4/0,6 mm ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, wobei das Polymer in Mengen von 11,6 bis 15,5 Gew.-%, bezogen auf das Gesamtgewicht der Koagulationsmischung, bereitgestellt wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die Koagulationsmischung einen flüssigen polymeren Anteil umfasst, wobei das Polymer **gekennzeichnet ist durch** einen Feststoffgehalt von 29 bis 31 Gew.-%, bezogen auf das Gewicht der Flüssigkeit, gelöst in einem organischen Lösungsmittel, eine Viskosität im Bereich zwischen 800 und 1200 DPA.S bei 25 °C unter dynamischer Rotation, eine Dehnungsrate von 350 %, 100 % Modul (MPa) von 3,5 und 300 % Modul (MPa) von 18.

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei das organische Lösungsmittel ein polares Lösungsmittel wie Methoxypropanol, Methylacetat und Dimethylformamid ist, das in Mengen im Bereich zwischen 50 und 60 Gew.%, bezogen auf das Gesamtgewicht der Koagulationsmischung, bereitgestellt wird.

7. Verfahren nach Anspruch 6, wobei das organische Lösungsmittel Dimethylformamid ist, das in Mengen von 50-60 Gew.-%, bezogen auf das Gesamtgewicht der Mischung, verwendet wird.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei die Koagulationsmischung Cellulosefaser in Mengen im Bereich zwischen 1 und 25 Gew.-%, bezogen auf das Gesamtgewicht der Mischung, umfasst.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei die erste Mischung ein Flammschutzmittel in Mengen im Bereich zwischen 1 und 20 Gew.-%, bezogen auf das Gewicht der Mischung, umfasst.

10. Verfahren nach einem der Ansprüche 1 bis 9, wobei die Abscheidung von einer oder mehreren Schichten der Koagulationsmischung so ausgeführt wird, dass eine Dicke im Bereich zwischen 0,1 und 2 mm gebildet wird.

11. Verfahren nach einem der Ansprüche 1 bis 10, umfassend die weiteren Schritte:

- Bereitstellen einer "Haut"-Flüssigkeitsmischung, umfassend ein Polymer aus Polyurethanen, Polyestern, sowohl aromatischen als auch aliphatischen Polyestern oder Polycarbonaten, in Lösung mit einer Mischung von organischen Lösungsmitteln;
- Abscheiden von wenigstens einer Schicht der Mischung auf der Schicht der koagulierten Mischung von dem gewebten oder nichtgewebten Substrat auf der koagulierten Seite;
- Härten der wenigstens einen "Haut"-Mischungsschicht.

12. Verfahren nach Anspruch 11, wobei der Abscheidungsschritt das Abscheiden der "Haut"-Mischung auf dem Substrat und das anschließende Leiten des Substrats durch ein Paar von Walzen umfasst, von denen wenigstens eine mit einer Oberfläche versehen ist, die Zeichnungen oder Muster trägt.

13. Verfahren nach Anspruch 11, wobei der Abscheidungsschritt umfasst:

- Abscheiden von wenigstens einer Schicht der "Haut"-Mischung auf einer Papierunterlage;
- Härten der wenigstens einen Schicht auf der Papierunterlage;
- Bereitstellen einer flüssigen Haftmischung, umfassend ein Polymer aus Polyurethanen, Polyestern, sowohl aromatischen als auch aliphatischen Polyestern oder Polycarbonaten, in Lösung mit wenigstens zwei organischen Lösungsmitteln;
- Abscheiden der Haftmischung auf der wenigstens einen Schicht der "Haut"-Mischung;
- Anordnen der koagulierten Unterlage auf der Haftmischungsschicht, so dass die koagulierte

Schicht der Substratmischung mit der Haftmischung in Berührung kommt;
- Härten der Haftmischung, so dass die Anhaftung zwischen dem Substrat und der Papierunterlage erhalten wird, um das Halbzeug zu bilden.

14. Verfahren nach Anspruch 13, wobei das Polymer der "Haut"-Mischung in Mengen im Bereich zwischen 1,9 und 18,9 Gew.-%, bezogen auf das Gesamtgewicht der Mischung, bereitgestellt wird und die wenigstens zwei organischen Lösungsmittel in Mengen zwischen 10 und 90 Gew.-%, bezogen auf das Gewicht der "Haut"-Mischung, bereitgestellt werden.

15. Verfahren nach Anspruch 14, wobei die wenigstens zwei organischen Lösungsmittel ausgewählt sind aus Toluol, Methylisobutylketon, Methoxypropanol, Methylacetat, Cyclohexanon, Aceton, Methylethylketon und Dimethylformamid.

16. Verfahren nach einem der Ansprüche 11 bis 15, wobei die "Haut"-Mischung einen flüssigen polymeren Anteil umfasst, wobei das Polymer durch einen Feststoffgehalt von 19 bis 21 Gew.-%, bezogen auf das Gewicht der Mischung, durch eine Viskosität im Bereich zwischen 300 und 600 DPA.S bei 25 °C unter dynamischer Rotation, eine Dehnungsrate von 330 %, 100 % Modul (MPa) von 20 und 300 % Modul (MPa) von 46,5 **gekennzeichnet** ist.

17. Verfahren nach einem der Ansprüche 11 bis 15, wobei die "Haut"-Mischung 28 % DMF und 7 % MEK (Methylethylketon), bezogen auf das Gesamtgewicht der Mischung, als die organischen Lösungsmittel umfasst.

18. Verfahren nach einem der Ansprüche 11 bis 17, wobei die "Haut"-Mischung Siliconöle in Mengen im Bereich zwischen 0,05 und 5 Gew.-%, bezogen auf das Gewicht der Mischung, umfasst.

19. Verfahren nach einem der Ansprüche 13 bis 18, wobei der Schritt der Härtung der Hautmischung auf einer Papierunterlage so stattfindet, dass eine Dicke im Bereich zwischen 0,50 mm und 1,05 mm erzeugt wird.

20. Verfahren nach einem der Ansprüche 13 bis 19, wobei die Haftmischung ein Polymer umfasst, das identisch ist mit dem für die Koagulationsmischung verwendeten Polymer, verdünnt mit einer Mischung von wenigstens zwei organischen Lösungsmitteln, ausgewählt aus Toluol, Methylisobutylketon, Methoxypropanol, Methylacetat, Cyclohexanon, Aceton, Methylethylketon und Dimethylformamid.

21. Verfahren nach einem der Ansprüche 13 bis 20, wobei das Polymer der Haftmischung in Mengen von 2,9 bis 12,4 Gew.-%, bezogen auf das Gesamtgewicht der Mischung, bereitgestellt wird.

22. Verfahren nach einem der Ansprüche 13 bis 21, wobei die Lösungsmittel DMF und MEK (Methylethylketon) in Mengen von 14 bzw. 20 %, bezogen auf das Gewicht der Mischung, sind.

23. Verfahren nach einem der Ansprüche 13 bis 22, wobei eine Schicht der Haftmischung mit einer Dicke im Bereich zwischen 0,5 und 1 mm aufgetragen wird.

Revendications

1. Procédé de préparation d'un matériau semi-fini pour la fabrication d'articles textiles semblables au cuir ou enduits, lequel comprend les étapes consistant :

- à fournir un substrat tissé ou non tissé ;
- à fournir un mélange liquide de coagulation comprenant un polymère de polyuréthane à base de polycarbonate aliphatique ou aromatique, un solvant organique et éventuellement de l'eau ;
- à déposer au moins une couche dudit mélange liquide sur ledit substrat ;
- à faire coaguler ledit mélange sur ledit substrat ;

caractérisé en ce que ledit substrat est mouillé avec de l'eau éventuellement mélangée avec un solvant organique avant le dépôt du mélange de coagulation.

2. Procédé selon la revendication 1, dans lequel le substrat tissé ou non tissé est choisi parmi des textiles de polyester et/ou de coton, des non-tissés de microfibre de polyester, d'élastomère de polyester, de polyamide, d'élastomère de polyamide, de polyester viscose, de polyamide polyester, de viscose polyamide aiguilleté, non tissé, mono ou multicouche lacé et/ou filé et/ou cardé.

3. Procédé selon la revendication 1 ou 2, dans lequel le substrat est une étoffe de textile tissé, à armure croisée de polyester et de coton, épaisseur de 0,4 à 0,6 mm, densité linéaire de trame Ne 6 $\pm$ 1, 100 % de coton, 14 boucles par unité de surface $\pm$ -1, densité linéaire de chaîne Ne 16 $\pm$ -1, non-tissé de 25 fils de polyester (65 %) coton (35 %) ou de 100 % de polyester, 150 g/m^2 de lacé, densité linéaire 1 950 dtex, épaisseur 0,4/0,6 mm.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ledit polymère est fourni dans des quantités de 11,6 % à 15,5 % en poids par rapport

au poids total du mélange de coagulation.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ledit mélange de coagulation comprend une portion polymère liquide dans laquelle le polymère est **caractérisé par** une teneur en matière solide de 29 % à 31 % en poids par rapport au poids du liquide dissous dans un solvant organique, la viscosité étant comprise entre 800 et 1 200 DPA.S à 25°C sous rotation dynamique, taux d'allongement de 350 %, module à 100 % (MPa) de 3,5 et module à 300 % (MPa) de 18.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel ledit solvant organique est un solvant polaire, tel que le méthoxypropanol acétate de méthyle et le diméthylformamide, fourni dans des quantités comprises entre 50 % et 60 % en poids par rapport au poids total du mélange de coagulation.

7. Procédé selon la revendication 6, dans lequel ledit solvant organique est le diméthylformamide utilisé dans des quantités de 50-60 % en poids par rapport au poids total du mélange.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel ledit mélange de coagulation comprend de la fibre de cellulose dans des quantités comprises entre 1 % et 25 % en poids par rapport au poids total du mélange.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel ledit premier mélange comprend un retardateur de flamme dans des quantités comprises entre 1 % et 20 % en poids par rapport au poids du mélange.

10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel le dépôt d'une ou plusieurs couches dudit mélange de coagulation est réalisé afin de former une épaisseur comprise entre 0,1 et 2 mm.

11. Procédé selon l'une quelconque des revendications 1 à 10 comprenant les étapes supplémentaires consistant :

- à fournir un mélange liquide de "peau" comprenant un polymère de polyuréthanes, de polyesters, de polyesters ou de polycarbonates à la fois aromatiques et aliphatiques, en solution avec un mélange de solvants organiques ;
- à déposer au moins une couche dudit mélange sur ladite couche de mélange coagulé dudit substrat tissé ou non tissé sur le côté coagulé ;
- à faire durcir ladite au moins une couche de mélange de "peau".

12. Procédé selon la revendication 11, dans lequel l'étape de dépôt comprend le dépôt du mélange de "peau" sur ledit substrat et le passage subséquent du substrat à travers une paire de rouleaux dont au moins un est muni d'une surface portant des dessins ou des motifs.

13. Procédé selon la revendication 11, dans lequel l'étape de dépôt comprend les étapes consistant :

- à déposer au moins une couche dudit mélange de "peau" sur un support de papier ;
- à faire durcir ladite au moins une couche sur ledit support de papier ;
- à fournir un mélange liquide d'adhérence comprenant un polymère de polyuréthanes, de polyesters, de polyesters ou de polycarbonates à la fois aromatiques et aliphatiques, en solution avec au moins deux solvants organiques ;
- à déposer ledit mélange d'adhérence sur ladite au moins une couche dudit mélange de "peau" ;
- à placer ledit support coagulé sur ladite couche de mélange d'adhérence de telle sorte que la couche coagulée du mélange de substrat est mise en contact avec ledit mélange d'adhérence ;
- à faire durcir ledit mélange d'adhérence afin d'obtenir l'adhérence entre ledit substrat et ledit support de papier pour former le matériau semi-fini.

14. Procédé selon la revendication 13, dans lequel ledit polymère dudit mélange de "peau" est fourni dans des quantités comprises entre 1,9 % et 18,9 % en poids par rapport au poids total du mélange et lesdits au moins deux solvants organiques sont fournis dans des quantités comprises entre 10 % et 90 % en poids par rapport au poids dudit mélange de "peau".

15. Procédé selon la revendication 14, dans lequel lesdits au moins deux solvants organiques sont choisis parmi le toluène, la méthylisobutylcétone, le méthoxypropanol acétate de méthyle, la cyclohexanone, l'acétone, la méthyléthylcétone et le diméthylformamide.

16. Procédé selon l'une quelconque des revendications 11 à 15, dans lequel ledit mélange de "peau" comprend une portion polymère liquide dans laquelle le polymère est **caractérisé par** une teneur en matière solide de 19 % à 21 % en poids par rapport au poids du mélange, par une viscosité comprise entre 300 et 600 DPA.S à 25°C sous rotation dynamique, un taux d'allongement de 330 %, un module à 100 % (MPa) de 20 et un module à 300 % (MPa) de 46,5.

17. Procédé selon l'une quelconque des revendications

11 à 15, dans lequel ledit mélange de "peau" comprend 28 % de DMF et 7 % de MEK (méthyléthylcétone) par rapport au poids total dudit mélange en tant que solvants organiques.

18. Procédé selon l'une quelconque des revendications 11 à 17, dans lequel ledit mélange de "peau" comprend des huiles de silicone dans des quantités comprises entre 0,05 % et 5 % en poids par rapport au poids du mélange.

19. Procédé selon l'une quelconque des revendications 13 à 18, dans lequel l'étape de durcissement dudit mélange de peau sur un support de papier a lieu afin de créer une épaisseur comprise entre 0,50 mm et 1,05 mm.

20. Procédé selon l'une quelconque des revendications 13 à 19, dans lequel le mélange d'adhérence comprend un polymère identique à celui utilisé pour le mélange de coagulation, dilué avec un mélange d'au moins deux solvants organiques choisis parmi le toluène, la méthylisobutylcétone, le méthoxypropanol acétate de méthyle, la cyclohexanone, l'acétone, la méthyléthylcétone et le diméthylformamide.

21. Procédé selon l'une quelconque des revendications 13 à 20, dans lequel le polymère dudit mélange d'adhérence est fourni dans des quantités de 2,9 % à 12,4 % en poids par rapport au poids total du mélange.

22. Procédé selon l'une quelconque des revendications 13 à 21, dans lequel les solvants sont DMF et MEK (méthyléthylcétone) dans des quantités respectives de 14 % et de 20 % par rapport au poids du mélange.

23. Procédé selon l'une quelconque des revendications 13 à 22, dans lequel une couche dudit mélange d'adhérence est appliquée avec une épaisseur comprise entre 0,5 et 1 mm.

REFERENCES CITED IN THE DESCRIPTION

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