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

(11) Publication number: **0 305 596 A1**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **87117815.8**

(51) Int. Cl.4: **D06N 3/00 , D06P 3/24**

(22) Date of filing: **16.06.84**

(43) Date of publication of application: **08.03.89 Bulletin 89/10**

(60) Publication number of the earlier application in accordance with Art.76 EPC: **0 165 345**

(84) Designated Contracting States: **BE CH DE FR GB IT LI NL**

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(54) **Grained artificial leather having good colour fastness and dyeing method of ultrafine polyamide fibers.**

(57) This invention presents an artificial leather and a dyeing method of ultrafine polyamide fibers, particularly a grained artificial leather, having bright, deep colour, good colour fastness to dry cleaning with charged soap, delicate touch free from undesirable rubber-like feeling as well as high durabilites.

The object of this invention is attained partly by using a super-entangled fiber base comprising ultrafine polyamide fibers and/or bundles thereof, and applying thereon a polyurethane including polyoxyethylene of molecular weights of 500 - 5,000 as a soft segment. The object of this invention is also partly attained by dyeing the polyamide ultrafine fibers with a metal-dye complex and a fixing agent treatment.

This invention is most suitable for manufacturing grain artificial leathers especially for clothing. Other uses are such as for shoes, belts, bags, gloves and balls.

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GRAINED ARTIFICIAL LEATHER HAVING GOOD COLOUR FASTNESS AND DYEING METHOD OF ULTRAFINE POLYAMIDE FIBERS

The present invention relates to a grained artificial leather having good colour fastness and to a process for dyeing ultrafine polyamide fibers into deep, bright colours, keeping good colour fastness to dry cleaning in charged system.

The grain layer of conventional artificial leathers are made by providing a porous or/and non-porous layer of a resin such as polyurethane on porous sheets made of elastomeric polymers and a fiber base such as woven, nonwoven or knitted fabrics. However, such resins do not show good dyeability and colour fastness, especially when subjected to dry cleaning processes.

Therefore, dope dyeing has been applied to the resins of grained surface. However, dope dyeing is not suitable for manufacturing small quantities of artificial leathers of many colours. Further, the appearance of artificial leathers which are dope dyed is monotonous and opaque due to lack of transparancy and lusters.

On the other hand, Japanese Patent Publication No. 28041/1973, teaches that some kinds of polyurethane whose soft segment is polyethyleneglycol (PEG-type PU) can be dyed with a metal complex dye. However, artificial leathers comprising PEG-type PU and a fiber base of ultra-fine fibers have no great practical value because they do not have good colour fastness as a whole, owing to an insufficient colour fastness of the ultra-fine fibers. Further, when the fiber base is impregnated or coated with porous resins, the porous resins, exhibit poor colour fastness when exposed to dry cleaning and spoil the appearance, not only of the back surface but also, of the grain surface of the artificial leather. The faded porous polyurethane affect even appears through the dyed grained surface.

On the other hand, a number of proposals have been made as to leather-like fabrics made of ultrafine fibers, such as suede-like, nubuk-like, woven or knitted fabrics, as well as grained artificial leathers. And, now, extra ultrafine fiber around or less than 0.01 denier is attracting our interests to obtain a softer hand or a more dense appearance.

However, as fibers become more fine, dyeing deeply and brightly become more difficult because of increased surface reflection of the extra fine fibers.

For example, though polyamide fibers such as nylon-6 and nylon-66 have such advantages over polyester fibers as softness, high wear resistance and brightness of colour, the use of polyamide ultrafine fibers for clothing has been delayed so far because dyes are very liable to come off in washing and dry cleaning.

Japanese Patent Publication No. 8128/1981 mentions the attempts to improve colour fastness by increasing molecular orientation of the ultrafine nylon fibers. However their colour fastness is insufficient when exposed to dry cleaning in which charge soap is used. Extra-ultrafine fibers around or less than 0.01 denier always show complete fading of colour even if they are dyed with the dyes said to give highest colour fastness to fibers of ordinary thickness.

Though thren-type vat dyes (vat dyes derivatived from anthraquinone), whose colour fastness is best amongst other dyes, can be also applied to the composite sheet of ultrafine polyamide fiber and polyurethane (Laid-Open Japanese Patent Application Publication No. 1365/1980), they can neither give any heavy shade nor show good resistance to the synthetic solvents used in dry cleaning. Further, not only do they cause photo-tendering for some hues, but also the strong base used in the dyeing process leads to deterioration of the polyurethane.

The object of this invention is to provide a dyeable artificial leather, particularly a dyeable grained artificial leather, having good colour fastness, bright, deep colours, excellent lusters, soft hand and high durabilities. The object can be achieved, most preferably by dyeing an artificial leather comprising a super-entangled ultrafine fiber base and PEG-type PU applied thereon with a metal dye complex.

This invention provides also a method for dyeing extra ultrafine polyamide fibers comprising dyeing with, preferably, a metal dye complex and fixing with tannin and a metal salt. The dyeing method makes it possible to provide deep and bright colours whilst maintaining sufficient colour fastness to enable dry cleaning of the extra-ultrafine polyamide fibers.

The grained surface preferably comprises, a super-entangled surface made mainly of ultrafine fibers and/or their bundles and polyurethane having at least 5% by weight of polyoxyethylene chain of molecular weights of 500 - 5,000 based on total weight of the soft segment.

The leathers of the invention are obtainable with at least the following four steps (1) to (4) combined.

(1) A step for making a fiber sheet being mainly comprising ultrafine fibers or ultrafine fiber formable fibers.

(2) A step for entangling said fiber sheets by applying high-velocity fluid streams to at least one surface thereof.

(3) A step for applying a polyurethane, to said surface to which said high-velocity fluid streams are applied, wherein at least 5 weight % of the soft-segment constituents of the polyurethane is polyoxyethylene chain having molecular weight of 500 to 5,000.

(4) A step for dyeing said polyurethanes with at least one dye selected from the group consisting of metal dye complexes, acid dyes and reactive dyes.

It is preferable for the facility of processing and handling to convert ultrafine fiber formable fibers into ultrafine fibers or bundles thereof at an appropriate stage. They can however be manufactured directly by methods such as wet spinning, super-drawing or melt-blow spinning.

Ultrafine fiber formable fibers include the chrysanthemum-like cross-section fibers in which one component is radially sandwiched between other components, multi-layered bicomponent fibers, radially multi-layered bicomponent hollow fibers, and islands-in-sea type composite fibers having fixed or unfixed cross section along the fiber axis. They may be used by mixing more than two of the fibers.

For obtaining leathers having soft hand and smooth surface, the thickness of the ultrafine fibers which can be obtained from the ultrafine fiber formable fibers should be less than 0.2 deniers, preferably less than 0.05 denier, more preferably less than 0.01 denier.

As materials for the ultrafine fibers, polyamides such as nylon-6 and nylon-66, polyesters such as polyethylene and polybuthylene terephthalate, polyacrylonitrile, and their copolymers are preferable among others. Polyamides are particularly preferable because even less than 0.01 denier they can be deeply coloured with good colour fastness by the dyeing method stated later.

As binding components (sea components) for ultrafine fiber formable fibers, those readily-separable type ultrafine fiber components or those different in the solubility are selected. For the facility of spinning and removal, polystyrene, polyethylene, their copolymers, and copolymerized polyesters are preferably used. Particularly the copolymers of styrene with acrylic acid and/or methacrylic acid are preferable amongst them for obtain ing strong fibers due to easiness of applying a high drawing ratio.

In this invention, to improve colour fastness, it is preferable to increase drawing ratio to achieve high molecular orientation or high degree of crystallinity. Drawing ratio more than 2.0 times, preferably more than 2.5 times, are usually preferable, provided the spinning speeds of 600 to 1,500 m/min. are used.

The ultrafine fibers of the grained surface should preferably have a size less than 0.2 denier. If not, a smooth grained surface is difficult to form because the excessive fiber stiffness affects their smoothness, the surface can produce unsightly creases and cracks, and crumpling readily causes cracks and surface unevenness. The ultrafine fibers of less than 0.2 denier, preferably of less than 0.05 denier, more preferably of less than 0.01 denier can be densely entangled so that a surface which is highly smooth, flexible, and not liable to cause cracks, and has a soft touch feeling is obtainable.

The fiber structure of or just beneath the grained surface should preferably have ultrafine fibers and/or their bundles, mutually super-entangled. They should preferably be such that the distance between the fiber entanglement points (defined later) is less than 200 microns. The fiber structures with less entanglement such as entangled only by needle punching are not preferable because they are apt to fluff or crack when subjected to friction, crumpling, or repeated shearing or bending. Such fiber bases require reinforcement with a great quantity of porous resins to maintain their strength and dimensional stability and, consequently, such sheets are poor in dyeing fastness. For the purpose of reducing the amount of porous resins for eliminating such defects, the distance between the fiber entanglement points should preferably be less than 200 microns or more preferably less than 100 microns.

The term "the distance between the fiber entanglement points" is defined in Laid-Open Japanese Patent application Publication No. 191280/1983 (Tokkai-sho 58-191280).

A short average distance between points of entanglement produces a high density of entanglement.

The average distance between the fiber entanglement points is measured in the following manner. When observed from the surface with a scanning electron microscope, the fibers are considered to form an entanglement point when an upper fiber which has passed over and across a lower fiber then passes under and across another fiber. It will be assumed that the constituent fibers are f_1, f_2, f_3, ..., the point at which two fibers f_1 and f_2 are entangled with each other is a_1 and another point at which the upper fiber f_2 is entangled with another fiber with the fiber f_2 being the lower fiber is a_2 (the entanglement point between f_2 and f_3). Similarly, the entanglement points a_3, a_4, a_5, ... are determined. The linear distances a_1a_2, a_2a_3, a_3a_4, a_4a_5, a_5a_6, a_6a_7, a_7a_3, a_3a_8, a_8a_7, a_7a_9, a_9a_6, ... measured along the surface are the distance between the fiber entangling points and their average is taken.

In the present invention, the fibers of the surface portion preferably have an average distance between the fiber entangling points of less than about 200 microns as measured by this method. In fiber structures where the average distance between the entangling points is greater than about 200 microns, such as in those fiber structures in which the entanglement of the fibers is effected only by needle punching, only little entanglement of the fibers occurs.

If fiber entanglement is so dense that the distance between its points is less than 200 microns, the amount of polyurethanes applied thereto can be decreased. Namely it is possible to decrease porous polyurethane to be impregnated in the fiber base or to decrease the thickness of polyurethane layer applied to the surface. The former spoils colour fastness and the latter spoils soft hand and delicate appearance. The fiber base may be nonwoven, laminated nonwoven or woven or knitted fabrics laminated and entangled with a nonwoven. Amongst them, nonwoven a fiber base comprising a surface portion of super-entangled ultrafine fibers and/or their bundles, said ultrafine fibers and/or their bundles being branched from the ultrafine bundles of the inner portion, is most preferable. It is.preferable that the degree of branching and entanglement vary at the boundary between the surface and inner portions. By applying water jet streams to the ultrafine formable fiber sheet, entanglement and branching often occur throughout its thickness. The dense entanglement and branching around the surface portion brings about the sheet a smooth surface and excellent stability such as against fluff and deformation. Looser entanglement than the surface of the inner portion brings about softness to the sheet.

The amount of resin depends on the intended purposes for the leather. For clothing, however, it should preferably be 0 to 50% and more preferably less than 20% based on the fiber weight.

The resins used for the grain layer in accordance with the invention are required to be the urethane polymers having at least 5% by weight of polyoxyethylene chains with molecular weights of 500 to 5,000 based on total weight of the soft segment. If the amount of polyoxyethylene chains is less than 5% by weight, bright colours are difficult to obtain by dyeing. The molecular weight of polyoxyethylene chains is required to be 500 to 5,000 for keeping the softening temperature, resistance to flexing and solvent within their practicable range.

Polyurethanes whose soft segment contains polyoxyethylene chains should preferably be dyed with anionic dyes such as metal dye complexes, acid dyes and reactive dyes because they are highly affinitive thereto and particularly dyeable with metal dye complexes and have good colour fastness.

They may of course be blended or copolymerized with a proper quantity of another polyether, polyester and copolymerized polyesters for improving mechanical strength.

Polyurethane polymers in accordance with the invention are not limited to linear type and may be the cross-linked type such as cross-linked with hexamethylene diisocyanate trimer. Cross-linked polyurethanes generally improve resistances to scratch, scuff, organic solvent and hot water, but is defective in flex resistance. However, in the present invention, flex resistance is much improved by virtue of super-entangled surface structure.

The soft segment of the polyurethane may be polyoxyethylene glycol alone, but may also be its mixtures with polyether diols such as polyoxypropyleneglycol, polyoxytetramethyleneglycol and polyester diols such as polyethyleneadipate, polybuthyleneadipate, polyhexamethyleneadipate and polycaprolactone, and copolymers thereof.

PEG-type PU may be mixed with other polyurethanes so that the amount of polyoxyethylene segment is more than 5% by weight based on the total weight of the soft-segment.

Organic diisocyanates used to make the polyurethane include aromatic ones such as diphenylmethane-4 4′-diisocyanate, aromatic-aliphatic ones such as xylylenediisocyanate, aliphatic diisocyanates such as hexamethylenediisocyanate, and alicyclic ones such as isophoronediisocyanate and hydrogenated diphenylmethane-4,4′-diisocyanate. Amongst them, aromatic diisocyanates, particularly diphenylmethane-4 4′-diisocyanate, is preferable for obtaining good physical characteristics such as thermal stability, solution stability and fracture strength.

Alicyclic diisocyanates such as isophorone ones are preferable for obtaining anti-yellowed (not easily coloured even when exposed to sun) type polyurethanes.

Chain extenders for the polyurethane include water, low-molecular diols such as ethyleneglycol and propyleneglycol, aromatic diamines such as ethylenediamine, aliphatic diamines such as 4,4′-daminodiphenylmethane, alicyclic diamines such as 4,4′-diaminodicyclohexylmethane and isopholonediamine, alkanolamines such as ethanolamine, hydrazines, and dihydrazide such as succinic one. Amongst them diamine compounds are preferable and 4,4′-diaminodiphenylmethane is particularly preferable for practical use because of its heat resistance and 4,4′-diaminodicyclohexylmethane is more preferable for light resistance. They may of course be used alone or in combination.

The polyurethanes are generally manufactured in the presence of solvents. Suitable solvents are dimethylformamide, (referred to DMF hereinunder), dimethylacetamide, ethylacetate and toluene. Amongst them DMF should be preferably used. Elastomers other than polyurethane such as polyamide, polyester, polyvinyl chloride, polyacrylic ester copolymers, neoprene, styrene-butadiene copolymers, acrylonitrile-butadiene copolymers, polyamino acid, polyamino acid-polyurethane copolymers, and silicone resins may be mixed with the polyurethanes, and if necessary may be applied in less than 10 microns thickness to the grained surface of the present invention. As a matter of course, plasticizers, fillers, stabilizers, crosslinking agent and so forth may be added thereto.

When flexibility and soft feeling are particularly demanded, the resin should be applied in great quantities to the uppermost very-thin portion of the grained surface and not at all or in small quantities to the other parts.

The deep luster and bright colour are obtainable by dyeing the leathers, with one or more dyes selected from anionic dyes which have a negative charge in aqueous solution such as metal dye complexes, acid dyes and reactive dyes. Further, when polyamide ultrafine fibers are used, the dyeing method described later is particularly preferable for obtaining heavy shade, and high colour fastness.

For ultrafine fibers other than polyamide, on the other hand, the polyurethanes and ultrafine fibers can be coloured independently.

The colour of the urethane polymers may be improved by preliminarily adding dyes and/or pigments thereto.

For making ultrafine fibers, islands-in-sea type fiber are representative. It is produced, for example, by using a spinning system mentioned in Japanese Patent Application Publication No. 18369/1969 (Tokko-sho 44-18369) or dope mixed spinning. Usually ultrafine fiber formable fibers are cut into short fibers, crimped with stuffing box, formed into web and subjected to needle punching. Or, continuous filaments are spread into sheet without cutting and subjected to needle punching. Further the ultrafine fiber formable fibers may be placed on and entangled with other nonwoven, woven knitted fabrics. After that or occasionally without needle-punching, high-velocity fluid streams are applied to the sheet. Water is most preferably used amongst other fluids. The branching and entanglement of the fibers are achieved through the treatment. The ultrafine fiber formable fibers may be converted into bundles of ultrafine fibers before treatment with high pressure fluid streams. In such a case, the pressure of the fluids may be 5 - 100 kg/cm^2. Even before conversion, a similar pressure may be applied for easy separable fibers. However, 100 - 300 kg/cm^3 is preferable for the fibers not liable to separation. The degree of branching and entanglement can also be changed by contact times. Pressure may be changed each time of contact. The degree of ultrafining can be controlled by treating the fiber sheets with solvents for at least a part of components. The dissolution of part of the fibers can be carried out even after impregnating or coating with resins. In this case, products become softer because many spaces where the part of components were formed along the fiber axis in the products.

The resin solution or dispersion for the grained surface may be applied by reverse roll coater, gravure coater, knife coater, slit coater, spraying and other methods. The coated surface is pressed and if necessary heated for smoothing or embossing the surface. Sometimes pressing the fiber sheets before coating the resin is also effective for improving smoothness.

In this invention, heavy shade, high colour fastness of polyamide ultrafine fibers is attainable through the colour fixing after dyeing with metal dye complexes.

Generally speaking, polyamide fibers such as nylon-6, can be dyed beautifully with acid dyes, disperse dyes or metal dye complexes. However, ultrafine polyamide fibers less than 0.2 denier is inferior to ordinary fibers in colour fastness. This trend is remarkable for as extra-ultrafine fibers with less than 0.01 denier.

We found that the ultrafine polyamide fibers can be deeply dyed using metal dye complexes such as mordant dyes, acid mordant dyes, 1:1 metal-complex dyes, 2:1 premetallized dyes and metal complex direct dyes of molecular weights more than 700, more preferably of more than 900. The methods for this dyeing include dip drying, pad steam drying and pad drying and are not limited. Amongst the dyes, 2:1 premetallized dyes of larger molecular weights are easy to be produced. We also found that the ultrafine fibers of less than 0.01 denier, particularly with 0.001 denier, can unexpectedly be dyed with so-called Irgaran-type metal complex dyes having low hydrophilicity groups such as sulfonamide and sulfonmethyl groups.

The metal dye complexes enhance dye bonding with the fibers by forming complex salts between the dye molecules and chrome or other metal atoms and can provide ordinary fibers with good colour fastness but in ultrafine fibers almost all colour fade by dry cleaning with charge-soap containing synthetic solvents.

We, however, discovered that remarkable effects are obtained by fixing synthetic tannins and tannic acid derivatives (synthetic and natural) or tannins and metal salts in combination after dyeing with metal dye complex dyeing. The fixing after dyeing with metal dye complexes has been said to be neither effective nor necessary for ordinary fibers at all. However, the fixing with tannins and metal salts ensures good colour fastness even to the extra ultrafine fibers in dry cleaning with synthetic solvents (such as perchlene which is said to have the strongest cleaning power).

Term "tannins" in accordance with the invention is generically given to hydrolysable tannins, condensed tannins and the complex tannins which has both properties. They are contained in the barks, leaves, roots and fruits of plants. Preferable tannins amongst them are gallotannins (tannic acid) classified in the category of hydrolytic tannins that are represented by Chiness gallotannin and gallic acid.

The metal salts in accordance with the invention include antimonty complex salts, iron salts, chrome salts, copper salts, bismuth salts and their complex compounds. Preferable amongst them is potassium antimonyl tartrate in the category of antimonide complex compounds.

Such fixing methods may be conducted by continuous 2-bath process or may be carried out by separate 2-bath process, namely, impregnation with tannins solution, drying the impregnated sheet, impregnation with metal salts solution and drying, in this order. In the former, temperature can be set at 25 to 100 °C. Too low temperatures lower the solubility and adsorbability of the fixing agent. On the contrary, too high temperature causes dissolving out of the absorbed dye into the treating solutions. Temperatures of 40 to 85 °C, particularly 50 to 80 °C, are therefore preferable and result in satisfactory fixing effects.

The mechanism of fixing is not known in detail, but it can be assumed that a layer of the fixing agent is formed on the surface of the ultrafine fibers and the layer multiplicatively enhances the affinity between the dyes and fibers so that dyes become difficult to move. Though such fixing treatment tends to harden the sheets, it is however also amazing that the above effects are kept even after finishing through mechanical crumpling.

Such crumpling methods are not limited and include dry heat mechanical crumpling and wet heat and hot water tumbler crumpling. Further it can be carried out simultaneously with the fixing by using liquid flow dyeing machines.

The fiber sheets thus obtained may be further subjected to washing and finishing agent treatment, if necessary, after the dyeing and fixing. Further the addition of polyurethanes or raising such as buffing can be applied either before or after the dyeing and fixing. Surface active agent treatment is preferable for dyeing the fiber sheets impregnated with high-molecular elast omer other than PEG-type PU. That is, because other type polyurethanes suitable for impregnation are extremely inferior in colour fastness, it is rather preferable to preliminarily remove the dyes absorbed to the impregnated elastomers with surface active agents.

Amongst such surface active agents, anionic, nonionic and amphoteric surfactants are effective. Particularly the latter two are preferable. Particularly preferable amongst them are polyoxyalkylene nonionic and betaine amphoteric surface active agents. The former include plyoxyalkylenealkylamine, polyoxyethylenealkylether, polyoxyethylenealkylarylether, polyoxyethylenealkylether, polyoxyethylenealkylester, polyoxyethylenealkylamide, polyoxyethylenepolyoxypropylene, polyoxyethylenealkylpheonol and polyoxyethylenephenylether for example.

When the fiber sheets are prepared with the multilayered ultrafine fiber formable fibers made of polyamide and polyester and the products are subjected to multi-colour dyeing, a melange coloured product having good colour fastness can be obtained.

Heretofore, description has been mainly made as to fiber dyeing and fixing after sheet formation. However, it is needless to say that the order of the sheet formation and the dyeing may be changed arbitrarily.

Example 1

A staple of islands-in sea type fiber (4 denier, 51mm length) having 7 islands, each islands consist of many islands-in-island (I-I-I) and a sea-in-island (S-I-I), was obtained by spinning at a speed of 1,200 m/min, drawing at 2.6 times, being subjected to crimping and cutting. The islands-in-sea type fiber is composed of 65 parts of acrylic acid-styrene copolymer (referred as AS resin hereinunder) as the sea and the S-I-I component and 35 parts of nylon-6 as I-I-I component. The average thickness of the I-I-I was 0.002 denier.

A web was formed through card, cross-lapper and needle-punched with single barbed needles for entanglement. The sheet has a weight 430 gr./m^2, an apparent density of 0.17 gr./cm^3 and an average distance between the entanglement points of 378. Both surfaces of the sheet were treated one time respectively with high-velocity fluid streams of 100 kg/cm^2 pressure from a nozzle having 0.25 mm diameter holes arranged in one row at 2.5 mm intervals, while oscillating the nozzle. The nonwoven sheet thus obtained showed the super-entangled structure in which the islands-in-sea type fibers were branched into extra ultrafine fibers and/or their bundles, and the average distance between the fiber entanglement points was 56 microns at the surface.

Next the nonwoven sheet was shrunk in 85 °C hot water, dried and smoothed between rubber roll and hot iron roll having smooth surface.

A prepolymer obtained from polyoxyethyleneglycol of molecular weight of 600 and isophronediisocyanate was chain extended with 4,4′-diaminodicyclohexylmethane, terminated at the end with ethanolamine and cross-linked with 15 parts of a hexamethylenediisocyanate trimer. Then the cross-linked polyurethane was coated with gravure coater, on the smoothed surface. The amount of coating was 5 gr./m^2. The coated surface was pressed with a hot emboss roll, for embossing and integrating the coated resin with the super-entangled surface.

Thereafter AS resin was almost completely removed with tricloroethylene and the islands-in-sea type fibers were ultrafined.

A sheet thus obtained was subjected to dyeing and fixing using a wince dyeing machine under the following condition.

Dyeing:

Dye stuff: Iregalan Black GBL 200%, 10% owf
Dyeing temperature × time: 98 °C × 60 min.

Fixing:

Fixing agents: tannic acid and tartar emetic
Treating method: treatment with weakly acidic bath containing 10% owf tannic acid at 50 °C, for 50 min. and,
treatment with weakly acidic bath containing 5% owf tartar emetic at 50 °C, for 50 min.

Next, after adding a finishing agent, the sheet was softened with a tumbler crumpling machine and dried.

Both the grained surface and the reverse surface of thus-obtained sheet were coloured dark black. It showed a softness free from undesirable rubber-like feeling and the grained surface has deep luster, resistances against scuff and repeated bending. Its washing and dry cleaning fastness according to JIS-L0844 LO860 (2% charge soap content) was good.

Comparative Example 1

A grained artificial leather was obtained according to the same manner except using anti-yellowed (not easily coloured even when exposed to sun light) type polyester polyurethane instead of the PEG-type PU.

It showed a natural leather-like appearance as that of Example 1. However the grained surface was dyed into dark-blue not into dark black. Further, the colour of the grained surface was seriously faded by dry cleaning containing 2% charge soap.

Comparative Example 2

The sane needle-punched sheet as Example 1 was immersed in a 15% aqueous solution of polyvinyl alcohol (referred to PVA hereinafter) at 85 °C, shrunk simultaneously, dried, impregnated with a 10% DMF solution of polyester polyurethane, coagulated with 30% DMF aqueous solution and sufficiently washed in 80 °C hot water for removing PVA and DMF.

Next, the sheet was subjected to the surface smoothing with a hot roll and the same treatment as Example 1. The sheet showed unevenly coloured lines or portions like stood veins along ultrafine fiber bundles, and cracks arised during the dyeing, and ultrafine fibers were exposed therefrom. Further it had hard touch, unbright colour and feeling not natural leather-like as compared with Example 1.

Further when picked up by fingers, so bent as to have an acute angle, and rubbed against a thigh part of trousers with a large pressure applied, the Comparitive Example 2 leathers showed peeled grained surface and exposed raising while the leather of Example 1 did not change in appearance at all.

Example 2 - 5, Comparative Example 3 and 4

The needle-punched sheet obtained in Example 1 was super-entangled with the high-velocity fluid streams on one side thereof in the same manner as Example 1, immersed in an 8% aqueous PVA solution at 85° C for PVA impregnation and for the sheet shrinkage at a time and dried.

Next a 7% DMF solution of polyester polyurethane to which a small quantity of carbon black was added was impregnated and coagulated with water and sufficiently washed in hot water at 80° C for removing PVA and DMF.

Thereafter the super-entangled surface of the impregnated sheet was coated with a DMF solution containing 10% polyurethanes obtained by chain extending the prepolymers between diphenylmethane-4,4'-diisocyanate and high molecular weight diol mixtures composed of polyoxyethyleneglycol (molecular weight, 2,000) and polyethylenebutyleneadipate (molecular weight, 2,000) of the mixing ratios of:

(A) 100/0 (Example 2)
(B) 50/50 (Example 3)
(C) 10/90 (Example 4)
(D) 5/95 (Example 5)
(E) 3/97 (Comparative Example 3)
(F) 0/100 (Comparative Example 4) in which the chain extending reaction was carried out adding small amount of 1,2,2,6,6-pentamethyl-4-hydroxy-peperidine. The coating of the DMF solution was carried out with gravure coater so that the amount of applied polyurethanes were 6 gr./m^2 (base on solid weight). Then the coated sheets were dried, and pressed with a hot emboss roll so that the base sheet and the coated layer were integrated.

Next, the embossed sheet was immersed in tricloroethylene and repeatedly subjected to immersion and squeezing for removal of AS resin.

Further the other side not embossed was raised through buffing.

The sheets (A), (B), (C), (D), (E) and (F) thus obtained were dyed with vinylsuphone reactive dye, Dlamira Brill Red F3B, at a bath ratio of 1:50, a dye concentration of 20 gr/lit. and a temperature of 50° C using a liquid flow dyeing machine for 60 minutes and finished by an ordinary method.

The leathers thus obtained looks like natural grain leathers, have softness free from rubbery elasticity and show comparatively-long ultrafine fiber nap on one side, and a grained surface with a high quality appearance. Further, as shown in Table 1, the leathers (A), (B), (C) and (D) showed a grained surface with a deep luster and a bright colour, while that (E) showed an uneven-dyeing spot pattern though it was improved in colour depth and that (F) was short of commodity value because of considerable uneven colouring, the resin part of the grained surface being little coloured.

The dyeing fastness properties of the leathers (A), (B), (C), and (D) were not problematic as shown in Table 1.

The distances between the entanglement points of the component fibers at the grained surface were measured after removing the polyurethane and finishing agents with solvent extraction. The measured value of all were about 60 microns.

TABLE 1

Leather Sheet	Colour Depth L-value	Colour Depth Naked eye judgement	Colour Fastness (grade)	Quality Naked eye judgement
(A)	55.9	good	4 4 4 - 5	good
(B)	56.8	good	4 4 4 - 5	good
(C)	57.8	good	4 4 4 - 5	good
(D)	58.4	good	4 4 4 - 5	good
(E)	60.1	improved	4 4 4 - 5	improved
(F)	62.4	poor	4 4 4 - 5	poor

1) The measurements by MS-2000 Colour Difference Meter manufactured by Macbeth

2) The dry cleaning fastness properties measured under JIS L-0860. The numeral values of discoloration and fading, contamination and colour-off are listed in the order of mention.

Example 7

A similar type of staple (3.5 denier, 51 mm length, 7 islands) fiber consisting of 60 parts of an AS resin as sea and S-I-I component and 40 parts of nylon-6 as I-I-I component was obained by spinning at 1,200 m.min., drawing 3.0 times, crimping and cutting. The I-I-I has a mean thickness of 0.003 denier.

The staple fibers were subjected to a card, cross lapper to form webs. The web was needle-punched with single barbed needles. The needle punched sheet had 380 gr./m^2 in weight and an apparent density of 0.12 gr./cm^3. High-velocity fluid streams were applied to the both surfaces of the needle-punched sheet two times respectively at a pressure of 100 kg/cm^2 with a nozzle with the 0.25 mm diameter holes arranged in one row at 2.5 mm intervals while the nozzle was oscillated. The sheet thus obtained showed the ultrafine fibers and/or their bundles super-entangled at the surface and branched from the islands-in-sea type fiber of the inner portion.

Next, the super-entangled sheet was shrunk in 85° C hot water, dried, and repeatedly subjected to immersion in tricloroethylene and squeezing for the almost-complete extraction removal of AS resin. Thereafter a raised sheet was obtained by lightly buffing one side of the nonwoven sheet using a roll sander type buffing machine.

Next, the raised sheet was subjected to dyeing and fixing with a wince dyeing machine under the following conditions.

Dye stuff: Irgalan Red Brown RL-200%, 10% owf

Drying temperature × time: 98° C × 60 min.

Fixing agent: tannic acid, tartar emetic

Treating method: treatment with weakly acidic bath of 10% owf of tannic acid at 50° C for 50 min. and, treatment with a weakly acidic bath of 5% owf tartar emetic at 50° C for 50 min.

The sheet was washed with hot water, and dried. A wine-coloured nubuk type artificial leather was obtained. Though no polyurethane binder was added, the sheet showed excellent dimensional stability and had an extra ultrafine fiber nap at the surface (raised), a soft touch free from undesirable elasticity, a high drapability, a heavy shade dyeing and as elegant an appearance as natural nubuks. Further it showed little discoloration and fading (colour-off) even through the dry cleaning with a synthe tic solvent with 2% content of charge soap.

Comparative Example 5

A nubuk type artificial leather was obtained according to Example 6 except without the fixing with the tannic acid and tartar emetic in Example 6. The nubuk type artificial leather showed the same high-grade appearance as Example 6 but when subjected to the dry cleaning with a charge-soap containing synthetic solvent almost all colour came off and considerable fading occurred.

Example 7

A 76 denier/20 filament yarn similar to that of Example 1 (the mean size of I-I-I: 0.008 denier) was obtained through spinning and drawing at a ratio of 3. The filament consists of 60 parts of AS resin as sea and S-I-I component and 40 parts of nylon-6 as I-I-I component and had 12 island components per filament. A double weave was obtained by weaving the filament yarn as the first weft and 75-denier/100 nylon-6 textured yarn as the warp and second weft. The weave has 5-leaves satin construction mainly composed of the islands-in-sea fiber at the surface and a 2/3 twill construction mainly composed of the textured filaments at the reverse surface. The density of this weaving was 110 warps/inch and 165 wefts/inch.

The textile was immersed in 85° C hot water, for removing sizing agent of the warp and for shrinkage at a time, and dried.

Next, the textile was subjected to tricloroethylene immersion and squeezing repeatedly for almost complete extraction removal of the As resin and to the ultrafining of the weft yarn. Next, after a raising oil agent was added, it was raised using a raising machine. Thereafter it was subjected to dyeing and fixing using a liquid flow dyeing machine under the following conditions.

Dyeing conditions:

Dye stuff: Irgalan Navy Blue B 10% owf
Dyeing temperature × time: 98 °C × 60 min.

Fixing conditions:

Fixing agents: tannic acid, tartar emetic
Treating method: treatment with weakly acidic bath containing 10% owf tannic acid at 60 °C for 30 min. and,
treatment with weakly acidic bath containing 5% owf tartar emetic at 60 °C and 30 min.

Thereafter the textile was washed in a hot water, dried and treated with a finishing agent.

The textile showed a very dense naps a soft surface touch, a lustrous navy-blue colour and a high-grade nubuk type appearance.

The textile showed good colour fastness, causing little colour-off and surface (raised part) fading, even on the dry cleaning with the perchloroethylene with 2% content of charge soap.

Comparative Example 6

A nubuk type textile was manufactured by the same manner as Example 7 except that Nylosan Blue F-GBL (high fasteness type acidic dye) and Nylon Fix-TH (multivalent phenol derivative) as fixing agent were used. The textile was dyed into greyish blue.

When washed with the perchloroethylene with 2% content of charge soap, it was quite short of commodity value because the colour of the raised ultrafine fibers of its surface bad-lookingly faded.

Example 8

Islands-in-sea fibers (3.5 denier, 51 mm length, 36 islands, thickness of each island is 0.05 denier) composed of 50 parts of AS resin as sea component and 50 parts of nylon-6 as islands component was subjected to a card, cross lapper to form webs, needle punched with single barbed needles.

Next the needle punched sheet was immersed in a 12% PVA aqueous solution at 85 °C, for shrinking and impreg nating with PVA at a time, and dried. Thereafter the AS resin was almost completely removed by extracting with tricloroethylene. Next it was impregnated with a 12% DMF solution of polyether-polyurethane, solidified in water, and subjected to removing of PVA and DMF in hot water.

Thereafter the both surfaces of the nonwoven sheet were buffed and a sheet with a 30% content of polyurethane was obtained.

The sheet was subjected to dyeing and fixing using a liquid flow dyeing machine under the following conditions.

Dyeing conditions:

Dye: Irgalan Red Brown RL 200% 10% owf
Kayakalan Red BL 2% owf
Dyeing temperature × time: 98 °C × 50 min.

Fixing conditions:

The same as Example 7

Thereafter the sheet was washed with water and treated with a 20 gr./lit. aqueous solution of Bisnol A-30 (alkylamine type nonionic surface active agent manufactured by Ipposha Yushi Co.) at 60 °C for 20 minutes. It was further washed with hot and cold waters.

The artificial suede thus obtained had soft hand, heavy shaded and high colour fastness, and showed no colour fading even after dry cleaning with a synthetic solvent (perchlene) with 2% content of charge soap.

Reference is directed to our copending application No. 84304074.2-2108 (Publication No. 0165345) from which the present application is divided.

Claims

1. A process for dyeing polyamide ultrafine fibers, which comprises dyeing with a metal dye complex and treating with a fixing agent.

2. A process according to Claim 1, wherein tannin and metal salt are used as said fixing agents.

3. A process according to Claim 1, wherein said metal dye complex has molecular weight more than 700.

4. A process according to Claim 1, wherein said metal dye complex is a 2:1 premetallized dye.

5. A process for manufacturing an artificial leather according to Claim 1, wherein a crumpling is carried out after said dyeing.

6. A process for dyeing polyamide ultrafine fibers according to Claim 1, wherein said artificial leather is a raised and/or grained artificial leather.

7. A process for dyeing a polyamide ultrafine fiber sheet containing a porous elastomer applied thereto, which comprises dyeing with a metal dye complex and treatment with a fixing agent and a surface active agent.

8. A process for dyeing a polyamide ultrafine fiber sheet, as claimed in Claim 7, wherein said surface active agent is a polyoxyalkylene nonionic type and/or a betaine amphoteric type.

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EUROPEAN SEARCH REPORT

Application Number

EP 87 11 7815

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,X	CHEMICAL ABSTRACTS, vol. 103, no. 8, August 1987, page 56, abstract no. 55191p, Columbus Ohio, US; & JP-A-60 75 689 (TORAY INDUSTRIES INC.) 30-04-1985 * Abstract *	1-4,7	D 06 N 3/00 D 06 P 3/24
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A	CHEMICAL ABSTRACTS, vol. 96, no. 18, 3rd May 1982, page 82, abstract no. 144370a, Columbus, Ohio, US; J. GUTHRIE: "The effect of tanning agents on the rate of alkaline desorption of acid dyes from nylon 6." & COLOURAGE 1982, 29(4), 3-9 * Abstract *	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl.4) D 06 N D 06 P
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05-09-1988	PFANNENSTEIN H.F.

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Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	CHEMICAL ABSTRACTS, vol. 95, no. 14, %th October 1981, page 76, abstract no. 117007k, Columbus, Ohio, US; & JP-A-81 73 167 (TORAY INDUSTRIES, INC.) 17-06-1981 * Abstract *	1	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05-09-1988	PFANNENSTEIN H.F.

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