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(54) **SUEDE TYPE ARTIFICIAL LEATHER WITH SOILING PROTECTION PROPERTY AND PREPARATION THEREFOR**

VELOURSARTIGES KUNSTLEDER MIT FÄULNISVERHINDERNDER EIGENSCHAFT UND HERSTELLUNGSVERFAHREN DAFÜR

CUIR ARTIFICIEL DE TYPE SUÉDINE PRÉSENTANT UNE PROPRIÉTÉ D'ANTISALISSURE, ET PROCÉDÉ DE PRÉPARATION DE CELUI-CI

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**Description****[Technical Field]**

5 **[0001]** The present invention relates to a suede type artificial leather having soiling protection properties, and more particularly to a simple method of preparing an artificial leather impregnated with a modified polyurethane having an soiling protection property, which the addition of an additive having an soiling protection function is not needful.

**[Background Art]**

10 **[0002]** Artificial leather is prepared by impregnating a polymer elastomer in a nonwoven fabric formed by three-dimensionally interlacing ultrafine fibers. The artificial leather has a smooth texture and unique appearance which is similar to natural leather and is widely used in various fields such as shoes, clothes, gloves, miscellaneous goods, furniture and automobile interior materials.

15 **[0003]** Artificial leather requires various characteristics according to its use. For example, the properties required for artificial leather for clothing include high durability, high sensitivity, excellent dyeability which can be stained with various colors and concentrations and high fastness.

20 **[0004]** In order to improve the durability among these demand characteristics, artificial leather is required to be provided with an soiling protection function including a water-repellent and oil-repellent function for inhibiting the occurrence of fouling even after a long-term use.

**[0005]** To provide an soiling protection property to artificial leather, a fluorine-based or silicone-based surfactant can be mixed with polyurethane and a mixture can be impregnated in a nonwoven fabric, thereby arranging a fluorine chain or a silicone chain on the surface of the artificial leather. The occurrence of fouling can be suppressed from the outside of the artificial leather accordingly.

25 **[0006]** However, fluorine-based or silicone-based surfactants are generally inactive additives, and in case that they are mixed with polyurethane, there is a problem that they are not chemically bonded to each other, thus they are free to move in the urethane molecular structure and as a result, transition of the surfactants to the surface of artificial leather occurs causing a surface change with the passage of time thereof.

30 **[0007]** Korean Patent No. KR100969839 B discloses a modified urethane to which fluorine is bonded and a method of preparing leathery sheet object using the modified urethane without the addition of a fluorine-based compound.

**[0008]** According to the patent, a urethane compound modified with fluorine-containing side chain in which

(i) 3 to 12 fluorine-containing side chains having a molecular weight of 200 to 1,000 are bonded to a urethane bond-containing compound having a molecular weight of 500 to 5,000

35 (ii) the fluorine content is 20 to 60 weight% in terms of fluorine atoms, and

(iii) containing 6 to 36 urethane bonds per a molecule,

improves water repellency and water resistance at the cut cross section of the leathery sheet object, are disclosed.

40 **[0009]** However, according to the patent, the urethane compound modified with fluorine-containing side chain is used together with polyurethane which is an elastomer constituting the treatment liquid of a leathery sheet object, and exhibits an effect as a water-repellent agent as an additive.

**[0010]** On the other hand, the development of providing an soiling protection effect by an elastomer impregnated in artificial leather without adding an soiling protection additive is progressing.

45 **[0011]** EP 1 143 063 A2 discloses an artificial leather having a base sheet impregnated with a resin layer comprising a polyurethane having side chains derived from a fluorine-containing diol.

**[Disclosure]****[Technical Problem]**

50 **[0012]** To solve the above problems, an object of the present invention is to provide artificial leather impregnated with a novel modified polyurethane, having an soiling protection property without adding an additive having an soiling protection property.

**[Technical Solution]**

55 **[0013]** To achieve the object of the present invention, an aspect of the present invention provides a suede type artificial leather according to claim 1, having soiling protection property in which a polymeric elastomer is impregnated in a

nonwoven fabric formed by three-dimensionally interlacing ultrafine fibers and raising is formed, wherein the polymeric elastomer is a fluorine-containing modified polyurethane, and the fluorine-containing modified polyurethane is a product obtained by a polymerization reaction between a urethane prepolymer having isocyanate groups at terminals, obtained by reacting a diol and a diisocyanate, and a fluorinated carbon compound having hydroxy functional groups at both terminals, and has a weight average molecular weight (Mw) of 500,000 to 800,000, wherein the urethane prepolymer has a weight average molecular weight (Mw) of 400,000 to 700,000.

**[0014]** The present invention also provides a method of preparing a suede type artificial leather according to claim 2, having soiling protection property in which a polymeric elastomer is impregnated in a nonwoven fabric formed by three-dimensionally interlacing ultrafine fibers and raising is formed, wherein the polymeric elastomer is a fluorine-containing modified polyurethane, and the fluorine-containing modified polyurethane is prepared by a method comprising: preparing a urethane prepolymer having a weight average molecular weight (Mw) of 400,000 to 700,000 by reacting a diol and a diisocyanate; and preparing a polymerization product having a weight average molecular weight (Mw) of 500,000 to 800,000 by reacting the prepolymer and a fluorinated carbon compound having hydroxy functional groups at both terminals.

#### **[Advantageous Effects]**

**[0015]** According to the present invention, artificial leather impregnated with a fluorine-containing modified polyurethane elastomer having soiling protection property also exhibits excellent water repellency in addition to the soiling protection property.

**[0016]** In addition, the artificial leather of the present invention can decrease the surface change with the passage of time, as compared with artificial leather produced by separately adding a fluorine-containing surfactant having the large occurrence of surface change with the passage of time due to the migration of the surfactant.

**[0017]** Further, since the separate addition of the fluorine-based surfactant is not required, the manufacture method can be simplified.

#### **[Description of Drawings]**

##### **[0018]**

Figure 1 illustrates a polymerization reaction scheme of a fluorine-containing modified polyurethane according to an embodiment of the present invention.

Figure 2 shows a drawing of an apparatus for evaluating water repellency of the artificial leather.

Figure 3 is a rating criterion for the water repellency evaluation.

#### **[Best Mode]**

**[0019]** The present invention relates to a suede type artificial leather having soiling protection property in which a polymeric elastomer is impregnated in a nonwoven fabric formed by three-dimensionally interlacing ultrafine fibers and raising is formed, wherein the polymeric elastomer is a fluorine-containing modified polyurethane.

**[0020]** The fluorine-containing modified polyurethane is a product obtained by a polymerization reaction between a urethane prepolymer having isocyanate groups at terminals and a weight average molecular weight (Mw) of 400,000 to 700,000, obtained by reacting a diol and a diisocyanate, and a fluorinated carbon compound having hydroxy functional groups at both terminals, and has a weight average molecular weight (Mw) of 500,000 to 800,000.

**[0021]** The diol may be used alone or in combination with diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, ethylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol or polytetramethylene glycol.

**[0022]** The diisocyanate may be 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- to 1,4-diiisocyanate, 1-isocyanate-3-isocyanatemethyl-3,5,5-trimethylcyclohexane(isophorone diisocyanate), bis-(4-isocyanatecyclohexyl) methane(hydrogenated MDI), 2- to 4-isocyanatecyclohexyl-2-isocyanatecyclohexylmethane, 1,3- to 1,4-tetramethylxylene diisocyanate, 2,4- to 2,6-diisocyanate toluene, 2,2-2,4- to 4,4'-diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate, xylene diisocyanate or diphenyl-4,4-diisocyanate, and the like, but are not limited thereto.

**[0023]** In the present invention, when the diol is reacted with the diisocyanate, the proportion to be reacted needs an excess amount of all NCO groups rather than all OH groups. By adjusting the ratio of the diol and the diisocyanate to react as such, the resulting urethane prepolymer may have an isocyanate group terminal in side chains thereof.

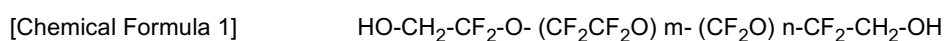
**[0024]** At this time, the molar ratio of the diol and the diisocyanate is preferably 1:1.2 to 1:1.4 because the fluorine-containing modified polyurethane having the weight average molecular weight range of the present invention can be produced.

**[0025]** When the molar ratio is less than 1:1.2, a side reaction occurs due to moisture or active hydrogen, etc. in the air, or the isocyanate reacts with each other to manifest a property of isocyanate for forming a trimer and to decrease the polymerization efficiency due to the increase of inactive NCO. When the molar ratio is more than 1:1.4, the excess of NCO groups causes an insufficient OH group so that it is difficult to raise the degree of polymerization.

**[0026]** In order to ensure the mechanical properties required in case that the fluorine-containing modified polyurethane of the present invention is applied to artificial leather, it is necessary to increase the polymerization molecular weight to an appropriate level easily and to do so, a urethane prepolymer can be prepared first.

**[0027]** If the weight average molecular weight (Mw) of the urethane prepolymer is less than 400,000, the molecular weight of the fluorine-containing modified polyurethane is lowered, and the mechanical properties such as tear strength, etc. and the chemical properties such as thermal stability and hydrolysis resistance, etc. are lowered. If it exceeds 700,000, the gelation phenomenon may occur in the production of the fluorine-containing modified polyurethane, and the viscosity of the fluorine-containing modified polyurethane may be high to reduce the workability in blending of an elastomer impregnation solution, and the resulting fluorine-containing modified polyurethane may be hardened, which may deteriorate the sensual quality in artificial leather.

**[0028]** The fluorinated carbon compound having hydroxy functional groups at both terminals is represented by the following Chemical Formula 1, has 8 to 14 fluorine groups bonded to one side chain and fluorine content of 50 to 70mol% in one functional group and is an ether diol having hydroxy functional groups at both terminals.



**[0029]** The fluorine-containing modified polyurethane obtained by reacting the ether diol of the Chemical Formula 1 with the urethane prepolymer can provide water-repellent and oil-repellent functions because the fluorine which is present as the diatomic molecule in the element state, in the side chain of the urethane polymer is bonded to prevent that the modified polyurethane is bonded to other atoms or molecules. Thus, by the fluorine-containing modified polyurethane of the present invention, the artificial leather can be suppressed deposition of an external contaminant and easily removed contaminants on the coated surface.

**[0030]** A commercialized product of a fluorinated carbon compound having hydroxy functional groups at both terminals is Solvay's FLUOROLINK.

**[0031]** The polymerization of the fluorine-containing modified polyurethane of the present invention can be carried out through the addition-polymerization by adding dropwise the fluorinated carbon compound having hydroxy functional groups at both terminals to the urethane prepolymer until the desirable molecular weight is reached. At this time, the addition amount of the fluorinated carbon compound corresponds to the moles of excess isocyanate in preparing the urethane prepolymer.

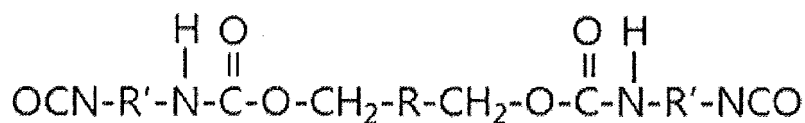
**[0032]** When a fluorinated carbon compound having hydroxy functional groups at both terminals is added at a time, the fluorinated carbon compound is partially bound to the urethane prepolymer, so that the dispersion of the fluorine groups in the fluorine-containing modified polyurethane becomes insufficient and as a result it is difficult to develop the uniform soiling protection performance. Therefore, it is preferable to slowly add dropwise.

**[0033]** The fluorine-containing modified polyurethane of the present invention is polymerized by the above-mentioned method and is characterized by having a weight average molecular weight (Mw) of 500,000 to 800,000. If the weight average molecular weight (Mw) is less than 500,000, the mechanical strength such as tear strength, etc. and chemical properties such as thermal stability, hydrolysis resistance, and the like in artificial leather may be reduced. When the weight average molecular weight (Mw) is more than 800,000, the viscosity of the fluorine-containing modified polyurethane may be high to reduce the workability in blending of an elastomer impregnation solution, and the resulting fluorine-containing modified polyurethane may be hardened, which may deteriorate the sensual quality in artificial leather.

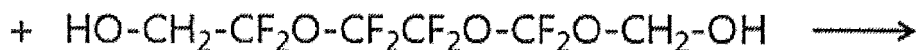
**[0034]** It is preferable that the fluorine-containing modified polyurethane of the present invention has a fluorine content of 5 to 20mol%. When the content is less than 5mol%, the soiling protection performance is insufficient, and when the content is more than 20mol%, the water repellency is too strong so that the fluorine-containing modified polyurethane cannot undergo the substitution solidification in the manufacturing process of the artificial leather.

**[0035]** An example of the synthesis reaction of the fluorine-containing modified polyurethane described above can be represented by the following reaction:

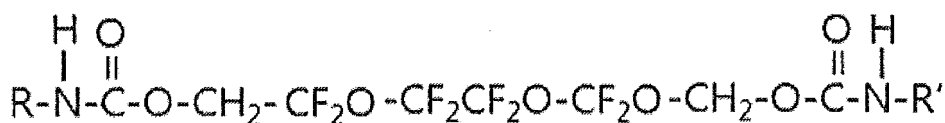
[Reaction Scheme]



Urethane prepolymer in which isocyanate is coupled to both ends thereof



Fluorinated carbon compound



Fluorine-containing modified polyurethane

[0036] Here, R and R' are each independently an alkyl group.

[0037] Generally, artificial leather can be prepared by impersing a nonwoven fabric formed by three-dimensionally interlacing ultrafine fibers in an impregnating liquid comprising a polymeric elastomer such as polyurethane, impregnating the polymeric elastomer to solidify the elastomer in the nonwoven fabric, raising by grinding and dyeing.

[0038] In the present invention, the fluorine-containing modified polyurethane of the present invention can be used as a polymeric elastomer of the impregnating liquid. The fluorine-containing modified polyurethane may be used as an impregnating liquid by diluting it in dimethyl formamide of 100 to 200wt% in respect of the weight of the fluorine-containing modified polyurethane.

[0039] The present invention will be described more fully hereinafter with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown.

[Preparation Example 1]

[0040] Polytetramethylene glycol (Mw: 1,500-2,500) of 0.45mol, ethylene glycol of 0.47mol and 1,4-butanediol of 0.08mol were subjected to addition polymerization with 1.2mol of 4,4'-diphenylmethane diisocyanate, and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 40% by weight to prepare an NCO-terminated polyurethane prepolymer having a weight average molecular weight (Mw) of 700,000.

[0041] The prepared prepolymer was subjected to addition polymerization with 0.2mol of a fluorinated carbon compound having hydroxy functional groups at both terminals in a side chain (trade name: FLUOROLINK D10-H, manufactured by Solvay, Mw: 1,400) and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 30% by weight to prepare a fluorine-containing modified polyurethane having a weight average molecular weight (Mw) of 800,000.

[Preparation Example 2]

[0042] Polytetramethylene glycol (Mw: 1,500-2,500) of 0.45mol, ethylene glycol of 0.47mol and 1,4-butanediol of 0.08mol were subjected to addition polymerization with 1.3mol of 4,4'-diphenylmethane diisocyanate, and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 40% by weight to prepare an NCO-terminated polyurethane prepolymer having a weight average molecular weight (Mw) of 600,000.

[0043] The prepared prepolymer was subjected to addition polymerization with 0.3mol of a fluorinated carbon compound having hydroxy functional groups at both terminals in a side chain (trade name: FLUOROLINK D10-H, manufactured by Solvay, Mw: 1,400) and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 30% by weight to prepare a fluorine-containing modified polyurethane having a weight average molecular weight (Mw) of 700,000.

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[Preparation Example 3]

5 **[0044]** Polytetramethylene glycol (Mw: 1,500-2,500) of 0.45mol, ethylene glycol of 0.47mol and 1,4-butanediol of 0.08mol were subjected to addition polymerization with 1.4mol of 4,4'-diphenylmethane diisocyanate, and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 40% by weight to prepare an NCO-terminated polyurethane prepolymer having a weight average molecular weight (Mw) of 400,000.

10 **[0045]** The prepared prepolymer was subjected to addition polymerization with 0.4mol of a fluorinated carbon compound having hydroxy functional groups at both terminals in a side chain and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 30% by weight to prepare a fluorine-containing modified polyurethane having a weight average molecular weight (Mw) of 500,000.

[Preparation Example 4]

15 **[0046]** Polytetramethylene glycol (Mw: 1,500-2,500) of 0.45mol, ethylene glycol of 0.47mol and 1,4-butanediol of 0.08mol were subjected to addition polymerization with 1.0mol of 4,4'-diphenylmethane diisocyanate, and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 70% by weight to prepare a reaction-terminated polyurethane having a weight average molecular weight (Mw) of 700,000.

[Preparation Example 5]

20 **[0047]** Polytetramethylene glycol (Mw: 1,500-2,500) of 0.45mol, ethylene glycol of 0.47mol and 1,4-butanediol of 0.08mol were subjected to addition polymerization with 1.7mol of 4,4'-diphenylmethane diisocyanate, and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 40% by weight to prepare an NCO-terminated polyurethane prepolymer having a weight average molecular weight (Mw) of 350,000.

25 **[0048]** The prepared prepolymer was subjected to addition polymerization with 0.7mol of a fluorinated carbon compound having hydroxy functional groups at both terminals in a side chain and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 30% by weight to prepare a fluorine-containing modified polyurethane having a weight average molecular weight (Mw) of 450,000.

30 [Preparation Example 6]

35 **[0049]** Polytetramethylene glycol (Mw: 1,500-2,500) of 0.45mol, ethylene glycol of 0.47mol and 1,4-butanediol of 0.08mol were subjected to addition polymerization with 1.0mol of 4,4'-diphenylmethane diisocyanate, and the produced polymerization product was diluted and dissolved in dimethylformamide so as to be a total solid content of 70% by weight to prepare a reaction-terminated polyurethane having a weight average molecular weight (Mw) of 700,000.

[Example 1]

40 **[0050]** The fluorine-containing modified polyurethane of the Preparation Example 1 was diluted with 150% by weight of dimethylformamide in respect of the weight of the polyurethane to prepare an impregnating liquid.

**[0051]** The nonwoven fabric in which the polyester fibers (0.3 denier, fiber length: 51mm) was entangled was immersed in the impregnation solution, taken out and carried out coagulating process in an aqueous solution diluted with 20% by weight of dimethylformamide to form the fluorine-containing modified polyurethane elastomer impregnated nonwoven fabric in which a fine porous layer was formed in the fiber structure.

45 **[0052]** Thereafter, a suede type artificial leather was produced by raising finishing on the surface of the elastomer impregnated nonwoven fabric.

[Example 2]

50 **[0053]** A suede type artificial leather was produced in the same manner as in Example 1, except that the fluorine-containing modified polyurethane of Preparation Example 2 was used to prepare an impregnation solution.

[Example 3]

55 **[0054]** A suede type artificial leather was produced in the same manner as in Example 1, except that the fluorine-containing modified polyurethane of Preparation Example 3 was used to prepare an impregnation solution.

[Comparative Example 1]

**[0055]** A suede type artificial leather was produced in the same manner as in Example 1, except that the fluorine-containing modified polyurethane of Preparation Example 4 was used to prepare an impregnation solution.

[Comparative Example 2]

**[0056]** A suede type artificial leather was produced in the same manner as in Example 1, except that the fluorine-containing modified polyurethane of Preparation Example 5 was used to prepare an impregnation solution.

[Comparative Example 3]

**[0057]** A suede type artificial leather was produced in the same manner as in Example 1, except that the reaction-terminated polyurethane of Preparation Example 6 is diluted with a mixture of 150% by weight of dimethylformamide and 0.5% of a fluorine-based surfactant (trade name FC-4430, 3M) with respect of the weight of the polyurethane, to prepare an impregnation solution.

**[0058]** The weight average molecular weights (Mw) of the polymer prepared in the above Examples and Comparative Examples were measured using gel permeation chromatography (GPC) (RI-8000, manufactured by Tosoh Corporation) passing through the column connected TSKgel super HM-L, TSKgel super HM-M and TSKgel super HM-N (Tosoh) in series with tetrahydrofuran (flow rate: 1mL/min) as a mobile phase and the column oven at temperature of 40 °C.

**[0059]** The raw material composition ratio for the polymerization in the above Preparation Examples and the weight average molecular weight of the polymerization product are shown in the following Table 1.

[Table 1]

	Preparation Example 1	Preparation Example 2	Preparation Example 3	Preparation Example 4	Preparation Example 5	Preparation Example 6
diol	1 mol	1 mol	1 mol	1 mol	1 mol	1 mol
Diisocyanate	1.2 mol	1.3 mol	1.4 mol	1 mol	1.7 mol	1 mol
prepolymer	700,000	600,000	400,000	700,000	350,000	700,000
FLUOROLINK D10-H	0.2 mol	0.3 mol	0.4 mol	-	0.7 mol	-
Fluorine-containing modified polyurethane	800,000	700,000	500,000	-	450,000	-
surfactant (FC-4430)	-	-	-	-	-	0.5%
The value of the surfactant is that in elastomer impregnation solution.						

**[0060]** The properties of the artificial leather prepared in the above Examples and Comparative Examples were evaluated according to the following soiling protection property evaluation method, and the results are shown in Table 2 below.

#### Evaluation method of soiling protection property

**[0061]** An artificial leather sample was cut into a size of 5x15cm and placed in a rubbing fastness tester (model name DL-2007) and a test fabric (product name: IEC carbon black/mineral oil, manufactured by EMPA) was placed on the surface of the fouled sample and rubbed by 10 times reciprocating motion, and the soiled sample was visually compared to give a soiling degree.

(Standard of soiling grade, 5: no visible soiling 4: slightly visible but almost inconspicuous soiling 3: slightly soiled and visible, 2: slightly severe soiling 1: significant soiling)

#### Water repellency evaluation method

**[0062]** The artificial leather sample was fixed (diameter 10cm) as shown in Figure 2 and then tilted at an angle of 45°. Then, 100ml of water was injected into the spray-type funnel located at the upper part, and the degree of distribution of the water droplets on the surface of the sample after the completion of the spraying was observed to give a rating according to Figure 3.

[Table 2]

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Soiling grade	3.5	3.5	3.5	2.0	2.5	3.5
Water repellency rating	3.5	4.0	4.5	2.5	3.0	2.5

**[0063]** As shown in the above Table 2, it can be confirmed that, the artificial leather of the Example according to the present invention, in which the fluorine-containing modified polyurethane is impregnated as an elastomer has the same soiling protection performance as the artificial leather (Comparative Example 3) in which the fluorine-containing surfactant was separately added, and exhibits improved water repellency at the same time.

**[0064]** The artificial leather according to the present invention is an artificial leather in which a fluorine-containing modified polyurethane having an soiling protection property is impregnated. The fluorine-containing surfactant does not need separately for the soiling protection property during the production of artificial leather so that productivity increase is possible. The artificial leather according to the present invention exhibits an excellent soiling protection performance that suppresses the surface change with the passage of time of the artificial leather caused by using a fluorine-containing surfactant, thereby improving the appearance quality of the artificial leather.

#### Claims

1. A suede type artificial leather having soiling protection property in which a polymeric elastomer is impregnated in a nonwoven fabric formed by three-dimensionally interlacing ultrafine fibers and raising is formed, wherein the polymeric elastomer is a fluorine-containing modified polyurethane, and the fluorine-containing modified polyurethane is a product obtained by a polymerization reaction between a urethane prepolymer having isocyanate groups at terminals, obtained by reacting a diol and a diisocyanate, and a fluorinated carbon compound having hydroxy functional groups at both terminals, and has a weight average molecular weight (Mw) of 500,000 to 800,000, wherein the urethane prepolymer has a weight average molecular weight (Mw) of 400,000 to 700,000.
2. A method of preparing a suede type artificial leather having soiling protection property in which a polymeric elastomer is impregnated in a nonwoven fabric formed by three-dimensionally interlacing ultrafine fibers and raising is formed, wherein the polymeric elastomer is a fluorine-containing modified polyurethane, and the fluorine-containing modified polyurethane is prepared by a method comprising:
  - preparing a urethane prepolymer having a weight average molecular weight (Mw) of 400,000 to 700,000 by reacting a diol and a diisocyanate; and
  - preparing a polymerization product having a weight average molecular weight (Mw) of 500,000 to 800,000 by reacting the prepolymer and a fluorinated carbon compound having hydroxy functional groups at both terminals.
3. The method of preparing a suede type artificial leather according to claim 2, wherein the diol and the diisocyanate is reacted at a molar ratio of 1: 1.2 to 1: 1.4 to prepare the urethane prepolymer.

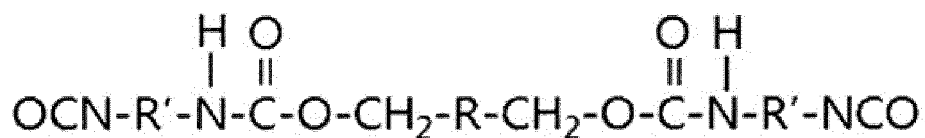
**Patentansprüche**

- 5 1. Veloursartiges Kunstleder, das eine Verschmutzungsschutzeigenschaft aufweist, wobei ein polymeres Elastomer in einen Vliesstoff imprägniert ist, gebildet durch dreidimensionales Verflechten ultrafeiner Fasern, und aufgekraust ist,  
wobei das polymere Elastomer ein fluorhaltiges modifiziertes Polyurethan ist,  
das fluorhaltige modifizierte Polyurethan ein Produkt ist, das durch eine Polymerisationsreaktion zwischen einem Urethanprepolymer, das Isocyanatgruppen als Terminale aufweist und durch Reagieren eines Diols und eines Diisocyanats erhalten wird, und einer fluorierten Kohlenstoffverbindung, die hydroxyfunktionelle Gruppen an beiden  
10 Terminalen aufweist, erhalten wird, und ein gewichtsdurchschnittliches Molekulargewicht (Mw) von 500.000 bis 800.000 aufweist, erhalten wird,  
wobei das Urethanprepolymer ein gewichtsdurchschnittliches Molekulargewicht (Mw) von 400.000 bis 700.000 aufweist.
- 15 2. Verfahren für die Herstellung eines veloursartigen Kunstleders, das eine Verschmutzungsschutzeigenschaft aufweist, wobei ein polymeres Elastomer in einen Vliesstoff imprägniert wird, der durch dreidimensionales Verflechten ultrafeiner Fasern gebildet wird, und aufgekraust wird,  
wobei das polymere Elastomer ein fluorhaltiges modifiziertes Polyurethan ist und das fluorhaltige modifizierte Polyurethan durch ein Verfahren hergestellt wird umfassend:
- 20 Herstellen eines Urethanprepolymers, das ein gewichtsdurchschnittliches Molekulargewicht (Mw) von 400.000 bis 700.000 aufweist, durch Reagieren eines Diols und eines Diisocyanats; und  
Herstellen eines Polymerisationsprodukts, das ein gewichtsdurchschnittliches Molekulargewicht (Mw) von 500.000 bis 800.000 aufweist, durch Reagieren des Prepolymers und einer fluorierten Kohlenstoffverbindung,  
25 die hydroxyfunktionelle Gruppen an beiden Terminalen aufweist.
3. Verfahren für die Herstellung eines veloursartigen Kunstleders nach Anspruch 2, wobei das Diol und das Diisocyanat in einem Molverhältnis von 1:1,2 bis 1:1,4 reagiert werden, um das Urethanprepolymer herzustellen.

**Revendications**

- 30 1. Un cuir artificiel de type daim ayant une propriété de protection contre la salissure dans lequel un élastomère polymère est imprégné dans un tissu non tissé formé par des fibres ultrafines à entrelacement tridimensionnel et une surélévation est formée,  
35 dans lequel l'élastomère polymère est un polyuréthane modifié contenant du fluor, et  
le polyuréthane polymère contenant du fluor est un produit obtenu par une réaction de polymérisation entre un prépolymère d'uréthane ayant des groupes isocyanate terminaux, obtenu par la réaction d'un diol et d'un diisocyanate, et un composé carboné fluoré ayant des groupes fonctionnels hydroxyle aux deux extrémités, et présente un  
40 poids moléculaire moyen en poids (Mw) de 500.000 à 800.000,  
dans lequel le prépolymère d'uréthane a un poids moléculaire moyen en poids (Mw) de 400.000 à 700.000.
2. Un procédé de préparation d'un cuir artificiel de type daim ayant une propriété de protection contre la salissure, dans lequel un élastomère polymère est imprégné dans un tissu non tissé formé par des fibres ultrafines à entrelacement tridimensionnel et une surélévation est formée,  
45 dans lequel l'élastomère polymère est un polyuréthane modifié contenant du fluor, et le polyuréthane polymère contenant du fluor est préparé par un procédé comprenant :
- la préparation d'un prépolymère d'uréthane ayant un poids moléculaire moyen en poids (Mw) de 400.000 à 700.000 en faisant réagir un diol et un diisocyanate ; et  
50 la préparation d'un produit de polymérisation ayant composé carboné fluoré ayant un poids moléculaire moyen en poids (Mw) de 500.000 à 800.000 en faisant réagir le prépolymère et un composé carboné fluoré ayant des groupes fonctionnels hydroxyle aux deux extrémités.
- 55 3. Le procédé de préparation d'un cuir artificiel de type daim ayant une propriété de protection contre la salissure selon la revendication 2, dans lequel le diol et le diisocyanate sont mis à réagir dans un rapport molaire de 1 : 1,2 à 1 : 1,4 pour préparer le prépolymère d'uréthane.

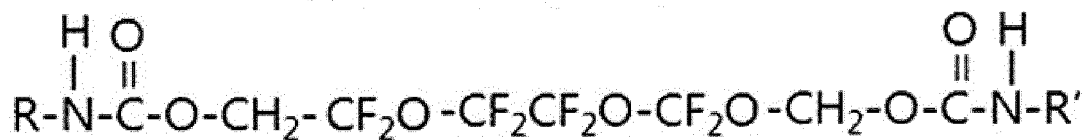
[FIG. 1]



Urethane prepolymer in which isocyanate is coupled to both ends thereof

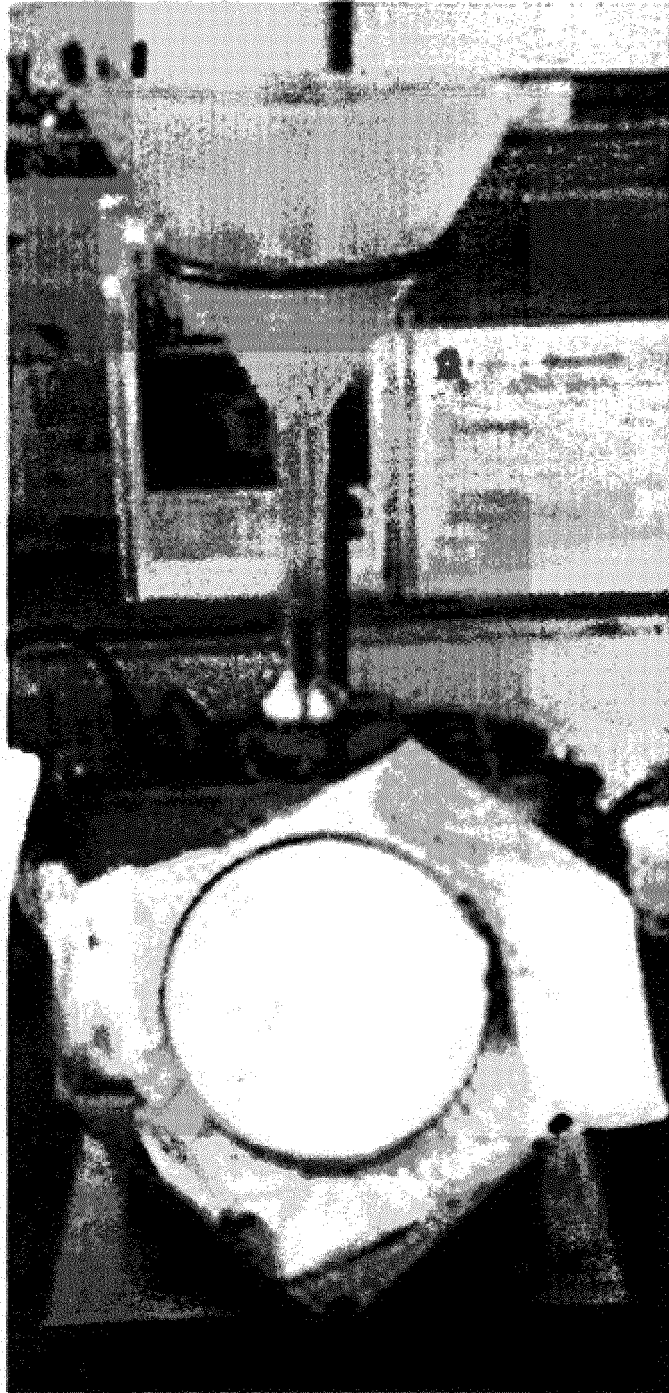


Fluorinated carbon compound

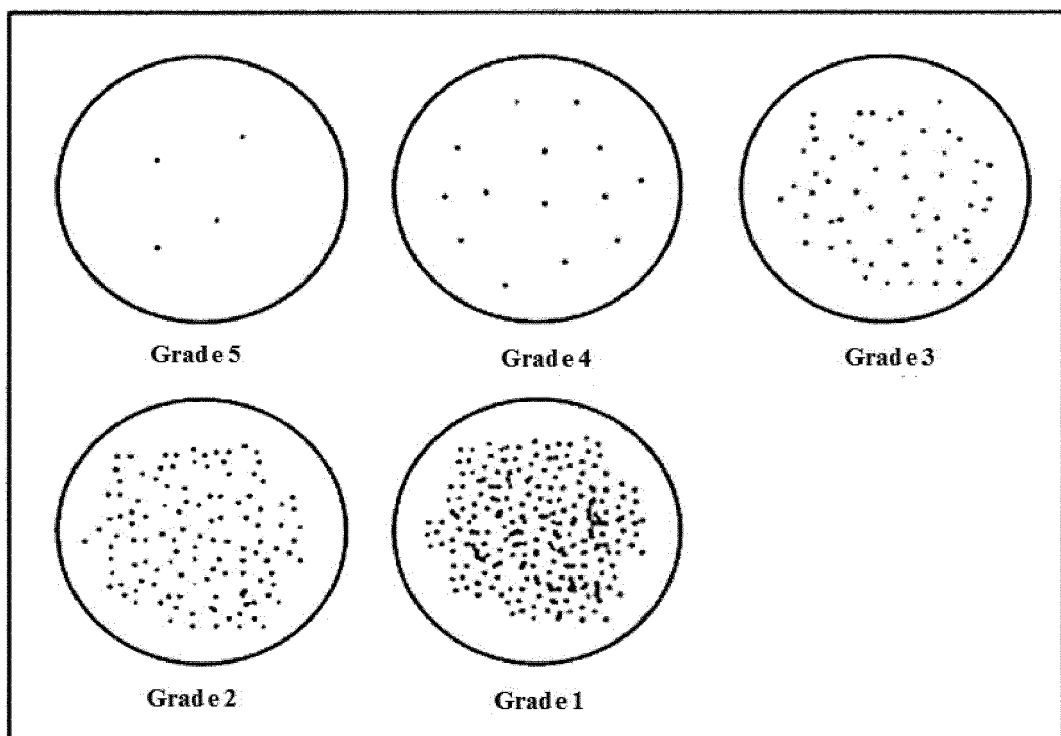


Fluorine-containing modified polyurethane

[FIG. 2]



[FIG. 3]



**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

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