



(51) International Patent Classification:

C08G 18/12 (2006.01)

C14C 11/00 (2006.01)

C09D 175/04 (2006.01)

(21) International Application Number:

PCT/CN2019/076936

(22) International Filing Date:

05 March 2019 (05.03.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicants: DOW GLOBAL TECHNOLOGIES LLC

[US/US]; 2040 Dow Center, Midland, Michigan 48674

(US). DOW SILICONES CORPORATION [US/US];

2200 West Salzburg Road, Midland, Michigan 48686-0994

(US).

(72) Inventors; and

(71) Applicants (for SC only): HU, Xiaolian [CN/CN]; No.

936 Zhang Heng Road, Shanghai Pilot Free Trade Zone,

Shanghai 201203 (CN). ZHANG, Chao [CN/CN]; No.

936 Zhang Heng Road, Shanghai Pilot Free Trade Zone,

Shanghai 201203 (CN). TAI, Xiangyang [CN/CN]; No.

936 Zhang Heng Road, Shanghai Pilot Free Trade Zone,

Shanghai 201203 (CN). FENG, Yanli [CN/CN]; No. 936

Zhang Heng Road, Shanghai Pilot Free Trade Zone, Shang-

hai 201203 (CN). SHI, Lili [CN/CN]; No. 936 Zhang Heng

Road, Shanghai Pilot Free Trade Zone, Shanghai 201203

(CN). XIONG, Jiawen [CN/CN]; No. 936 Zhang Heng

Road, Shanghai Pilot Free Trade Zone, Shanghai 201203

(CN). MA, Biao [CN/CN]; No. 936 Zhang Heng Road,

Shanghai Pilot Free Trade Zone, Shanghai 201203 (CN).

(74) Agent: SHANGHAI PATENT & TRADEMARK LAW

OFFICE, LLC; 435 Guiping Road, Shanghai 200233

(CN).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,

CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,

DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,

HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: WATERBORNE POLYURETHANE DISPERSION AND METHOD FOR PREPARING THE SAME

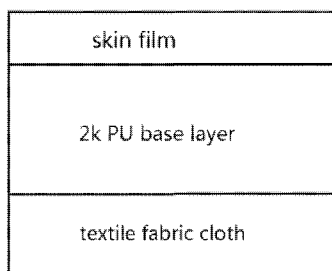


Figure 1

(57) Abstract: Provided is a waterborne polyurethane dispersion. The waterborne polyurethane dispersion is prepared in the presence of a hydrophilic amino siloxane compound and exhibits good anti-stickiness while retaining superior mechanical properties. A laminated synthetic leather article prepared with said waterborne polyurethane dispersion as well the method for preparing the synthetic leather article are also provided.

WATERBORNE POLYURETHANE DISPERSION AND METHOD FOR PREPARING THE SAME

FIELD OF THE INVENTION

5 The present disclosure relates to a waterborne polyurethane dispersion and a method for preparing the same, a laminated synthetic leather article comprising a skin film derived from the waterborne polyurethane dispersion and a method for preparing the same. The laminated synthetic leather article prepared by said waterborne polyurethane dispersion exhibits superior anti-stickiness and mechanical properties.

INTRODUCTION

10 Synthetic leather gets popular applications in people's daily life, from clothes, footwear, bag and luggage, home upholstery to seats in automobile. It provides similar performance and hand feeling to natural leather with much better cost advantage. Synthetic leather is fabricated by coating polymer(s) on a fabric substrate or impregnating polymer(s) into a fabric substrate, and the most commonly used polymer is polyurethane. Traditional processes are performed with the solution of polyurethane resin(s) in volatile organic solvents such as dimethylformamide (DMF), methylethyl ketone (MEK) and toluene. Porous structure of PU is created by precipitating PU polymer chain in a controlled manner through leading the coated or impregnated fabric substrate into water bath. Such a porous structure is very critical and essential to endow the synthetic leather with a similar hand feeling as that of natural leather. However, the volatile organic solvents are very hazardous to plant operators, consumers and environment. Therefore, synthetic leather industry is pushed to solvent free fabrication process, to minimize the use of volatile organic solvents in the manufacturing of PU synthetic leather.

20 Waterborne polyurethane dispersion (PUD) is a green alternative to PU solution in the volatile organic solvents such as DMF. Currently, most of the waterborne PUD's are based on polyester polyol and aliphatic isocyanates due to their good mechanical properties (such as tensile strength and modulus). However, polyester polyol based PUD's have many problems, e.g. poor hydrolysis resistance, high cost and low dispersity in water due to high viscosity of polyester prepolymer). Polyether polyol based PUD's don't have such problems, but the

mechanical properties and anti-stickiness performance are poor due to the intrinsic softness of polyether polyol. A newly developed technology for producing a synthetic leather is to laminate a externally emulsified skin layer derived from a polyurethane dispersion with a non-solvent 2k PU foam layer, but the skin layer of the laminated synthetic leather exhibits unfavorable anti-stickiness performance which cannot meet the requirements of the synthetic leather application as any slight stickiness in the skin film would not be acceptable to the customer.

After persistent exploration, we have surprisingly found that siloxane compound with both hydrophilic group and amine group can be used in the preparation of said PUD and impart the resultant synthetic leather article with significantly improved anti-stickiness performance while maintaining good PUD film mechanical properties like tensile strength, elongation and modulus.

SUMMARY OF THE INVENTION

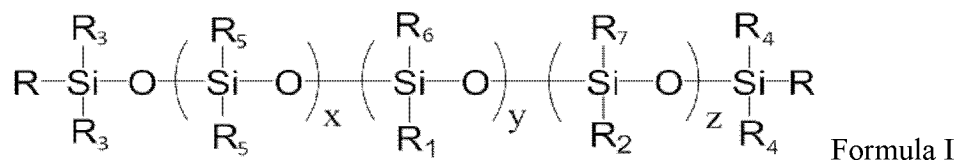
The present disclosure provides a unique waterborne polyurethane dispersion and a laminated synthetic leather article prepared by using the same.

In a first aspect of the present disclosure, the present disclosure provides a waterborne polyurethane dispersion comprising polyurethane particles dispersed in water, wherein the waterborne polyurethane dispersion is derived from:

(A) an isocyanate component comprising one or more compounds having at least two isocyanate groups;

(B) an isocyanate-reactive component comprising one or more compounds having at least two isocyanate-reactive groups;

(C) a hydrophilic amino siloxane compound represented Formula I:



wherein each R independently represents methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, n-pentyl, i-pentyl, tert-pentyl, neo-pentyl, cyclohexyl, phenyl, vinyl, allyl or $-(\text{OCH}_2\text{CH}_2)_a-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$;

R_1 is $-(\text{CH}_2)_m\text{NH}_2$ or $-(\text{CH}_2)_s-\text{NH}-(\text{CH}_2)_t\text{NH}_2$;

R_2 is $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$; and

each of R_3 , R_4 , R_5 , R_6 and R_7 is independently selected from the group consisting of methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, n-pentyl, i-pentyl, tert-pentyl, neo-pentyl, cyclohexyl and phenyl;

wherein a is an integer of 1 to 10; x is an integer of 20-500; y is an integer of 1-10; z is an integer of 1-10; m is an integer of 1-5; s is an integer of 1, 2, 3, 4 or 5; t is an integer of 1, 2, 3, 4 or 5; and n is an integer of 5-20;

(D) a catalyst;

(E) a surfactant;

(F) a chain extender; and

(G) water.

According to a preferable embodiment of the present disclosure, the waterborne polyurethane dispersion is an externally emulsified polyurethane that does not comprise cationic or anionic hydrophilic pendant group or a group which can be converted into the cationic or anionic hydrophilic pendant group covalently attached to the backbone chain of the polyurethane.

In a second aspect of the present disclosure, the present disclosure provides a method for producing the waterborne polyurethane dispersion of the first aspect, comprising (i) reacting the isocyanate component (A) with the isocyanate-reactive component (B) in the presence of the catalyst (D) to form a prepolymer comprising free isocyanate groups; and (ii) reacting the prepolymer with the hydrophilic amino siloxane compound (C) and the chain extender (F) in the presence of the surfactant (E) and water (G) to form the waterborne polyurethane dispersion.

In a third aspect of the present disclosure, the present disclosure provides a synthetic leather article, comprising, from top to bottom:

a polyurethane skin film derived from the waterborne polyurethane dispersion of the first aspect;

a base layer derived from a 2k PU composite composition; and

an optional backing substrate.

In a fourth aspect of the present disclosure, the present disclosure provides a method for preparing the synthetic leather article of the third aspect, comprising:

- a) providing the waterborne polyurethane dispersion of the first aspect;
b) forming the polyurethane skin film with the waterborne polyurethane dispersion;
c) applying the 2k PU composite composition onto one side of the polyurethane skin film to form the base layer; and
5 d) optionally, applying the backing substrate onto one side of the base layer opposite the polyurethane skin film.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of a cross-section of one embodiment of a synthetic leather article described herein.

DETAILED DESCRIPTION OF THE INVENTION

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. Also, all publications, patent applications, patents, and other references mentioned herein are incorporated by reference.

As disclosed herein, the term "composition", "formulation" or "mixture" refers to a physical blend of different components, which is obtained by mixing simply different components by a physical means.

As disclosed herein, "and/or" means "and, or as an alternative". All ranges include endpoints unless otherwise indicated.

The Isocyanate Component

In various embodiments, the isocyanate component (A) has an average functionality of at least about 2.0, preferably from about 2 to 10, more preferably from about 2 to about 8, and most preferably from about 2 to about 6. In some embodiments, the isocyanate component includes a polyisocyanate compound comprising at least two isocyanate groups. Suitable polyisocyanate compounds include aromatic, aliphatic, cycloaliphatic and araliphatic

polyisocyanates having two or more isocyanate groups. In a preferable embodiment, the polyisocyanate component comprises polyisocyanate compounds selected from the group consisting of C₄-C₁₂ aliphatic polyisocyanates comprising at least two isocyanate groups, C₆-C₁₅ cycloaliphatic or aromatic polyisocyanates comprising at least two isocyanate groups, C₇-C₁₅ araliphatic polyisocyanates comprising at least two isocyanate groups, and combinations thereof. In another preferable embodiment, suitable polyisocyanate compounds include m-phenylene diisocyanate, 2,4-toluene diisocyanate and/or 2,6-toluene diisocyanate (TDI), the various isomers of diphenylmethanediisocyanate (MDI), carbodiimide modified MDI products, hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene diisocyanate, hydrogenated MDI, naphthylene-1,5-diisocyanate, isophorone diisocyanate (IPDI), or mixtures thereof.

Alternatively or additionally, the polyisocyanate component may also comprise a isocyanate prepolymer having an isocyanate functionality in the range of 2 to 10, preferably from 2 to 8, more preferably from 2 to 6. The isocyanate prepolymer can be obtained by reacting the above stated monomeric isocyanate components with one or more isocyanate-reactive compounds selected from the group consisting of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,4-butyne diol, 1,5-pentanediol, neopentylglycol, bis(hydroxy-methyl) cyclohexanes such as 1,4-bis(hydroxymethyl)cyclohexane, 2-methylpropane-1,3-diol, methylpentanediols, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, dibutylene glycol and polybutylene glycols. Suitable prepolymers for use as the polyisocyanate component are prepolymers having NCO group contents of from 2 to 40 weight percent, more preferably from 4 to 30 weight percent. These prepolymers are preferably prepared by reaction of the di- and/or poly-isocyanates with materials including lower molecular weight diols and triols. Individual examples are aromatic polyisocyanates containing urethane groups, preferably having NCO contents of from 5 to 40 weight percent, more preferably 20 to 35 weight percent, obtained by reaction of diisocyanates and/or polyisocyanates with, for example, lower molecular weight diols, triols, oxyalkylene glycols, dioxyalkylene glycols, or polyoxyalkylene glycols having molecular weights up to about 800. These polyols can be employed individually or in mixtures as di- and/or polyoxyalkylene glycols. For example, diethylene glycols, dipropylene glycols, polyoxyethylene glycols,

ethylene glycols, propylene glycols, butylene glycols, polyoxypropylene glycols and polyoxypropylene-polyoxyethylene glycols can be used. Polyester polyols can also be used, as well as alkane diols such as butane diol. Other diols also useful include bishydroxyethyl- or bishydroxypropyl-bisphenol A, cyclohexane dimethanol, and bishydroxyethyl hydroquinone.

Also advantageously used for the isocyanate component are the so-called modified multifunctional isocyanates, that is, products which are obtained through chemical reactions of the above isocyanates compounds. Exemplary are polyisocyanates containing esters, ureas, biurets, allophanates and preferably carbodiimides and/or uretoneimines. Liquid polyisocyanates containing carbodiimide groups, uretoneimines groups and/or isocyanurate rings, having isocyanate groups (NCO) contents of from 12 to 40 weight percent, more preferably from 20 to 35 weight percent, can also be used. These include, for example, polyisocyanates based on 4,4'- 2,4'- and/or 2,2'-diphenylmethane diisocyanate and the corresponding isomeric mixtures, 2,4- and/or 2,6-toluenediisocyanate and the corresponding isomeric mixtures; mixtures of diphenylmethane diisocyanates and PMDI; and mixtures of toluene diisocyanates and PMDI and/or diphenylmethane diisocyanates.

Generally, the amount of the isocyanate component may vary based on the actual requirement of the synthetic leather article. For example, as one illustrative embodiment, the content of the isocyanate component can be from about 5 wt% to about 50 wt%, preferably from about 10 wt% to about 40 wt%, preferably from about 15 wt% to about 30 wt%, based on the total weight of all the components for preparing the prepolymer in the first stage, i.e., based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D).

The Isocyanate-Reactive Component

In various embodiments of the present disclosure, the isocyanate-reactive component comprises one or more polyols selected from the group consisting of aliphatic polyhydric alcohols comprising at least two hydroxy groups, cycloaliphatic or aromatic polyhydric alcohols comprising at least two hydroxy groups, araliphatic polyhydric alcohols comprising at least two hydroxy groups, polyether polyol, polyester polyol, vegetable oil having at least two hydroxyl groups and mixture thereof. Preferably, the polyol is selected from the group consisting of C2-C16 aliphatic polyhydric alcohols comprising at least two hydroxy groups,

C6-C15 cycloaliphatic or aromatic polyhydric alcohols comprising at least two hydroxy groups, C7-C15 araliphatic polyhydric alcohols comprising at least two hydroxy groups, polyester polyols having a molecular weight from 100 to 5,000, polyether polyols having a molecular weight from 1,500 to 12,000, and combinations thereof. According to a preferable embodiment, the polyol comprises a polyether polyols (e.g., a polyether polyols as stated above), a castor oil, or a mixture thereof.

In a preferable embodiment, the isocyanate-reactive component comprises a mixture of two or more different polyols, such as a mixture of two or more polyether polyols, a mixture of two or more polyester polyols, a mixture of at least one polyether polyols with at least one polyester polyols, a mixture of two or more vegetable oils having at least two hydroxyl groups, or a mixture of a polyether polyols and a castor oil.

In an alternative embodiment, the isocyanate-reactive component is a polyether polyols having a functionality (average number of isocyanate-reactive groups, particularly, hydroxyl group, in a polyol molecule) of 1.0 to 3.0 and a weight average molecular weight (Mw) of 1,500 to 12,000 g/mol, preferably from 2,000 to 8,000 g/mol, more preferably from 2,000 to 6,000 g/mol.

The polyether polyols is generally prepared by polymerization of one or more alkylene oxides selected from propylene oxide (PO), ethylene oxide (EO), butylene oxide, tetrahydrofuran and mixtures thereof, with proper starter molecules in the presence of catalyst. Typical starter molecules include compounds having at least 2, preferably from 4 to 8 hydroxyl groups or having two or more primary amine groups in the molecule. Suitable starter molecules are for example selected from the group comprising aniline, EDA, TDA, MDA and PMDA, more preferably from the group comprising TDA and PMDA, and most preferably TDA. When TDA is used, all isomers can be used alone or in any desired mixtures. For example, 2,4-TDA, 2,6-TDA, mixtures of 2,4-TDA and 2,6-TDA, 2,3-TDA, 3,4-TDA, mixtures of 3,4-TDA and 2,3-TDA, and also mixtures of all the above isomers can be used. By way of starter molecules having at least 2 and preferably from 2 to 8 hydroxyl groups in the molecule it is preferable to use trimethylolpropane, glycerol, pentaerythritol, castor oil, sugar compounds such as, for example, glucose, sorbitol, mannitol and sucrose, polyhydric phenols, resols, such as oligomeric condensation products of phenol and formaldehyde and Mannich condensates of phenols, formaldehyde and dialkanolamines, and also melamine. Catalyst for

the preparation of polyether polyols may include alkaline catalysts, such as potassium hydroxide, for anionic polymerization or Lewis acid catalysts, such as boron trifluoride, for cationic polymerization. Suitable polymerization catalysts may include potassium hydroxide, cesium hydroxide, boron trifluoride, or a double cyanide complex (DMC) catalyst such as zinc
5 hexacyanocobaltate or quaternary phosphazanium compound. In a preferable embodiment of the present disclosure, the polyether polyol includes (methoxy) polyethylene glycol (MPEG), polyethylene glycol (PEG), poly(propylene glycol) or copolymer of ethylene epoxide and propylene epoxide with primary hydroxyl ended group and secondary hydroxyl ended group.

In general, the content of the isocyanate-reactive component used herein may range
10 from about 50 wt% to about 95 wt%, preferably from about 60 wt% to about 85 wt%, based on the total weight of all the components for preparing the prepolymer in the first stage, i.e., based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D).

Catalyst

Catalyst may include any substance that can promote the reaction between the isocyanate group and the isocyanate-reactive group. Without being limited to theory, the catalysts can include, for example, glycine salts; tertiary amines; tertiary phosphines, such as trialkylphosphines and dialkylbenzylphosphines; morpholine derivatives; piperazine
20 derivatives; chelates of various metals, such as those which can be obtained from acetylacetone, benzoylacetone, trifluoroacetyl acetone, ethyl acetoacetate and the like with metals such as Be, Mg, Zn, Cd, Pd, Ti, Zr, Sn, As, Bi, Cr, Mo, Mn, Fe, Co and Ni; acidic metal salts of strong acids such as ferric chloride and stannic chloride; salts of organic acids with variety of metals, such as alkali metals, alkaline earth metals, Al, Sn, Pb, Mn, Co, Ni and
25 Cu; organotin compounds, such as tin(II) salts of organic carboxylic acids, e.g., tin(II) diacetate, tin(II) dioctanoate, tin(II) diethylhexanoate, and tin(II) dilaurate, and dialkyltin(IV) salts of organic carboxylic acids, e.g., dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate; bismuth salts of organic carboxylic acids, e.g., bismuth octanoate; organometallic derivatives of trivalent and pentavalent As, Sb and Bi and metal
30 carbonyls of iron and cobalt; or mixtures thereof.

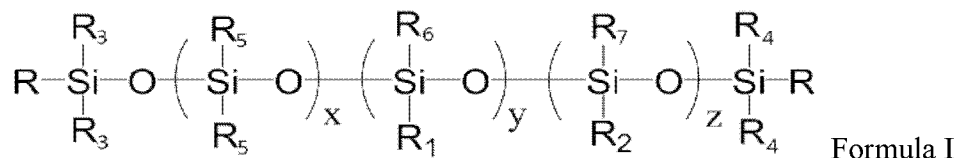
Tertiary amine catalysts include organic compounds that contain at least one tertiary

nitrogen atom and are capable of catalyzing the hydroxyl/isocyanate reaction. The tertiary amine, morpholine derivative and piperazine derivative catalysts can include, by way of example and not limitation, triethylenediamine, tetramethylethylenediamine, pentamethyldiethylene triamine, bis(2-dimethylaminoethyl)ether, triethylamine, tripropylamine, tributylamine, triamylamine, pyridine, quinoline, dimethylpiperazine, piperazine, N-ethylmorpholine, 2-methylpropanediamine, methyltriethylenediamine, 2,4,6-tridimethylamino-methylphenol, N,N',N''-tris(dimethyl amino-propyl)sym-hexahydro triazine, or mixtures thereof.

In general, the content of the catalyst used herein is larger than zero and is at most 1.0 wt%, preferably at most 0.5 wt%, more preferably at most 0.05wt%, based on the total weight of all the components for preparing the prepolymer in the first stage, i.e., based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D).

Hydrophilic Amino Siloxane compound

The hydrophilic amino siloxane compound is a compound comprising a silicon-oxygen back bone chain to which nitrogen-containing side chain and hydrophilic side chain are attached. The molecular structure of the hydrophilic amino siloxane compound may be represented by Formula I:



wherein each R independently represents methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, s-butyl, t-butyl, n-pentyl, i-pentyl, tert-pentyl, neo-pentyl, cyclohexyl, phenyl, vinyl, allyl or $-(\text{OCH}_2\text{CH}_2)_a-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$;

R_1 is $-(\text{CH}_2)_m\text{NH}_2$ or $-(\text{CH}_2)_s-\text{NH}-(\text{CH}_2)_t\text{NH}_2$;

R_2 is $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$; and

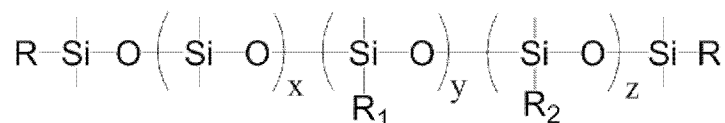
each of R_3 , R_4 , R_5 , R_6 and R_7 is independently selected from the group consisting of methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, n-pentyl, i-pentyl, tert-pentyl, neo-pentyl, cyclohexyl and phenyl;

wherein a is an integer of 1 to 10; x is an integer of 20-200; y is an integer of 1-10; z is an integer of 1-10; m is an integer of 1-5; s is an integer of 1, 2, 3, 4 or 5; t is an integer of 1, 2,

3, 4 or 5; and n is an integer of 5-20.

Without being limited to theory, the amine group in R_1 and the hydroxyl group in R_2 may react with the remaining isocyanate group in the prepolymer to produce a polyurethane comprising the above siloxane structure in the polyurethane back bone chain, thus significantly improve the anti-stickiness of the resultant PU skin film.

According to one preferable embodiment of the present disclosure, the hydrophilic amino siloxane compound has a structure presented by Formula II:



wherein R, R_1 , R_2 , x, y and z are as described above.

In general, the content of the hydrophilic amino siloxane compound used herein is from 2 wt% to 10 wt%, preferably from 2 wt% to 8 wt%, more preferably from 2 wt% to 5 wt%, based on the total weight of all the components for preparing the prepolymer in the first stage, i.e., based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D). It can be seen that the content of the hydrophilic amino siloxane compound is calculated as an additional amount while taking the total amount of the prepolymer as 100 wt%.

It's noted that the hydrophilic amino siloxane compound should be firstly dissolved/dispersed in water via mixing to get an aqueous solution and then degassed. In this invention, the amino silicone oil was added during the dispersion stage and was not added into polymer backbone during the prepolymer synthesis. The reason is that some degree of polymer gel will be formed if the siloxane was added during the prepolymer synthesis stage.

Surfactant

According to a preferable embodiment, the waterborne polyurethane dispersion is an externally emulsified dispersion, i.e., the waterborne polyurethane dispersion is preferably prepared exclusively by using "external surfactant/emulsifier" and substantially comprises no "internal surfactant/emulsifier".

The expression "externally emulsified polyurethane dispersion" as described herein refers to a polyurethane dispersion comprising limited amount of internally emulsifying ionic

components and thus mainly relying on the emulsifying function of “external surfactant/emulsifier” [i.e. ionically or nonionically emulsifiers that are not covalently bonded to the backbone chain within the polyurethane particles dispersed in the liquid medium, especially via the urethane bond derived from the reaction between an isocyanate group and an isocyanate-reactive group (such as a hydroxyl group)] so as to stabilize the polyurethane dispersion.

According to one embodiment of the present disclosure, the externally emulsified polyurethane dispersion is prepared by (i) reacting one or more monomeric or prepolymeric polyisocyanates with one or more compounds having at least two isocyanate-reactive groups as stated above to form a prepolymer comprising an urethane prepolymer chain and at least one, preferably at least two free isocyanate groups per molecule; (ii) dispersing the prepolymer obtained in step (i) in an aqueous solvent (e.g. water) with the presence of the external emulsifier to form an emulsion and optionally further adding the chain extender and the hydrophilic amino siloxane compound into the emulsion to react with the prepolymer obtained in step (i) and form the externally emulsified polyurethane dispersion. According to one embodiment of the present disclosure, the prepolymer prepared in the step (i) does not comprise any ionic internal emulsifier or residual moieties of the ionic internal emulsifier covalently bonded to the urethane prepolymer chain. According to another embodiment of the present disclosure, the polyurethane chain in the prepolymer prepared in the step (i) does not comprise any cationic or anionic pendant group.

The PUD prepared by using an internal surfactant/emulsifier is known as an “internally emulsified PUD”. According to the knowledge of the prior art, a typical process for preparing an internally emulsified PUD comprises the steps of (i) reacting an monomeric isocyanate or a prepolymer of the monomeric isocyanate with polyols and cationic or anionic precursor which has at least one isocyanate-reactive groups (i.e., an ionic internal emulsifier) to form a PUD prepolymer comprising pendant cationic or anionic hydrophilic groups attached to the PU chain; (ii) dispersing the PUD prepolymer into an aqueous solvent (e.g. water), with the cationic or anionic hydrophilic group attached to the PU chain as main emulsifier, optionally with the assistance of additional external emulsifier in this step; and optionally (iii) reacting the emulsion with additional chain extender to form the ionic internally emulsified polyurethane dispersion. It can be clearly seen that the externally emulsified PUD used in the

present disclosure is completely different from the ionic internally emulsified PUD of the prior art both in the preparation process and the composition of the resultant polyurethane particles. It shall be clarified that the polyurethane particles prepared by the present application comprise residual groups of the chain extenders and the hydrophilic amino siloxane compound attached to the polyurethane main chain, but these residual groups are different from the above stated ionic internal emulsification function groups at least in the charge neutrality and hence shall be excluded from the definition of the ionic internal emulsifying function groups. Besides, in a preferable embodiment, the emulsifying of the polyurethane is conducted mainly or solely by using the external emulsifier, and the chain extender and hydrophilic amino siloxane compound are not added until an emulsion of PU has been formed. That is why the PU dispersion of the present disclosure is identified as an externally emulsified system.

In one embodiment of the present disclosure, the above stated ionic internal emulsifying component (emulsifier) is not added during the preparation of the externally emulsified PUD. In a preferable embodiment of the present disclosure, the externally emulsified polyurethane dispersion is free of anionic or cationic salt group in the backbone chain of the polyurethane prepolymer particles dispersed in the externally emulsified PUD.

The waterborne polyurethane dispersion of the present disclosure may be prepared by using any anionic surfactant, cationic surfactant, amphoteric surfactant or non-ionic surfactant. Suitable classes of surfactant include, but are not restricted to, sulfates of ethoxylated phenols such as poly(oxy-1,2-ethanediyl) α -sulfo- ω (nonylphenoxy) salt; alkali metal fatty acid salts such as alkali metal oleates and stearates; alkali metal C₁₂-C₁₆ alkyl sulfates such as alkali metal lauryl sulfates; amine C₁₂-C₁₆ alkyl sulfates such as amine lauryl sulfates, more preferably triethanolamine lauryl sulfate; alkali metal C₁₂-C₁₆ alkylbenzene sulfonates such as branched and linear sodium dodecylbenzene sulfonates; amine C₁₂-C₁₆ alkyl benzene sulfonates such as triethanolamine dodecylbenzene sulfonate; anionic and nonionic fluorocarbon emulsifiers such as fluorinated C₄-C₁₆ alkyl esters and alkali metal C₄-C₁₆ perfluoroalkyl sulfonates; organosilicon emulsifiers such as modified polydimethylsiloxanes. Preferably, the surfactant is one that can react with a multivalent cation present in a neutral salt to form an insoluble multivalent cation water insoluble salt of an organic acid. Exemplary preferred surfactant includes disodium octadecyl sulfosuccinate, sodium dodecylbenzene sulfonate, sodium stearate and ammonium stearate.

According to an embodiment of the present disclosure, the content of the surfactant is larger than zero and no more than 10 wt%, preferably no more than 5 wt%, more preferably no more than 3.5 wt%, based on the total weight of all the components for preparing the prepolymer in the first stage, i.e., based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D). It can be seen that the content of the surfactant is calculated as an additional amount while taking the total amount of the prepolymer as 100 wt%.

Chain Extender

According to one embodiment of the present disclosure, the chain extender may be a diamine or an amine compound having another isocyanate reactive group, but is preferably selected from the group consisting of: an aminated polyether diol; piperazine; aminoethylethanolamine; C₂-C₁₆ aliphatic polyamine comprising at least two amine groups, e.g., ethylenediamine; C₄-C₁₅ cycloaliphatic or aromatic polyamine comprising at least two amine groups, such as cyclohexanediamine and p-xylenediamine; C₇-C₁₅ araliphatic polyamine comprising at least two amine groups; aminated C₂-C₈ alcohol, e.g., ethanolamine; and mixtures thereof. According to a preferable embodiment, the chain extender is a polyamine having a functionality of 2 and comprising primary amine group or secondary amine group. Preferably, the amine chain extender is dissolved in the water used to make the PU dispersion.

According to an embodiment of the present disclosure, the content of the chain extender is from 1.0 wt% to 15 wt%, preferably from 2 wt% to 10 wt%, more preferably from 3 wt% to 9 wt%, based on the total weight of all the components for preparing the prepolymer in the first stage, i.e., based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D). It can be seen that the content of the chain extender is calculated as an additional amount while taking the total amount of the prepolymer as 100 wt%.

The Waterborne Polyurethane Dispersion

According to an embodiment of the present application, the waterborne polyurethane dispersion is prepared by a two-stage reaction. In the first stage, a prepolymer is prepared by

reacting the isocyanate groups in the isocyanate component (A) with the isocyanate-reactive groups in the isocyanate-reactive component (B) in the presence of the catalyst (D). A polyurethane back bone chain can be formed in the prepolymer by the above stated reaction. In the second stage, the prepolymer is mixed with the surfactant (E) and reacts with the chain extender (F) and the hydrophilic amino siloxane compound (C). The chain extender (F) and the hydrophilic amino siloxane compound (C) comprise isocyanate-reactive groups, e.g. amine group, which react with the free isocyanate groups remained in the prepolymer, hence their structural moieties are also introduced into the resultant polyurethane back bone chain. During the second stage, the chain of the prepolymer is further extended by the chain extender (F) and the hydrophilic amino siloxane compound (C) so as to form the waterborne polyurethane dispersion comprising polyurethane particles dispersed in water. The waterborne polyurethane dispersion may be heated and dried to form a skin film exhibiting superior improved anti-stickiness performance while maintaining good PUD film mechanical properties.

The waterborne polyurethane dispersion may have any suitable solids loading of polyurethane particles, but the solids loading is generally between about 1% to about 70% solids by weight of the total dispersion weight, preferably at least about 2%, more preferably at least about 4%, more preferably at least about 6%, more preferably at least about 15%, more preferably at least about 25%, more preferably at least about 35%, most preferably at least about 40%, to at most about 70%, preferably at most 68%, more preferably at most about 65%, more preferably at most about 60% and most preferably at most about 50% by weight.

The waterborne polyurethane dispersion may also contain a rheological modifier such as thickeners that enhance the dispersability and stability of the dispersion. Any suitable rheological modifier may be used such as those known in the art. Preferably, the rheological modifier is one that does not cause the dispersion to become unstable. More preferably, the rheological modifier is a water soluble thickener that is not ionized. Examples of useful rheological modifiers include methyl cellulose ethers, alkali swellable thickeners (e.g., sodium or ammonium neutralized acrylic acid polymers), hydrophobically modified alkali swellable thickeners (e.g., hydrophobically modified acrylic acid copolymers) and associative thickeners (e.g., hydrophobically modified ethylene-oxide-based urethane block copolymers). Preferably the rheological modifier is a methylcellulose ether. The amount of thickener is from at least about 0.2% to about 5% by weight of the total weight of the waterborne polyurethane

dispersion, preferably from about 0.5% to about 2% by weight.

Generally, the waterborne polyurethane dispersion has a viscosity from at least about 10 cp to at most about 10,000 cp, preferably, from at least about 20 cp to at most about 5000 cp, more preferably, from at least about 30 cp to at most about 3000 cp.

5 In an embodiment of the present disclosure, the dispersion of the PU particles in the waterborne polyurethane dispersion can be promoted by the surfactant and high shear stirring action, wherein the shear force and stirring speed can be properly adjusted based on specific requirement.

According to one embodiment of the present disclosure, the waterborne polyurethane
10 dispersion may further comprise one or more pigment, dyes and/or colorant, all of which are generally termed as “color masterbatch” in the present disclosure. For example, the color masterbatch may be added so as to impart a transparent or translucent film with a desired color. Examples of pigments dyes and/or colorants may include iron oxides, titanium oxide, carbon black and mixtures thereof. The amount of the pigment, dyes and/or colorant may be 0.1% to
15 15%, preferably 0.5-10%, more preferably 1% to 5% by weight, based on the total weight of the waterborne polyurethane dispersion. Suitable commercially available black pigments useful in the present invention may include for example EUDERMTM black B-N carbon black dispersion available from Lanxess Deutschland GmbH.

20 **The Laminated Synthetic Leather Article**

Figure 1 is a schematic illustration of a cross-section of one embodiment of the synthetic leather article described herein. In one embodiment of the present disclosure, the synthetic leather article comprises, from top to bottom, a top skin film formed by the waterborne polyurethane dispersion, a 2K PU foam base layer, and a backing substrate (e.g. a
25 textile fabric cloth). Please note that the leather article is not necessarily shown in actual proportion, and the dimensions of one or more layers may be exaggerated so as to clearly show the configuration thereof.

The 2K PU foam used in the present disclosure is preferably a non-solvent PU foam and comprises a continuous PU matrix that defines a plurality of pores and/or cells therein. As
30 disclosed herein, the terms “solvent free”, “solventless” or “non-solvent”, can be used interchangeably for describing the PU foam or any other dispersion, mixture, etc., and shall be

interpreted that the mixture of all the raw materials used for preparing the PU foam or PU dispersion comprise less than 3% by weight, preferably less than 2% by weight, preferably less than 1% by weight, more preferably less than 0.5% by weight, more preferably less than 0.2% by weight, more preferably less than 0.1% by weight, more preferably less than 100 ppm by weight, more preferably less than 50 ppm by weight, more preferably less than 10 ppm by weight, more preferably less than 1ppm by weight of any organic or inorganic solvents, based on the total weight of the mixture of raw materials. As disclosed herein, the term "solvent" refers to organic and inorganic liquids whose function is solely dissolving one or more solid, liquid or gaseous materials without incurring any chemical reaction. In other words, although some organic compounds, e.g. ethylene glycol and propylene glycol, and water, which are generally considered as "solvent" in the polymerization technology, are used in the preparation of the 2k PU foam, none of them belongs to "solvent" since they mainly function as isocyanate-reactive functional substance, chain extending agent or foaming agent, etc. by incurring chemical reactions.

According to one embodiment of the present disclosure, the 2k PU foam layer has a thickness in the range from 0.01 μm to 2,000 μm , preferably in the range from 0.05 μm to 1,000 μm , more preferably in the range from 0.1 μm to 750 μm and more preferably in the range from 0.2 μm to 600 μm .

According to one embodiment of the present disclosure, the foamed polyurethane in the polyurethane foam layer is prepared with a solvent-free polyurethane system comprising (i) one or more second isocyanate components, (ii) one or more second isocyanate-reactive components, (iii) one or more foaming agent, second catalyst and any other additives. The second isocyanate component (i) includes one or more polyisocyanates and/or isocyanate prepolymers which are used for the isocyanate component (A). The second isocyanate-reactive components (ii) comprise compounds having two or more isocyanate-reactive groups selected from OH groups, SH groups, NH groups, NH_2 groups and carbon-acid groups, for example β -diketo groups. According to one embodiment of the present application, the isocyanate-reactive components (ii) comprise those used for (B). In one preferred embodiment of the present disclosure, the second isocyanate components (i) and second the isocyanate-reactive components (ii) react with each other in the presence of a foaming/blowing agent, and the foaming agent is used in combination with the isocyanate-reactive components. Useful

foaming agents include commonly known chemically or physically reactive compounds. Physical blowing agents may be selected from one or more of a group consisting of carbon dioxide, nitrogen, noble gases, (cyclo)aliphatic hydrocarbons having from 4 to 8 carbon atoms, dialkyl ethers, esters, ketones, acetal and fluoroalkanes having from 1 to 8 carbon atoms. The chemically reactive blowing agent preferably comprises water, which is preferably contained as a constituent of the blend with the isocyanate-reactive components (ii). The amount of the foaming agent is in the range from 0.05 to 10%, preferably in the range from 0.1 to 5%, more preferably from 0.1 to 2%, and most preferably from 0.1 to 0.5% by weight, based on the overall weight of all the raw materials used for preparing the 2k PU foam layer. The 2K PU layer typically has a density of 0.3 to 1.1 kg/liter and preferably has a density of 0.4 to 0.9 kg/liter.

In an embodiment of the present disclosure, the second isocyanate components (i) reacts with the second isocyanate-reactive components (ii) in the presence of a catalyst selected from organotin compounds, such as tin diacetate, tin dioctoate, dibutyltin dilaurate, and/or strongly basic amines such as diazabicyclooctane, triethylamine, triethylenediamine or bis(N,N-dimethylaminoethyl) ether in an amount from 0.01 % to 5% by weight, preferably from 0.05% to 4% by weight, more preferably from 0.05% to 3% by weight, based on the overall weight of all the raw materials used for preparing the 2k PU foam layer.

In an embodiment of the present disclosure, the categories and molar contents of the second isocyanate components (i) and the second isocyanate-reactive components (Bii) are particularly selected so that the overall equivalence ratio of NCO groups to NCO-reactive hydrogen atoms (e.g. hydrogen atom in the hydroxyl group) is in the range from 0.9:1 to 1.8:1, preferably from 0.92:1 to 1.6:1, preferably in the range from 0.95:1 to 1.5:1, and more preferably in the range from 1:1 to 1.45:1, more preferably in the range from 1.05:1 to 1.4:1, and more preferably in the range from 1.10:1 to 1.35:1.

Release Layer

Suitable release layers are typically known in the prior art as "release paper". Examples of suitable release layers include foils of metal, plastic or paper. In one preferred embodiment of the present disclosure, the release layer is a paper layer optionally coated with a plastic membrane. Preferably, the paper layer disclosed herein is coated with a polyolefin, more

preferably polypropylene. Alternatively, the paper layer is preferably coated with silicone. In an alternative embodiment, the release layer used herein is a PET layer optionally coated with plastic membrane. Preferably, the PET layer can be is coated with a polyolefin, more preferably polypropylene. Alternatively, the PET layer is preferably coated with silicone.

5 Examples of suitable release layers are commercially available. The release layers used in the present disclosure may have a flat, embossed or patterned surface so that corresponding or complementary surface profile can be formed on the outermost surface of the synthetic leather article. Preferably, the release layer is textured in the mode of leather grain so as to impart the synthetic leather article with good haptic property comparable with that of high grade natural
10 leather. The release layer generally has a thickness of 0.001 mm to 10 mm, preferably from 0.01 mm to 5 mm, and more preferably from 0.1 mm to 2 mm.

The material and the thickness of the release layer can be properly adjusted, as long as the release layer is able to endure the chemical reaction, mechanical processing and thermal treatments experienced during the manufacturing procedures and can be readily peeled from
15 the resultant synthetic leather without bringing about the delamination between the skin film and the 2k PU foam base layer.

Auxiliary Agents and Additives

The PU skin film and the 2K PU foam base layer may independently and optionally
20 comprise any additional auxiliary agents and/or additives for specific purposes.

In one embodiment of the present disclosure, one or more of the auxiliary agents and/or additives may be selected from the group consisting of fillers, cell regulators, release agents, colorants/pigments, surface-active compounds, handfeeling agents, dullers, thickeners, crosslinkers and stabilizers.

25 Examples of suitable fillers comprise glass fibers, mineral fibers, natural fibers, such as flax, jute or sisal for example, glass flakes, silicates such as mica or glimmer, salts, such as calcium carbonate, chalk or gypsum. The fillers are typically used in an amount from 0.5% to 60% by weight, preferably from 3% to 30% by weight, and more preferably from 3% to 10% by weight, based on the overall dry weight of the skin film or the 2K PU foam base layer.

Backing Substrate

In an embodiment of the present disclosure, the backing substrate has a thickness of in the range from 0.01 mm to 50 mm, preferably in the range from 0.05 mm to 10 mm and more particularly in the range from 0.1 mm to 5 mm. The backing substrate may comprise one or more selected from the group consisting of fabric, preferably woven or nonwoven fabric, impregnated fabrics, knit fabric, braid fabric or microfiber; foil of metal or plastic, e.g. rubber, PVC or polyamides; and leather, preferably split leather.

The backing substrate can be made of a woven or nonwoven textile. Preferably, the textile is a nonwoven textile. The textile may be made by any suitable method such as those known in the art. The textile may be prepared from any suitable fibrous material. Suitable fibrous materials include, but are not limited to, synthetic fibrous materials and natural or semi-synthetic fibrous materials and mixtures or blends thereof. Examples of synthetic fibrous materials include polyesters, polyamides, acrylics, polyolefins, polyvinyl chlorides, polyvinylidene chlorides, polyvinyl alcohols and blends or mixtures thereof. Examples of natural semi-synthetic fibrous materials include cotton, wool and hemp.

Manufacture Technology

The waterborne polyurethane dispersion may be applied by conventional coating technologies such as spraying coating, blade coating, die coating, cast coating, etc.

The skin film can be either partially or completely dried before the application of the next layer. Preferably, the skin film is completely dried so as to minimize the moisture entrapped therein, and then the next layer is applied thereon. In an alternative embodiment of the present application, only part of the moisture is removed from the skin film on the release layer, then the skin film is completely dried together with the 2K PU foam layer applied thereon.

According to one embodiment, the second isocyanate component (i) and the second isocyanate-reactive component (ii) for the 2K non-solvent PU foam are mixed together, applied to the skin film, and pre-cured by being heated in an oven at a temperature of e.g. from 70°C to 120°C, preferably from 75°C to 110°C for a short duration of 10 seconds to 5 minutes, preferably from 30 seconds to 2 minutes, more preferably from 45 to 90 seconds. Then the backing substrate (e.g. a textile fabric) is applied to the pre-cured 2k PU foam layer with the assistance of a pressing roller, followed by being post cured at a higher temperature of e.g.

from 100°C to 160°C, preferably from 110°C to 150°C for a longer duration of 3 to 20 minutes, preferably from 3 to 15 minutes, more preferably from 4 to 10 minutes. The above stated two-step curing process aims to ensure high adhesion strength between the pre-cured 2k PU foam and the backing substrate.

5 According to a preferable embodiment of the present disclosure, the release layer is removed after the 2k PU foam has been fully cured. The release layer can be peeled off via any ordinary technologies.

 According to a preferable embodiment of the present disclosure, after the removal of the release layer, a top finishing layer can be applied onto the surface of the synthetic leather
10 (i.e. on the outermost surface of the skin film) and dried to form a protection film layer. The presence of the finishing layer can further increase abrasion resistance of the multilayer synthetic leather. The protection film layer may be formed by using any suitable raw materials and technologies. The finishing layer may optionally comprise additives such as wetting agent, crosslinking agent, binder, matting agent, hand-feel modifier, pigments and/or colorants,
15 thickener or other additives used for the skin film. The synthetic leather disclosed herein can further comprise one or more than one optional additional layer such as a color layer between the skin film and the finishing layer. Other suitable optional additional layers can be selected from a water repellent layer, UV protective layer and tactile (touch/feel) modification layer. The process of the present invention may be carried out continuously or batchwise.

20 The multilayer structure synthetic leather disclosed herein can be cut or otherwise shaped so as to have a shape suitable for any desired purpose, such as shoe manufacturing. Depending on the intended application, the synthetic leathers can be further treated or post-treated similarly to natural leathers, for example by brushing, filling, milling or ironing. If desired, the synthetic leathers may (like natural leather) be finished with the customary
25 finishing compositions. This provides further possibilities for controlling their character. The multilayer structure disclosed herein may be used in various applications particularly suitable for use as synthetic leather, for example, footwear, handbags, belts, purses, garments, furniture upholstery, automotive upholstery, and gloves. The multilayer structure is particular suitable for use in automotive applications.

30

EXAMPLES

Some embodiments of the invention will now be described in the following Examples, wherein all parts and percentages are by weight unless otherwise specified.

The information of the raw materials used in the examples is listed in the following table 1:

5

Table 1. Raw materials used in the following examples

Raw Material	Description	Supplier
Isophorone diisocyanate (IPDI)	Aliphatic isocyanate, functionality=2	Evonik
T12	Catalyst (organic tin)	Air Product
Voranol 222-056 polyol	Ether polyol, Mw=2000, EO capped, EO content = 12 wt.%, Functionality=2	Dow Chemical
Voranol 4000LM polyol	Ether polyol, Mw=4000, Functionality=2	Dow Chemical
Voranol 4240 polyol	Ether polyol, Mw=4000, EO capped, EO content = 16.9 wt.%, Functionality=2	Dow Chemical
Castor oil	Polyol, with a OH value of 163 mg KOH/g, Functionality=2.7	-
MPEG1000	Ether polyol, Mw=2000, Functionality=1	Sinopharm.
Piperazine	chain extender, functionality=2	Sinopharm.
Sodium dodecyl benzene sulfonate (SDBS)	Surfactant	Sinopharm
Deionized water	Medium	N.A.
OFX-7700	a hydrophilic amino siloxane compound of the present application	Dow Chemical
OFX-8209	a hydrophobic amino siloxane compound	Dow Chemical
Euderm Black B-N	Black color master batch	Lanxess
Acrysol RM 825	Thickener	Dow Chemical
1,2-Propanediol (PG)	Fast drying agent	Sinopharm
A2 additive	A mixture of silicone and fluorine based slipping agent	Dow/DuPont
Polyol in 2k PU composite	See, Table 2	Dow Chemical
Prepolymer in 2k PU composite	Voralast* GE 143 ISO	Dow Chemical

The 2K non-solvent PU foam is prepared by combining the isocyanate prepolymer (VoralastTM GE 143 ISO) shown in table 1 and the raw materials listed in table 2.

Table 2. Raw materials used in 2K PU composite

Materials	Content / %	Vendor
SPECFLEX TM NC 701	28	Dow Chemical
VORANOL TM CP 6001	46	Dow Chemical
VORANOL TM 4240/EP 1900	18	Dow Chemical
Dipropylene glycol	4	Dow Chemical
Ethylene glycol	3	Dow Chemical
WATER	0.22	N.A.
Dow Corning 193	0.5	Dow Chemical
Polycat SA2LE	0.2	Evonik
Polycat SA-1	0.04	Evonik
Niax C-225	0.02	Evonik
Mixing ratio		
Above polyol formulation / Voralast TM GE 143 ISO		100/54

In the following Inventive and Comparative Examples, synthetic leather articles comprising a skin film derived from the waterborne polyurethane dispersion and a 2k PU foam base layer were prepared by the following Steps 1) to 4).

5 1) Preparation of two prepolymers for the waterborne polyurethane dispersion

A. The Prepolymer H1

Voranol 222-056 (317.5 g), castor oil (27.5 g) and MPEG1000 (10 g) were charged into a 1000 ml three neck flask and dehydrated at 115°C under 76 mmHg pressure for one hour, then naturally cooled down to a temperature of about 72 °C. IPDI (145 g) was poured
10 into the dehydrated polyol mixture at about 72 °C under the protection of nitrogen (N₂) flow and mechanical stirring, then the catalyst T12 (0.03 g) was added into the flask. The reaction lasted for one hour at about 72°C, and then was heated to a temperature of about 82°C and continued for additional 2.5 hours. The product (prepolymer H1) was packaged in a plastic bottle and stored hermetically under nitrogen protection. It was measured that the prepolymer
15 H1 had a NCO% of 7.3%.

B. The Prepolymer H2

Voranol 4000LM polyol (130 g), Voranol 4240 polyol (207.5 g), castor oil (27.5 g) and MPEG1000 (10 g) were charged into a 1000 ml three neck flask and dehydrated at 115°C under 76 mmHg pressure for one hour, then naturally cooled down to a temperature of about
20 72 °C. IPDI (125 g) was poured into the dehydrated polyol mixture at about 72 °C under the protection of nitrogen (N₂) flow and mechanical stirring, then the catalyst T12 (0.03 g) was

added into the flask. The reaction lasted for one hour at about 72°C, and then was heated to a temperature of about 82°C and continued for additional 2.5 hours. The product (prepolymer H2) was packaged in a plastic bottle and stored hermetically under nitrogen protection. It was measured that the prepolymer H2 had a NCO% of 7.1%.

5

2) Preparation of the waterborne polyurethane dispersion

100 gram of the prepolymer H1 or H2 was poured into a 500 ml plastic cup and stirred with a cowles mixer. 13 g of a 23wt% SDBS aqueous solution was gradually added into the prepolymer under a mixing speed of ~4000 rpm. After stirring for additional several minutes,
10 ice water was dropwisely added into the prepolymer under a mixing speed of ~4000 rpm. Phase reversion happened upon the addition of ice water and an oil-in-water emulsion was formed. The mixing speed was then lowered down to ~1500rpm. Aqueous solutions of the amino siloxane compound (the hydrophilic OFX-7700 or the hydrophobic OFX-8209) and the piperazine was dropwisely added into the emulsion. Once all the solution was added,
15 mechanical stirring was continued for additional 12 minutes. Finally, a polyurethane dispersion with ~40% solid content was obtained and stored in a plastic container with cover.

3) Preparation of the PUD skin film

22.5 gram of the polyurethane dispersion prepared in 2) was weighed and diluted with
20 equal amount of deionized water. The diluted PUD was transferred into a vacuum oven and degassed for ~10 minutes. Then the degassed PUD was poured into a plastic surface petri dish. The dish filled with PUD was transferred into an oven and heated at 48°C for 24 hours, after which the film was peeled from the dish, reversed and continuously dried for another 24 hours. The film was cooled down to room temperature for tensile and tear testing.

25

4) Fabrication of the synthetic leather article

The waterborne polyurethane dispersion prepared in 2) was mixed with color masterbatch, thickener, slipping agent and fast-drying agent as shown in table 3 at high speed (1000~3000 rpm) for several minutes. The formulated PUD was coated on a release paper to a
30 wet film thickness of 150 µm. The coated release paper was dried in oven at 100°C for 3 min and then at 130°C for 2 min. The release paper with dried PU skin layer was taken out of the

oven and cooled down to ambient temperature. The formulated 2k PU composite was coated on the dried PU skin film on the release paper to a wet film thickness of 300 μm . The release paper with the PU skin film and the coated 2k PU composite was transferred into a 100°C oven and precured for 75 seconds. A backing substrate (textile fabric cloth) was then carefully applied onto the 2k PU foam layer and pressed with a 3.5kg roller for 2 times. The specimen was put into a 140°C oven and post-cured for 5 minutes, and then taken out and cooled down.

Table 3. The raw materials used in Step 4)

Material	Dosage (phr)
PUD	93
Euderm Black B-N	5
PG (1,2-Propanediol)	5
Acrysol RM 825	2
A2 additive	0.5

Technologies for characterizing the products

(a) Mechanical properties of the PUD skin film formed in Step 3)

The tensile strength, elongation at break, modulus at 100% elongation and tear strength of the PUD skin films obtained in Step 3) were characterized according to the standard ASTM D412-15a.

(b) Anti-stickiness performance property of synthetic leather article prepared in Step 4)

The anti-stickiness of the synthetic leather articles prepared in above Step 4) were characterized according to the standard GB/T 8948-2008. In particular, two 90mm x 60mm samples of the synthetic leather article were pasted together face to face under a pressure of 1kg and heated in an oven at 85°C for 3 h. The anti-stickiness was ranked from 1 to 5 according to the degree of stickiness between the two samples during detaching of the two samples at room temperature:

Rank 1: not sticky completely;

Rank 2: can be detached with a little force;

Rank 3: can be detached with a certain force, and the surface is not destroyed;

Rank 4: can be detached with a large force and incomplete damage occurs on the surface; and

Rank 5: cannot be detached.

The formulations and characterization results of the Comparative Examples 1-2 and the Inventive Examples 1-2 were summarized in Table 4. The prepolymer H1 was prepared with a polyether polyol having a Mw of 2,000 and was used in the Inventive Example 1 and Comparative Example 1. The prepolymer H2 was prepared with a polyether polyol having a Mw of 4,000 and was used in the Inventive Example 2 and Comparative Example 2. The difference between the inventive examples and the comparative examples is that a hydrophilic amino siloxane compound (OFX-7700) was used in the inventive examples. Particularly speaking, in the inventive examples, a small amount of the OFX-7700, 2.5 wt% of the prepolymer weight, was added during the PUD preparation, while the comparative examples do not comprise said hydrophilic amino siloxane compound. Since the equivalent molecule weight of the hydrophilic amino siloxane (3700 g/mol) is significantly higher than that of piperazine (43 g/mol), the influence of the hydrophilic amino siloxane on chain extension coefficient can be ignored, thus the inventive example and comparative example had almost same chain extension coefficient (~88%).

The formulations and characterization results of the Comparative Examples 1-2 and the Inventive Examples 1-2

	Comparative Example 1	Comparative Example 2	Inventive Example 1	Inventive Example 2
PUD formulation				
Prepolymer-1	80		80	
Prepolymer-2		80		80
SDBS (23% aqueous)	10.4	10.4	10.4	10.4
Ice/water (50/50)	76	77.5	61	62.5
OFX-7700 (10% aqueous)	0	0	20	20
Piperazine (10% aqueous)	52.6	50.8	52.6	50.8
Solid content	40%	40%	40%	40%
PUD film				

mechanical properties				
Tensile strength (MPa)	29.9	17.7	27.6	17.8
Elongation (%)	749	757	807	719
Modulus at 100% Elongation (MPa)	4.3	3.8	4.1	4.0
Synthetic leather skin layer formulation	see Table 3			
Anti-stickiness rank	3	3	1	1
Tactility	Moderate	Moderate	Good	Good

The comparison between the Inventive Example 1 and Comparative Example 1 clearly shows that the incorporation of 2.5 wt% of hydrophilic amino siloxane compound can significantly improve the anti-stickiness performance of the PUD synthetic leather derived from a polyether polyol having a Mw of 2,000 from rank 3 to rank1. Only anti-stickiness performance with rank 1 can be qualified for different applications by the synthetic leather manufacturer. The greatly improved anti-stickiness performance leads to much better tactility of the synthetic leather. Besides, it can be found that the good mechanical properties of PUD film such as tensile strength, elongation (>500% is required for synthetic leather application) and modulus at 100% elongation (>2.5 MPa is required for synthetic leather application) can be maintained.

The same conclusion can be drawn based on the comparison between the Inventive Example 2 and the Comparative Example 2 which were conducted by using a polyether polyol having a Mw of 4,000.

Comparative Example 3 and Inventive Examples 3 to 4

Comparative Example 3, Inventive Example 3 and Inventive Example 4 were performed by repeating the procedures of the Inventive Example 1, except that the content of the hydrophilic amino siloxane compound (OFX-7700) was adjusted to 1.25 wt%, 3.75 wt% and 5.0 wt%, respectively, and the anti-stickiness rank were as follows:

Table 5: The formulations and anti-stickiness ranks of the Comparative Example 3 and

Inventive Examples 3 to 4

	Comparative Example 3	Inventive Example 3	Inventive Example 4
OFX-7700	1.25 wt%	3.75 wt%	5.0 wt%
Anti-stickiness rank	2	1	1

Comparative Example 4

The Comparative Example 4 was performed by following the procedures of the
5 Inventive Example 1, except that the OFX-7700 was replaced with a hydrophobic amino
siloxane compound (OFX-8209). It was found that there were many bulges on the PUD film,
implying that some gels were formed during the forming of the PUD. Since we cannot get a
homogeneous and transparent PUD film via this hydrophobic amino siloxane, we did not
prepare a synthetic leather with this PUD for further evaluation.

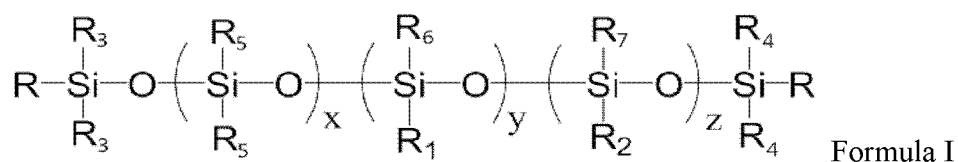
What is claimed is:

1. A waterborne polyurethane dispersion comprising polyurethane particles dispersed in water, wherein the waterborne polyurethane dispersion is derived from:

(A) an isocyanate component comprising one or more compounds having at least two isocyanate groups;

(B) an isocyanate-reactive component comprising one or more compounds having at least two isocyanate-reactive groups;

(C) a hydrophilic amino siloxane compound represented by Formula I:



wherein each R independently represents methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, n-pentyl, i-pentyl, tert-pentyl, neo-pentyl, cyclohexyl, phenyl, vinyl, allyl or $-(\text{OCH}_2\text{CH}_2)_a-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$;

R_1 is $-(\text{CH}_2)_m\text{NH}_2$ or $-(\text{CH}_2)_s-\text{NH}-(\text{CH}_2)_t\text{NH}_2$;

R_2 is $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$; and

each of R_3 , R_4 , R_5 , R_6 and R_7 is independently selected from the group consisting of methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, n-pentyl, i-pentyl, tert-pentyl, neo-pentyl, cyclohexyl and phenyl;

wherein a is an integer of 1 to 10; x is an integer of 20-500; y is an integer of 1-10; z is an integer of 1-10; m is an integer of 1-5; s is an integer of 1, 2, 3, 4 or 5; t is an integer of 1, 2, 3, 4 or 5; and n is an integer of 5-20; and wherein the content of the hydrophilic amino siloxane compound (C) is from 2.0 wt% to 10 wt%, based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B), and the catalyst (D);

(D) a catalyst;

(E) a surfactant;

(F) a chain extender; and

(G) water.

2. The waterborne polyurethane dispersion according to claim 1, wherein there is no

cationic or anionic hydrophilic pendant groups or groups which can be converted into the cationic or anionic hydrophilic pendant groups covalently attached to the backbone chain of polyurethane in the polyurethane particles, and the polyurethane is externally emulsified.

5 3. The waterborne polyurethane dispersion according to claim 1 or 2, wherein the one or more compounds having at least two isocyanate groups are selected from the group consisting of:

 a) C4-C12 aliphatic polyisocyanates comprising at least two isocyanate groups, C6-C15 cycloaliphatic or aromatic polyisocyanates comprising at least two isocyanate groups,
10 C7-C15 araliphatic polyisocyanates comprising at least two isocyanate groups, and a combination thereof; and

 b) an isocyanate prepolymer prepared by reacting one or more polyisocyanates of a) with one or more isocyanate-reactive components selected from the group consisting of C2-C16 aliphatic polyhydric alcohols comprising at least two hydroxy groups, C6-C15
15 cycloaliphatic or aromatic polyhydric alcohols comprising at least two hydroxy groups, C7-C15 araliphatic polyhydric alcohols comprising at least two hydroxy groups, polyester polyols having a molecular weight from 500 to 5,000, polycarbonate diols having a molecular weight from 200 to 5,000, polyetherdiols having a molecular weight from 200 to 5,000, C2 to C10
20 polyamine comprising at least two amino groups, C2 to C10 polythiol comprising at least two thiol groups, C2-C10 alkanolamine comprising at least one hydroxyl group and at least one amino groups, and a combination thereof, with the proviso that the isocyanate prepolymer comprises at least two free isocyanate terminal groups.

 4. The waterborne polyurethane dispersion according to claim 1 or 2, wherein the
25 content of the isocyanate component (A) is from 5 wt% to 50 wt%, based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D).

 5. The waterborne polyurethane dispersion according to claim 1 or 2, wherein the one or more compounds having at least two isocyanate-reactive groups are selected from the group
30 consisting of: C2-C16 aliphatic polyhydric alcohols comprising at least two hydroxy groups, C6-C15 cycloaliphatic or aromatic polyhydric alcohols comprising at least two hydroxy

groups, C7-C15 araliphatic polyhydric alcohols comprising at least two hydroxy groups, polyester polyols having a molecular weight from 500 to 5,000, polycarbonate diols having a molecular weight from 200 to 5,000, polyetherdiols having a molecular weight from 200 to 5,000, C2 to C10 polyamine comprising at least two amino groups, C2 to C10 polythiol comprising at least two thiol groups, C2-C10 alkanolamine comprising at least one hydroxyl group and at least one amino groups, vegetable oil having at least two hydroxyl groups, and a combination thereof.

6. The waterborne polyurethane dispersion according to claim 1 or 2, wherein the content of the isocyanate-reactive component (B) is from 50 wt% to 95 wt%, based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D).

7. The waterborne polyurethane dispersion according to claim 1 or 2, wherein the catalyst (D) is selected from the group consisting of: organotin compound, organic dismut compound, tertiary amine, morpholine derivative, piperazine derivative, and combination thereof; and

wherein the content of the catalyst (D) is 1.0wt% or less, based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D).

8. The waterborne polyurethane dispersion according to claim 1 or 2, wherein the surfactant (E) is selected from the group consisting of: poly(oxy-1,2-ethanediyl) α -sulfo- ω (nonylphenoxy) salt, alkali metal oleates and stearates, alkali metal C₁₂-C₁₆ alkyl sulfates, amine C₁₂-C₁₆ alkyl sulfates, alkali metal C₁₂-C₁₆ alkyl benzene sulfonates, amine C₁₂-C₁₆ alkyl benzene sulfonates, fluorinated C₄-C₁₆ alkyl esters, alkali metal C₄-C₁₆ perfluoroalkyl sulfonates, and the combination thereof; and

wherein the content of the surfactant (E) is 10wt% or less, based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D).

9. The waterborne polyurethane dispersion according to claim 1 or 2, wherein the chain extender (F) is selected from the group consisting of: C₂-C₁₆ aliphatic polyamine comprising at

least two amine groups, C₄-C₁₅ cycloaliphatic or aromatic polyamine comprising at least two amine groups, C₇-C₁₅ araliphatic polyamine comprising at least two amine groups; and

wherein the content of the chain extender (F) is from 1.0wt% to 15wt%, based on the total weight of the isocyanate component (A), the isocyanate-reactive component (B) and the catalyst (D).

10. The waterborne polyurethane dispersion according to claim 1 or 2, wherein the waterborne polyurethane dispersion has a solid content of 5 wt% to 50 wt%, based on the total weight of the waterborne polyurethane dispersion; and

the polyurethane particles have a volume average particle size of 20 nm to 5 μ m.

11. A method for preparing the waterborne polyurethane dispersion according to any of claims 1 to 10, the method comprising

(i) reacting the isocyanate component (A) with the isocyanate-reactive component (B) in the presence of the catalyst (D) to form a prepolymer; and

(ii) reacting the prepolymer with the hydrophilic amino siloxane compound (C) and the chain extender (F) in the presence of the surfactant (E) and water (G) to form the waterborne polyurethane dispersion.

12. A synthetic leather article, comprising, from top to bottom:

a polyurethane skin film derived from the waterborne polyurethane dispersion according to any of claims 1 to 10;

a base layer derived from a 2k PU composite composition; and

an optional backing substrate, wherein the polyurethane skin film directly contacts with the base layer, and the backing substrate, when present, directly contacts with the base layer.

13. A method for preparing the synthetic leather article according to claim 12, comprising:

a) providing the waterborne polyurethane dispersion according to any of claims 1 to 11;

b) forming the polyurethane skin film with the waterborne polyurethane dispersion;

c) applying the 2k PU composite composition onto one side of the polyurethane skin

film to form the base layer; and

d) optionally, applying the backing substrate onto one side of the base layer opposite the polyurethane skin film.

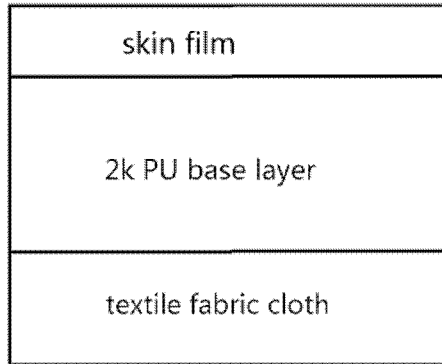


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2019/076936

A. CLASSIFICATION OF SUBJECT MATTER

C08G 18/12(2006.01)i; C09D 175/04(2006.01)i; C14C 11/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G 18/- C09D 175/- C14C11/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,CNKI,WPLEPODOC,STN: waterborne, polyurethane, dispers+, particle, isocyanate, hydrophilic, amino, polysiloxane, catalyst, surfactant, chain 1w extender, water, emulsif+, prepolymer, hydroxy, alcohol, polyol, diol, leather, film, article, OFX 7700, OFX 8209

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005222368 A1 (REINERS JUERGEN ET AL.) 06 October 2005 (2005-10-06) paragraphs [0021] to [0037]	1-13
A	US 2013078474 A1 (MUENTER JUERGEN ET AL.) 28 March 2013 (2013-03-28) paragraphs [0016] to [0024]	1-13
A	CN 108250390 A (WANHUA CHEM GROUP CO., LTD. ET AL.) 06 July 2018 (2018-07-06) paragraphs [0011] to [0020]	1-13
A	CN 101959914 A (DOW GLOBAL TECHNOLOGIES INC. ET AL.) 26 January 2011 (2011-01-26) claims 1-21	1-13
A	CN 106243316 A (ZHAOQING HAOCHENG RESIN TECH CO., LTD.) 21 December 2016 (2016-12-21) claims 1-10	1-13

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

14 November 2019

Date of mailing of the international search report

03 December 2019

Name and mailing address of the ISA/CN

National Intellectual Property Administration, PRC
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088
China

Authorized officer

ZHOU, Wen

Facsimile No. (86-10)62019451

Telephone No. 86-(10)-53962200

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2019/076936

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2005222368	A1	06 October 2005	US	2008305342	A1	11 December 2008
				EP	1582542	A1	05 October 2005
				DE	102004015430	A1	20 October 2005
US	2013078474	A1	28 March 2013	EP	2576647	A1	10 April 2013
				WO	2011147519	A1	01 December 2011
				UY	33182	A	30 December 2011
				US	2015307741	A1	29 October 2015
				RU	2012156068	A	27 June 2014
				AR	080831	A1	09 May 2012
				EP	2576647	B1	10 December 2014
				ES	2527024	T3	19 January 2015
				HK	1178552	A1	04 September 2015
				AU	2011257642	A1	16 August 2012
				TW	1511992	B	11 December 2015
				MX	338642	B	25 April 2016
				JP	5864552	B2	17 February 2016
				ZA	201205419	B	29 May 2013
				KR	20130075719	A	05 July 2013
				JP	2013528236	A	08 July 2013
				CN	102781988	B	24 September 2014
				CN	102781988	A	14 November 2012
				DE	102010021465	A1	01 December 2011
				TW	201141893	A	01 December 2011
				KR	101845690	B1	05 April 2018
				AU	2011257642	B2	02 April 2015
				MX	2012013641	A	24 January 2013
				US	9404019	B2	02 August 2016
				BR	112012029710	A2	02 August 2016
CN	108250390	A	06 July 2018	WO	2018120055	A1	05 July 2018
CN	101959914	A	26 January 2011	CN	101959914	B	12 February 2014
				JP	5492787	B2	14 May 2014
				EP	2271685	A1	12 January 2011
				TW	200936624	A	01 September 2009
				BR	PI0819586	A2	05 May 2015
				US	2010273939	A1	28 October 2010
				JP	2011508056	A	10 March 2011
				BR	PI0819586	B1	24 April 2019
				EP	2271685	B1	03 January 2018
				WO	2009085587	A1	09 July 2009
				US	8362142	B2	29 January 2013
CN	106243316	A	21 December 2016	None			