

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 18/08, C09J 175/06	A1	(11) International Publication Number: WO 97/19121 (43) International Publication Date: 29 May 1997 (29.05.97)
(21) International Application Number: PCT/US96/09501 (22) International Filing Date: 7 June 1996 (07.06.96) (30) Priority Data: 08/561,197 21 November 1995 (21.11.95) US (71) Applicant: H.B. FULLER LICENSING & FINANCING, INC. [US/US]; 1220 County Road E. West, Arden Hills, MN 55112 (US). (72) Inventors: DUAN, Youlu; Apartment C1009, 1530 South 6th Street, Minneapolis, MN 55454 (US). STAMMLER, Sonja; 11181 189th Street North, Marine on the St. Croix, MN 55047 (US). IERIEN, Jillian, H.; 1132 Iowa Avenue West, St. Paul, MN 55108 (US). MARTY, Brian, L.; 4801 Helena Road North, Oakdale, MN 55128 (US). (74) Agents: STEINKRAUS, Walter, J. et al.; Suite 1540, 920 Second Avenue South, Minneapolis, MN 55402 (US).		(81) Designated States: AU, BR, CA, CN, MX, NZ, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: IMPROVED WATER-BASED POLYURETHANES FOR FOOTWEAR (57) Abstract A water-based sulfonated polyurethane composition and footwear manufactured using the composition as an adhesive, coating and primer. The sulfonated polyurethane is a reaction product of (a) at least one polyisocyanate; (b) at least one alkylene diol; (c) at least one sulfonated polyester polyol wherein the sulfo groups thereof are present as alkali metal salts; and (d) at least one dihydroxy carboxylic acid, or salt thereof. The composition may also be modified to include a dispersed polymer or copolymer of an ethylenically unsaturated monomer. Such modified compositions may be obtained by preparing the sulfonated polyurethane in the presence of an ethylenically unsaturated monomer and subsequently subjecting the mixture to free-radical polymerization conditions.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

IMPROVED WATER-BASED POLYURETHANES FOR FOOTWEAR

5 Background of the Invention

Field of the Invention

This invention relates to water-based adhesives, coatings and primers. Specifically, it relates to water-based polyurethane compositions having improved characteristics such as adhesion, peel strength and heat resistance. More specifically, it relates to one-component water-based sulfonated polyurethane compositions useful as adhesives, coatings and primers in the manufacture of footwear and to footwear and a method of preparing footwear using such compositions.

Description of the Prior Art

It is generally known that water-based sulfonated polyurethanes are
15 useful in the manufacture of footwear. References describing such include the
following:

U.S. Pat. No. 5,334,690 (Hoechst Aktiengesellschaft, Fed.) discloses water-based sulfonated polyurethanes which are obtained by reacting ionic polyester polyols, polycarbonate polyols and polyether polyols or mixtures thereof with a polyisocyanate or mixtures of polyisocyanates. The water-based sulfonated polyurethane special feature are the ionic groups present in the polyol segment. These polymers are described as being especially useful in the production of adhesive bonds for the shoe industry.

German Pat. No. DE 3930352 (REIA GMBH) discloses a process for
25 bonding parts of shoes by applying water-based sulfonated polyurethane adhesives
and drying with a microwave heater before bringing the parts together. The
water-based sulfonated polyurethane Dispercoll U KA-8464 from Bayer Corporation
is referenced.

"Waterbased high performance adhesive materials", Warrach., Presented at
30 Proceedings of the ASC Division of Polymeric Materials Conference, Miami Beach,
FL., September 11-18, 1989. The article describes water-based sulfonated
polyurethane polymers, and their formulations, yielding good adhesion to substrates

often used in the manufacture of footwear like PVC, ABS, polyurethanes, nylon, leather and fabrics.

A draw back for these prior art compositions is their failure to pass minimum adhesion standards in footwear applications, set by the Association of
5 European Adhesive Manufacturers (FEICA), as one-component formulations. To pass minimum adhesion standards, two-component adhesive formulations are required. For example, bond strengths when subjected to thermal and mechanical stresses can be improved by the addition of water dispersible polyfunctional crosslinking agents selected from a group consisting of isocyanates, aziridines,
10 melamine resins, epoxies, oxazolines and carbodiimides. However, a disadvantage associated with two component formulations is their limited pot life due to coagulation, gelling and viscosity increase. Furthermore, two-component adhesives have to be mixed from separate components directly before use. This can give rise to unsatisfactory adhesive bonds or a shortened pot life through inexact metering of
15 the components making the system less user friendly. Also, exposure to latent crosslinking agents can pose a health risk through skin contact or inhalation.

There remains a need for improved one-component water-based adhesives, coatings and primers. One-component water-based compositions are easier to handle, safer and generally cost less. The present inventors have now
20 discovered new one-component water-based sulfonated polyurethane adhesives compositions which pass FEICA minimum specifications for sole bonding. The present inventors have also discovered two-component water-based sulfonated polyurethane compositions having improved performance over previously known two-component systems.

25 Summary of the Invention

The present invention is directed to new water-based sulfonated polyurethane compositions which are useful as adhesives, coatings and primers in the manufacture of footwear, comprising a dispersion in an aqueous vehicle of a reaction product of:

- 30
- a) at least one polyisocyanate component;
 - b) at least one alkylene diol component;
 - c) at least one sulfonated polyester polyol component wherein the sulfo groups are present in the form of alkali metal salts; and

d) at least one dihydroxy carboxylic acid or salt thereof selected from the group consisting of alkali metal salts, organic tertiary amine salts and mixtures thereof.

If the carboxyl groups of the dihydroxy carboxylic acid are not in the form of alkali metal salts and/or organic tertiary amine salts at the time of reaction to form the polyurethane polymer, they are converted thereto by the time the polymer is dispersed in the aqueous vehicle.

Surprisingly, the polymers of the invention are characterized as having low heat activation temperatures in a range from about 50°C to about 95°C and rapidly develop heat resistance greater than about 110°C, without internal or external crosslinking agents. The unique one-component water-based adhesives pass minimum adhesion standards set by the Association of European Adhesive Manufacturers (FEICA).

In order to meet requirements in footwear applications, such as wet out, viscosity, green strength, peel strength, water resistance, heat resistance and cost, it may be desirable to compound the water-based sulfonated polyurethanes. Further formulations of the invention comprise a mixture of:

- a) a water-based sulfonated polyurethane as previously described;
- b) at least one non-polyurethane based water dispersible polymer selected from the group consisting of acrylics, vinyl/acrylics, styrene/acrylics, vinyl-acetate/ethylene copolymers, polychloroprenes, styrene emulsions, styrene/butadiene emulsions, starches, dextrans, caseins, animal pectines and mixtures thereof;
- c) at least one compounding additive selected from a group consisting of thickening agents, surfactants, coalescing aids and plasticizers and mixtures thereof; and optionally,
- d) at least one water dispersible polyfunctional crosslinking agent selected from the group consisting of isocyanates, aziridines, melamine resins, epoxies and carbodiimides and mixtures thereof.

Because adhesion properties can vary with coating weights and substrates, two-component adhesives may be formulated to pass a particular manufacturer's specification. The present invention also comprises two-component water-based polyurethanes which exceed the performance characteristics of

two-component water-based adhesives currently available for use in the manufacture of footwear.

The water-based sulfonated polyurethane compositions of the present invention generate useful coatings and primers. As coatings, in the manufacture of footwear, the polymers are tough but flexible, offering a protective layer which acts as a barrier to water, oil, and as solvent. As a primer, the polymers are especially useful on difficult to adhere to surfaces such as oily leathers and porous substrates.

The present invention further comprises water-based sulfonated polyurethane/acrylic or water-based sulfonated polyurethane/vinyl polymers wherein the polyurethanes disclosed above are synthesized in the presence of ethylenically unsaturated monomers to generate useful water-based blends of polyurethane/acrylic-or-vinyl polymers. Such processes are described in U.S. Pat. No. 5,173,526 (Air Products and Chemicals, Inc.), U.S. Pat No. 4,644,030 (Witco Corporation) and EP-A-No. 95101621.1. These processes reduce the use of volatile organic compounds (VOC) and generate polymer blends with enhanced interpenetrating polymer networks which ultimately improve the physical properties of the dried films as adhesives, coatings and primers.

The water-based sulfonated polyurethane compositions and formulations of the present invention outperform existing waterbased products currently available for use in the manufacture of footwear. These characteristics are attributed to the unique properties of the sulfonated polyurethane polymers.

Detailed Description of the Invention

In the instant invention, the polyurethane is a water-based sulfonated polyurethane wherein the sulfonate functional group is in the soft segment of the polyurethane. The term "polyurethane" is defined as a polymer containing two or more urethane groups and is also intended to cover polyurethane-urea polymers. Examples of such polymers are described in copending application Serial No. 08/304/653, filed September 9, 1994.

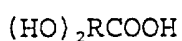
The diisocyanates which are used in forming the sulfonated polyurethane can be aliphatic or aromatic diisocyanates or their mixtures. Examples of suitable aliphatic diisocyanates are isophorone diisocyanate (IPDI), cyclopentylenediisocyanate, cyclohexylenediisocyanate, methylcyclohexylenediisocyanate, dicyclohexylmethanediisocyanate,

hexamethylenediisocyanate (HDI), dicyclohexylmethanediisocyanate (H12MDI), and tetramethylxylylenediisocyanate (TMXDI). Examples of suitable aromatic diisocyanates are phenylenediisocyanate, tolylenediisocyanate (TDI), xylylenediisocyanate, biphenylenediisocyanate, naphthylenediisocyanate and
 5 diphenylmethanediisocyanate (MDI).

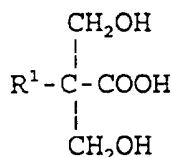
Preferably, the alkylene diol component of the sulfonated polyurethane is a C₂-C₈ alkylene diol or mixture thereof, most preferably a C₃-C₆ alkylene diol or mixture thereof. Examples of the diols are ethylene glycol, 1,3-propylene glycol, 1,4-butanediol (1,4-BD) and 1,6-hexanediol.

10 The sulfonated polyester polyols used to form the sulfonated polyurethane may be any polyester polyol which incorporates sulfonate groups via sulfonate functional dicarboxylic acid residues and/or sulfonate functional diol residues. The sulfonate functional groups are in alkali salt form. Typically such sulfonate functional dicarboxylic acid residues and/or sulfonate functional diol
 15 residues are a minor portion of the diol and/diacid moieties of the polyester, preferably 1.0%-10.0% by weight of the polyester. The non-sulfonated diacids and diols used in forming the sulfonated polyesters may be aromatic or aliphatic. Examples of the non-sulfonated diacids include adipic, azelaic, succinic, suberic and phthalic acids. Examples of the non-sulfonated diols include ethylene glycol,
 20 condensates of ethylene glycols, butanediol, butenediol, propanediol, neopentylglycol, hexanediol, 1,4-cyclohexane dimethanol, 1,2-propylene glycol and 2-methyl-1,3 propanediol. Examples of the sulfonate diacids include sulfoisophthalic acid, 1,3-dihydroxybutane sulfonic acid and sulfosuccinic acid. Examples of the sulfonate diols include 1,4 dihydroxybutane sulfonic acid and
 25 succinaldehyde disodium bisulfite.

The dihydroxy carboxylic acids used to form the sulfonated polyurethane are compounds of the formula:



wherein R represents a straight or branched, hydrocarbon radical containing 1 to 12
 30 carbon atoms. Preferably, the dihydroxy carboxylic acid is an α,α -dimethylol alkanoic acid represented by the formula:



5

where R¹ denotes hydrogen or an alkyl group with up to about 20 carbon atoms.

Examples of such compounds are 2,2-dimethylolacetic acid,

2,2-dimethylolpropionic acid, 2,2-dimethylolbutyric acid and 2,2-dimethylolpentanic

10 acid. The preferred dihydroxyalkanoic acid is 2,2-dimethylolpropionic acid (DMPA).

The carboxylate groups of the dihydroxy carboxylic acid is neutralized to form alkali or tertiary amine alkali groups in order to stabilize the dispersion of the sulfonated polyurethane. The neutralization may be accomplished before, or
15 during dispersion of the sulfonated polyurethane polymer in water.

The preferred water-based sulfonated polyurethane is a high molecular weight, crystalline, polyester based polyurethane polymer formed from mixtures of isophorone diisocyanate and hexamethylene diisocyanate. The water-based sulfonated polyurethane solids are present from about 15 parts to about 95 parts by weight, and
20 preferably from about 50 parts to about 95 parts by weight, based on 100 parts total solids. These polymers contain unique properties important in the development of improved adhesives, coatings and primers for footwear. The water-based sulfonated polyurethane compositions contain ionomers, in the soft and hard segments of the molecule, capable of strong hydrogen bonding and ionic dipole interactions. It is
25 surmised that the strong intermolecular forces and high degree of crystallization, inherent in these polymers, generate enhanced thermal and solvent resistance properties as well as good adhesion through mechanical interlocking. A surprising feature of the invention is that the polymers have low heat activation temperatures in a range from about 50°C to about 95°C and rapidly develop high heat resistant
30 bonds greater than about 110°C, preferably greater than about 120°C, without internal or external crosslinking agents.

The adhesives, coatings and primers of the invention may also include other non-polyurethane based water dispersible polymers and copolymers selected from a group consisting of acrylics, vinyl/acrylics, styrene/acrylics, vinyl
35 acetate-ethylene copolymers, polychloroprenes, styrene emulsions, styrene-butadiene emulsions, starches, dextrans, caseins, animal pectins and mixtures thereof. When

present in the formulations, the water-based polymer and copolymer solids comprise from about 5 parts to about 95 parts by weight, and preferably from about 5 parts to about 50 parts by weight based on 100 parts total solids.

- The adhesives, primers, and coatings of the invention may also
- 5 include compounding additives. Compounding additives include thickening agents, surfactants, coalescing aids and plasticizers. A preferred associative thickening agent is DSX-1550 from Henkel Corporation. A preferred non-ionic surfactant is Pentex 99 from Rhone Poulenc. A particularly preferred coalescing aid is Reentry KNI-2000 which is a terpene mixture from Environmental Solvents Corporation.
- 10 Useful plasticizers are selected from the group consisting of alkyl and aryl sulfonamides, benzoates esters, phthalate esters, adipates, citrates and mixtures thereof. A preferred plasticizer is Uniplex 108 from Initex Chemical Corporation. When compounding additives are present in the formulations, their solids content can vary from about 0.5 parts to about 30 parts by weight, and preferably from
- 15 about 0.5 parts to about 25 parts by weight, based on 100 parts total solids.

- As two-component adhesives, primers, and coatings, the formulations may include water dispersible polyfunctional crosslinking agents selected from the group consisting of isocyanates, aziridines, melamine resins, epoxies, oxazolines, and carbodiimides. Particularly preferred crosslinking agents are water dispersible
- 20 polyfunctional isocyanates. When present in the formulations, the amount of crosslinking agent solids can vary from about 3 parts to about 35 parts by weight, and preferably from about 8 parts to about 20 parts by weight, based on 100 parts total solids.

- As an adhesive, the water-based polymer compositions or formulations
- 25 of the invention can be accomplished in one-side mode or two-side mode. In the one-side mode, the adhesive is applied to one of two substrates and dried. The adhesive is heat activated and the substrates are brought together with pressure. In the two-side mode, the adhesive is applied to both substrates, dried, then heat activated and brought together with pressure. It is possible, in both modes, to dry
- 30 and heat activate the adhesive in the same step.

The adhesives can be used either in the aqueous form or in the form of a cast film and are useful in the construction of uppers made of leather, polyurethane, polyvinyl chloride, and textile materials. The adhesives are also useful

in sole bonding operations employing cup-sole, welt and stitch-down constructions and can be used for attaching direct injection molded soles.

To successfully prepare the adhesive, primer, and coating formulations a sequential mix process is used. The water-based sulfonated polyurethane and water-based sulfonated polyurethane/acrylic-or-vinyl polymers are blended with other non-polyurethane based water dispersible polymers and copolymers. Compounding additives are then blended in with mild agitation. If two-component formulations are required, the water dispersible polyfunctional crosslinking agents must be mixed into the formulations directly before use.

The present invention is further illustrated by the following non-limiting examples.

Examples

Example 1 & Comparative Example 1-C

Example 1 describes the synthesis of a preferred water-based sulfonated polyurethane polymer, useful as an adhesive, coating and primer in the manufacture of footwear.

To a reaction flask was charged 21.43 grams (0.021 hydroxyl equivalents) of molten Rucoflex® XS-5483-55 which is a sulfonated polyester polyol from Ruco Polymer Corporation, 1.00 grams (0.015 hydroxyl equivalents) dimethylolpropionic acid, and 1.127 grams (0.025 hydroxyl equivalents) 1,4-butanediol. The mixture was heated to 55°C then charged with 3.11 grams (0.0279 isocyanate equivalents) isophorone diisocyanate, 4.71 grams (0.056 isocyanate equivalents) 1,6-diisocyanatohexane, and 7.01 grams (solvent) anhydrous acetone. The mixture was heated at 70°C for approximately 3 hours then cooled to 55°C. The isocyanate terminated prepolymer was charged with 0.60 grams (.006 moles) triethylamine then stirred for 10 minutes. The prepolymer was then dispersed in 55.43 grams deionized water and chain extended with a solution containing 0.54 grams (0.02 amine equivalents) ethylenediamine and 5.0 grams deionized water. The aqueous properties are described below:

pH = 8.0
Solids = 35%
Viscosity = 250 mPa.s
Color wet = White

The formulation of comparative Example 1-C is Dispercoll U KA-8464, a commercially available water-based sulfonated polyurethane from Mobay Corporation. The formulations of Example 1 and Example 1-C were tested for peel adhesion failure temperatures according to the test method described below:

5 180° Peel Adhesion Failure Temperature Procedure:

The wet samples were drawn down on untreated, pressed, and polished polyvinyl chloride (PVC) sheets with a #40 Meyer rod and dried twenty four hours at ambient room temperature. A second PVC sheet was placed over the dried films and 2.54 x 15.24 centimeter strips were cut. The individual strips were
 10 heat activated, using variable temperatures, on a Sentinel heat sealer at 3.515 kilograms per square centimeter for 30 seconds. After 7 days of aging, at ambient room temperature, the strips were placed in a Tenny® oven using 0.1 kilogram weights and subjected to a 25°C increase each hour until bond failure. Bond failure
 15 temperatures were recorded up to 126°C by the Tenny® oven sensing unit, and the results are provided below:

Test Sample	51.6°C	65.5°C	79.4°C	93.3°C
Example 1 polymer	> 126°C	> 126°C	> 126°C	> 126°C
Example 1-C	93°C	104°C	105°C	106°C

20 Example 2 & Comparative Example 2-C

Example 2 was made to compare the 180° peel strengths, bonding various substrates using Dispercoll U KA-8464 and the polymer described in example 1. The adhesive formulations, test procedures and results are described below.

25 The water-based sulfonated polyurethane viscosities were increased to approximately 3000 mPa.s with the associative thickener DSX-1550 from Henkel Corporation. The surfactant Pentex 99 from Rhone Poulenc was also added to improve the formulations' wet out characteristics. The formulations were as described below:

	Materials	Example 2 (grams)	Comparative Example 2-C (grams)
	Example #1 Polymer	99.18	---
	Dispercoll U KA-8464	---	94.40
	DSX-1550/water (50/50)	0.56	0.32
5	Pentex 99	0.26	0.24
	Desmodur DA	---	5.0

Test procedures were performed in accordance with the Association of European Adhesive Manufacturers (FEICA). Initially, 2.54 centimeter by 15.24 centimeter strips of substrate were surface treated using the following materials and methods:

	Substrate	Surface Preparation
	Leather	roughed with 36 grit sandpaper using a belt sander
	Styrene-Butadiene Rubber(SBR)	roughed with 36 grit sandpaper using a belt sander
15	Nitrile Rubber (NBR)	roughed with 36 grit sandpaper using a belt sander
	Thermoplastic Rubber (SBS or TPR)	halogenated with a 2% solution of trichloroisocyanuric acid (TCICA) in ethyl acetate, allowed to air dry for 1 hour before applying adhesive
	Polyvinylchloride (PVC)	wiped with ethyl acetate

The adhesive formulations were then coated on each of the two pieces to be bonded using Meyer rods to generate a total dried coat weight of approximately 175 g/m². The dry adhesive films were heat activated at 70°C and pressed at 85 psi for 15 seconds. After 5 days aging at 23°C and 50% relative humidity, 180° peel strengths were tested on an Instron* 1123 using a cross-head speed of 100 mm/min. The peel strengths were recorded in N/mm.

The FEICA specification for sole bonding adhesives is 5.0 N/mm, with an industry standard coat weight of 175 g/m². The results of these samples are shown below, with coating weights normalized to the standard coating weight.

5		leather/SBR	SBR/SBR	NBR/NBR	PVC/PVC	SBS/SBS
	Example 2	3.47	3.89	2.40	5.36	7.60
	Comparative Example 2-C	2.80	1.63	3.20	1.46	1.27

Different coating weights, actual, were also made for bonding PVC to PVC. The results of these weight variations, and the peel adhesion differences, are shown below:

	Coat Weight (g/m ²)	76	~ 152	~ 228	~ 304	~ 380
15	Example 2	3.66	4.87	6.48	8.63	11.49

Example 3 & Comparative Example 3-C

Example 3 was made to compare the adhesive properties of a two-component water-based sulfonated polyurethane of the present invention with a two-component water-based sulfonated polyurethane currently available for use in the manufacture of footwear. The formulation of Example 2 above was further blended with 5 parts crosslinker per 95 parts of wet sample. The crosslinker employed was Desmodur DA which is a water dispersible polyfunctional isocyanate from Miles Inc. The formulations were tested exactly as described in Example 2 bonding SBR to SBR. At an approximate dried coat weight of 130 g/m², Example 3 exhibited an average peel strength of 7.00 N/mm while the average peel strength of Example 3-C was 4.75 N/mm. Example 3-C is the same as 2-C, except at a coating weight of 135 g/mm.

Example 4

This example describes the synthesis and properties of a preferred water-based sulfonated polyurethane/acrylic polymer.

To a reaction flask was charged 213.8 grams (0.21 hydroxyl equivalents) of molten Rucoflex XS-5483-55 which is a sulfonated polyester polyol from Ruco Corporation, 10.05 grams (0.15 hydroxyl equivalents) dimethylolpropionic acid, 6.75 grams (0.15 hydroxyl equivalents) 1,4-butanediol,

37.97 grams methyl methacrylate and 37.97 grams butyl acrylate. The mixture was heated to 55°C then charged with 25.9 grams (0.23 isocyanate equivalents) isophorone diisocyanate and 39.2 grams (0.46 isocyanate equivalents) 1,6-diisocyanatohexane. The mixture was heated at 70°C for approximately 3 hours.

- 5 The isocyanate terminated sulfonated polyurethane prepolymer/monomer mixture was then charged with 8.0 grams (0.8 moles) triethylamine and stirred for 10 minutes. The prepolymer was dispersed in 554.5 grams deionized water. To the dispersion was charged, over a 10 minute period, a solution containing 0.20 grams ammonium peroxydisulfate and 20 grams deionized water. Free radical emulsion
- 10 polymerization was completed by heating to 80°C for approximately 3 hours. The aqueous and dried polymer properties are described below:

pH = 7.7

Viscosity = 900 mPa.s

Effective diameter = 228 nm

- 15 Mean diameter = 494 nm

Adhesion testing:

- The wet sample was drawn down on an untreated, pressed and polished PVC sheet using a number 40 Meyer rod and dried 24 hours at ambient room temperature. A second PVC sheet was placed over the dried film and 2.54 cm
- 20 x 15.24 cm strips were cut. The individual strips were heat activated, using variable temperatures, on a Sentinel® heat sealer at 3.515 kilograms per square centimeter for 30 seconds. After 24 and 168 hours aging, at ambient room temperature, the strips were tested on a Intellect® 500 for 180° peel values. The results are provided below:

Aging	51.6°C	65.5°C	79.4°C	93.3°C
25 24 hours	2.1 kg/cm	3.0 Kg/cm	4.4 Kg/cm	5.3 Kg/cm
168 hours	3.2 Kg/cm	SF	SF	SF

SF = Substrate Failure

- The 180° peel adhesion failure temperature was tested using the
- 30 procedure as described in example 2. The results are provided below:

Heat activation Temperature	51.6°C	65.5°C	79.4°C	93.3°C
Failure Temperature	58.7°C	> 126°C	> 126°C	> 126°C

Example 5

This was made in the same manner as Example 1 except the composition of this example did not contain a chain extender.

Example 6

- 5 The polymer of Example 5 was used to prepare a formulation as follows:

	Example 6
Example 5 polymer	99.45
DSX-1550/water (50/50)	0.05
10 Surfynol 465	0.05

The Example 6 formulation was tested in the same manner as described in Example 2 and the results are shown below:

	Leather/SBR	SBR/SBR	NBR/NBR	PVC/PVC	SBS/SBS
15 Example 6	3.84	7.30	7.43	11.30	11.47
Comparative Example 2-C	2.80	1.63	3.20	1.46	1.27

Claims

What is claimed is:

- 5 1. An improved water-based sulfonated polyurethane composition particularly useful as an adhesive, coating and primer in the manufacture of footwear, said sulfonated polyurethane being a reaction product of
- a) at least one polyisocyanate;
 - b) at least one alkylene diol;
 - 10 c) at least one sulfonated polyester polyol wherein the sulfo groups thereof are present as alkali metal salts; and
 - d) at least one dihydroxy carboxylic acid, or salt thereof;
- the carboxyl groups of said dihydroxy carboxylic acid being present in said dispersion as alkali metal salts, organic tertiary amine salts or mixtures thereof.
- 15
2. A composition as in claim 1 wherein said polyisocyanate is an aliphatic polyisocyanate.
- 20 3. A composition as in claim 2 wherein said dihydroxy carboxylic acid is dimethylolpropionic acid.
4. A composition as in claim 2 wherein said polydiisocyanate is selected from the group consisting of isophorone diisocyanate, hexamethylene diisocyanate and mixtures thereof.
- 25
5. A composition as in claim 1 wherein said composition is characterized as having a dried film heat activation temperature in the range of from about 50°C to about 95°C and heat resistant bonds of greater than 110°C.
- 30
6. A composition as in claim 1 further comprising at least one water dispersible polyfunctional crosslinking agent.

7. A composition as in claim 6 wherein said crosslinking agent is selected from the group consisting of isocyanates, aziridines, melamine resins, epoxies, oxazolines and carbodiimides.
- 5 8. A composition as in claim 7 wherein said crosslinking agent is present in the composition in an amount from about 8 to about 20 parts by weight, based on 100 parts total solids.
9. A composition as in claim 8 wherein said water dispersible
10 polyfunctional crosslinking agent is a water dispersible polyfunctional isocyanate.
10. A composition as in claim 9 wherein said composition is characterized
15 as having a dried film heat activation temperature in a range from about 50°C to about 95°C and heat resistant bonds greater than about 110°C.
11. A composition as in claim 1 further comprising at least one
dispersible non-polyurethane based polymer and copolymer selected from the
group consisting of acrylics, vinyl/acrylics, styrene/acrylics,
20 vinyl-acetate/ethylene copolymers, polychloroprenes, styrene,
styrene/butadiene, starches, dextrans, caseins, animal pectins and mixtures thereof.
12. An improved water-based sulfonated polyurethane composition,
25 particularly useful as an adhesive, coating or primer in the manufacture of footwear, the composition comprising an aqueous dispersion of a sulfonated polyurethane polymer formed in the presence of at least one ethylenically unsaturated monomer.
- 30 13. A composition as in claim 12 wherein said ethylenically unsaturated monomer is selected from the group consisting of methyl methacrylate, butyl acrylate and mixtures thereof.

14. A composition as in claim 13 wherein said at least one ethylenically unsaturated monomer is free radically polymerized after formation of said sulfonated polyurethane to form a water-based sulfonated polyurethane/acrylic interpreting network.
- 5
- 15 A composition as in claim 14 wherein said composition is characterized as having a dried film heat activation temperature in a range from about 50°C to about 95°C and heat resistant bonds of greater than 110°C.
- 10
16. A composition as in claim 14 further comprising at least one water dispersible polyfunctional crosslinking agent.
17. A composition as in claim 16 wherein said crosslinking agent is selected from the group consisting of isocyanates, aziridines, melamine resins, epoxies, oxazolines and carbodiimides.
- 15
18. A composition as in claim 17 wherein said crosslinking agent is present in the composition in an amount from about 8 to about 20 parts by weight, based on 100 parts total solids.
- 20
19. A footwear adhesive as in claim 17 wherein said water dispersible polyfunctional crosslinking agent is a water dispersible polyfunctional isocyanate.
- 25
20. A composition as in claim 14 further comprising at least one water dispersible non-polyurethane based polymer or copolymer selected from the group consisting of acrylics, vinyl/acrylics, styrene/acrylics, vinyl-acetate/ethylene copolymers, polychloroprenes, styrene, styrene/butadiene, starches, dextrans, casein, animal pectin and mixtures thereof.
- 30

21. A method of bonding a pair of substrates comprising applying a composition as in claim 1 to at least one of said substrates, drying said composition and then joining the two substrates with heat and pressure.
- 5 22. A bonded assembly prepared by the method of claim 21 wherein at least one of said substrates is a member selected from the group consisting of leather, polyvinyl chloride, polyurethane, cloth, nylon fabric, vulcanized rubbers, ethylene vinyl acetate, polypropylene, polyamide, styrene butadiene copolymers, natural rubber, fiberboard, polyester, polystyrene, wood, nylon
10 and polyethylene.
23. In a method of manufacturing an article of footwear wherein a composition comprising an aqueous dispersion of a polyurethane polymer is utilized as an adhesive, coating or primer on at least one portion of said
15 article of footwear,
the improvement wherein the polyurethane polymer is a reaction product of
- a) at least one polyisocyanate;
 - b) at least one alkylene diol;
 - c) at least one sulfonated polyester polyol wherein the sulfo
20 groups are present as alkali metal salts; and
 - d) at least one dihydroxy carboxylic acid, or salt thereof;
- the carboxyl groups of said dihydroxy carboxylic acid being present in said dispersion as alkali metal salts, organic tertiary amine salts and mixtures thereof.
- 25
24. An article of footwear having an adhesive, coating or primer layer on at least one portion thereof, said layer comprising a polyurethane polymer, said polyurethane polymer being a reaction product of
- a) at least one polyisocyanate;
 - b) at least one alkylene diol;
 - c) at least one sulfonated polyester polyol wherein the sulfo
30 groups are present as alkali metal salts; and

- d) at least one dihydroxy carboxylic acid, or a salt thereof selected from the group consisting of alkali metal salts, organic tertiary amine salts and mixtures thereof.

- 5 25. An article of footwear as in claim 24 wherein said layer comprises a dried film of an aqueous dispersion comprising said polyurethane polymer and or copolymer of an ethylenically unsaturated compound.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/09501

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G18/08 C09J175/06

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)

IPC 6 C08G C09J

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,96 07540 (H.B. FULLER) 14 March 1996 see the whole document	1-11
A	EP,A,0 368 172 (TOYO BOSEKI) 16 May 1990 see claim 1; examples	1
A	US,A,5 455 293 (WOOD ET AL) 3 October 1995 see column 2, line 60 - column 6, line 6; claims 1-3,6	1,9,12
A	EP,A,0 259 679 (BAYER) 16 March 1988 see page 2, line 41 - page 5, line 22; claims 1-4; examples	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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 document 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.
- *Z* document member of the same patent family

Date of the actual completion of the international search

8 October 1996

Date of mailing of the international search report

16 OCT 1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Bourgonje, A

INTERNATIONAL SEARCH REPORT

Inte al Application No
PCT/US 96/09501

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,95 08583 (H.B. FULLER) 30 March 1995 see page 6, line 10 - page 17, line 6; claims & US,A,4 870 129 cited in the application ---	1
A	DE,A,39 30 352 (RENIA-GESELLSCHAFT) 21 March 1991 cited in the application see claims 1-7,12 ---	1
A	EP,A,0 666 275 (AIR PRODUCTS) 9 August 1995 see page 3, line 36 - page 6, line 9; claims 1-9 -----	1,12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PLI/US 96/09501

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9607540	14-03-96	AU-A- 1556895	27-03-96
EP-A-368172	16-05-90	JP-A- 2128316	16-05-90
		DE-D- 68909002	14-10-93
		DE-T- 68909002	05-01-94
		US-A- 5009960	23-04-91
US-A-5455293	03-10-95	NONE	
EP-A-259679	16-03-88	DE-A- 3630045	17-03-88
		CA-A- 1315454	30-03-93
		DE-A- 3772303	26-09-91
		JP-A- 63069882	29-03-88
		US-A- 4870129	26-09-89
WO-A-9508583	30-03-95	AU-A- 7055994	10-04-95
DE-A-3930352	21-03-91	NONE	
EP-A-666275	09-08-95	CA-A- 2141715	09-08-95
		JP-A- 7242866	19-09-95