Title: SULFONATE-CONTAINING POLYURETHANE DISPERSIONS VIA NON-SOLVENT PROCESS

Abstract: The invention relates to a water-dispersible polyurethane and a process of making same without solubilizing amounts of organic solvent.
SULFONATE-CONTAINING POLYURETHANE DISPERSIONS
VIA NON-SOLVENT PROCESS

BACKGROUND OF THE INVENTION

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority from U.S. Provisional Application No. 60/193,272 filed on March 30, 2000.

1. Field of the Invention

The invention pertains to a water-dispersible polyurethane and a high-yield process of making same that does not require use of solubilizing amounts of an organic solvent. In a preferred practice of the invention, the process uses no organic solvent.

2. Description of the Prior Art

Polyurethanes are commercially significant inasmuch as they are adaptable to a variety of applications and end uses, including coatings, paints, adhesives, fibers and solid articles of manufacture. Given the importance of this class of polymers, much effort has been invested in developing processes to produce same that are increasingly flexible and economic.

For certain applications --for example, in coatings, adhesives and the like-- the polyurethane is provided in the form of a dispersion. Older processes in this regard took advantage of the fact that polyurethanes are typically more soluble in organic solvents than they are in water, in which the polymer generally has little, if any, solubility. Organic solvent based polyurethane dispersions have, however,
become disfavored given pressing environmental concerns: disposal of the solvents became problematic in some instances, and issues of safety and toxicity arose in others.

The detriments attendant organic solvent polyurethane dispersions have impelled the development of water as the dispersing medium. Because polyurethanes ordinarily exhibit poor solubility in water, these techniques commonly involve the introduction of salt groups at some point into the polymer thereby creating the requisite solubility. In one approach, sulfonate groups, which lend solubility, are so introduced.

While the ultimate sulfonate-containing polyurethane dispersion in this regard is aqueous --and thus does not manifest the problems hereinbefore described-- the processes to make same still typically utilize organic solvents, especially low boiling organics such as acetone. Representative processes of this type are found in British Patents GB 1305880, GB 1329565, GB 1335891 and GB 1336050; and in US Patent Nos. 4289672, 4870129 and 5432228.

Generally speaking, these known processes employ the following steps: a polyether or polyester is reacted with a diisocyanate in quantities to yield an isocyanate-terminated (-N=C=O; or NCO) polymer known as a prepolymer. The prepolymer is not soluble in water to any great degree, but is soluble in certain organic solvents. Industrially, low boiling, volatile solvents such as acetone, tetrahydrofuran, methyl ethyl ketone, tertiary butanol and the like are used for this purpose. In practice, the organic solvent is added to the reactor to create a dilute solution in which the prepolymer disperses. Usually, large amounts of solvent are required to achieve the desired effect.
e.g. the solvent can account for up to 70% weight of the total ingredients.

The solubilized prepolymer is then chain extended to increase molecular weight. The chain extenders are solvent soluble and, to impart water solubility to the polymer, they are sulfonated. Sulfonate-containing water soluble amine chain extenders have been favored in this regard; these include salts of aliphatic aminosulphonic acids, such as 1-propanesulfonic acid, 2-[[2-aminoethyl]amino]propionamido]-2-methyl-, monosodium salt; monosodium salt of ethylenediamino-2-ethanesulfonic acid; monosodium salt of ethylenediamino-3-propanesulfonic acid.

The chain extended, high molecular weight polymer, now containing sulfonate groups, is then dispersed in water to generate a fully reacted, NCO-free polyurethane in water. Thereafter, the volatile solvent is stripped off to beget a solvent-free, aqueous polyurethane dispersion.

While adequate to obtain an aqueous dispersion of polyurethane, these processes are nevertheless cumbersome to implement and suffer numerous disadvantages: they require liberal quantities of organic solvent to make the prepolymer solution, which solvent must later be stripped off to make the aqueous dispersion product -- all of which leads to increased cost and creates safety and environmental concerns during manufacturing. And although the solvent is eventually stripped off, there is still some residue in the final product, which in turn gives rise to VOC problems. Finally, the yield per production batch in these processes is usually very low, which is antithetical to the economics of commercial scale production.
In view of these drawbacks, interest in developing solvent-free processes has arisen. Among the efforts in this regard is that described in commonly-assigned U.S.S.N. 09/531,831, filed March 21, 2000. The process thereof reacts a polyisocyanate with a sulfonate-containing polyester polyol, such as poly(butylene adipate) glycol, the latter having greater than 40 milliequivalents (meq) of sulfonate groups per hundred grams of polyester. The process is conducted free of organic solvents; the solid polyurethane elastomer thereby created is dispersed in water to form a stable, aqueous polyurethane dispersion. When the sulfonate value is 40 meq or lower, however the elastomer does not form an adequate dispersion.

Although this process is a marked advance in aqueous polyurethane dispersion technology, the need for still further improvement exists.

SUMMARY OF THE INVENTION

Consistent with the foregoing desiderata, the present invention relates to a water-dispersible, sulfonate-containing polyurethane and a high-yield process to make same without organic solvents.

The polyurethane of the invention comprises the product obtained by contacting a sulfonated polyol with a polyisocyanate under conditions effective to form a NCO-terminated prepolymer that is dispersible in water only with agitation; and contacting said prepolymer with an amine-containing chain extender that is sulfonated sufficient to provide a water dispersible polyurethane, wherein said contacting steps occur without solubilizing amounts of organic solvent.
DETAILED DESCRIPTION OF THE INVENTION

In one aspect, the invention utilizes controlled introductions of water soluble sulfonate groups into the polymer system whereby a water dispersible polyurethane is eventually obtained. In a preferred practice, a portion of the sulfonate groups are introduced by way of a polyol component, as defined hereinafter, which is reacted with a polyisocyanate to form a prepolymer. The amount of sulfonation introduced at this point is sufficient to render the prepolymer dispersible in water, but only with agitation. That is to say, a stable prepolymer water dispersion will not form, and agitation must be continued throughout to maintain the dispersive state. If stopped, the prepolymer will settle out in an unacceptably short period of time. Further sulfonation is then introduced by way of a sulfonated amine-containing chain extender. The amount of sulfonation introduced at this point is sufficient to render the polyurethane thereby obtained water dispersible such that a stable aqueous polyurethane dispersion eventuates where agitation is no longer required.

The practice of the present invention occurs without solubilizing amounts of organic solvent such as acetone and the like. Thus in one embodiment of the present invention, organic solvent may be present at less than 30% solvent (by weight total ingredients), which amount is insufficient to solubilize the polymer. In a more preferred embodiment, de minimus amounts of organic solvent are present, e.g. about 1 to about 5% weight; in the most preferred practice of the invention, no organic solvents are present.
**Polyol:** Without limitation, serviceable polyols include polyhydroxyl compounds known in the polyurethane fabrication arts, such as polyester, polyethers and polyamides; these are hydroxyl terminated, preferably at both ends.

In a particular practice of the invention, the polyol is a polyester formed by conventional condensation polymerization between a diacid and a diol.

Diacid in this regard refers to dicarboxylic acids and anhydrides thereof. Without restriction, dicarboxylic acids include: aliphatic dicarboxylic acids, alicyclic dicarboxylic acids, aromatic dicarboxylic acids, ethylenically unsaturated alkenyl dicarboxylic acids. Preferred are alkyl dicarboxylic acids having 2 to 12 carbon atoms, and aromatic dicarboxylic acids having 6 to 12 carbon atoms. By way of exemplification only, specific diacids include: oxalic acid, malonic acid, dimethylmalonic acid, succinic acid, glutaric acid, adipic acid, trimethylmalonic acid, pimelic acid, dodecanedioic acid, 2,2-dimethylglutaric acid, azelaic acid, sebacic acid, suberic acid, maleic acid, fumeric acid, 1,3-cyclopentanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, phthalic acid, terephthalic acid, isophthalic acid, tetrahydrophthalic acid, 2,5-norbornanedicarboxylic acid, 1,4-naphthalic acid, diphenic acid, 4,4'-oxydibenzoic acid, diglycolic acid, thiodipropionic acid, 4,4'-sulfonyldibenzoic acid and 2,5-naphthalene dicarboxylic acid. Anhydrides of the foregoing are also contemplated.

Diols include, without limitation, those having 2 to 12 carbon atoms. Nonrestrictive examples include: ethylene glycol, diethylene glycol, 1,3-propylene
glycol, 1,2-propylene glycol, 2,2-diethyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2-ethyl-2-isobutyl-1,3-propanediol, 1,3-propanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 2,4-dimethyl-2-ethylhexane-1,3-diol, 1,2-cyclohexanediol, 1,3-cyclohexanediimethanol, 1,4-cyclohexanediimethanol, p-xylenediol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol. Other suitable diols include polyethylene glycol, poly(propylene glycol), copoly(ethylene/propylene)glycol and polybutylene glycol as well as corresponding poly(alkylene ether)glycols such as poly(ethylene ether)glycol, poly(propylene ether)glycol, copoly(ethylene ether)glycol and poly(butylene ether)glycol.

The polyl may be sulfonated using methods known in the art. Particularly preferred methods include those described in commonly-assigned US Patent Nos. 5698626 and 5753774 and European Patent Published Application EP 0849299, the contents of each and all of which are fully incorporated herein by reference. In the present invention, the sulfonated polyl is typically associated with a Group I cation, e.g. Na, K and Li.

In the practice of the invention, the polyl is sulfonated just enough to render the resultant prepolymer dispersible in water only under conditions of agitation. That is, there is inadequate sulfonation provided by the polyl alone to render the resultant prepolymer water dispersible without agitation. Consistently, the polyl may be sulfonated with up to 40 meq of sulfonate groups per hundred grams of polyl, but no more inasmuch as greater than 40 meq results in a prepolymer that is water soluble and stable as such without agitation. In a preferred practice, the polyl
contains about 5 to about 30 meq of sulfonate groups per hundred grams of polyol. In a more preferred embodiment, the polyol contains about 5 to about 20 meq of sulfonate groups per hundred grams of polyol. In a still more preferred embodiment, the polyol contains about 10 to about 15 meq of sulfonate groups per hundred grams of polyol.

**Polyisocyanate:** The invention contemplates the use of any organic polyisocyanate including diisocyanates, triisocyanates and higher isocyanates. Preferred polyisocyanates have the formula \( Q(NCO)_{2} \) wherein \( Q \) is an aliphatic hydrocarbon group having 4 to 12 carbon atoms, a cycloaliphatic hydrocarbon group having 6 to 15 carbon atoms, an aromatic hydrocarbon group having 6 to 15 carbon atoms or an araliphatic hydrocarbon group having 7 to 15 carbon atoms. The preferred polyisocyanate is a diisocyanate, particularly isophorone diisocyanate. Other diisocyanates in this regard include without limitation: tetramethylene diisocyanate, hexamethylene diisocyanate, dicyclohexylmethane diisocyanate, dodecamethylene diisocyanate, 1,4-diisocyanato-cyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanato-cyclohexane, 4,4'-diisocyanatodicyclohexylmethane, 4,4'-diisocyanatodicyclohexyl-propane-(2,2), 1,4-diisocyanatobenzene, toluene diisocyanates such as 2,4-diisocyanatotoluene and 2,6-diisocyanatotoluene, 4,4'-diphenylmethane diisocyanate, 4,4'-diisocyanatodiphenyl-propane-(2,2), p-xylene-diisocyanate, a,a,a',a'-tetramethyl-m or p-xylene diisocyanate.

**Amine-Containing Chain Extender:** Typically useful chain extenders in this regard include without restriction, alkyl and aromatic diamines and triamines wherein the alkyl moiety has 2 to 12 carbon atoms and the aromatic moiety has 6 to 10 carbon atoms. Examples
include: ethylene diamine, diethylene triamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane and 3,3,5-trimethyl-5-aminomethylcyclohexylamine. In a first preferred practice, the amine-containing chain extender has the formula I:

\[
RR_1N-\text{CH}_2\text{-CHR}_2-C(O)\text{NH-}CR_4\text{-CHR}_5\text{-SO}_3M \quad (I)
\]

wherein R and R₁ are each independently hydrogen, C₁-C₆ alkyl or C₅-C₉ cycloalkyl which may be unsubstituted or substituted with an amino or C₁-C₆ alkylamino group with the proviso that if R is hydrogen R₁ can also be 4-(4-aminocyclohexylmethyl)-cyclohexyl, 3-(3-aminopropoxy)-n-propyl or 3-(3-aminopropyl-methylamino)-n-propyl; R₂, R₃, R₄ and R₅ are each independently hydrogen or a C₁-C₆ alkyl, and M is a Group I cation. Amine-containing chain extenders of formula I include monosodium salt of ethylenediamino-2-ethanesulfonic acid, and monosodium salt of methylenediamino-3-propanesulfonic acid. The most preferred chain extender is 1-propanesulfonic acid, 2-[3-[(2-aminoethyl)amino]proionamido]-2-methyl, monosodium salt, also known as SSAMPS, having the structure

\[
\text{H}_2\text{N-CH}_2\text{CH}_2\text{-NH-CH}_2\text{CH}_2\text{-C-NH-C-CH}_2\text{-SO}_3\text{Na} \quad (II)
\]

where in formula I: R₁, R₂, and R₅ are each hydrogen, R₃ and R₄ are each methyl, and R is a C₂ alkyl (ethyl) substituted with an amino group at its terminal end. In a second preferred practice the amine-containing chain extender has the formula II:
wherein R₆ and R₇ are each independently hydrogen or a C₁-C₆ alkyl; R₈ and R₉ are each independently a C₁-C₆ alkylene (such as methylene, ethylene, trimethylene etc) which can be unsubstituted or substituted with one or more C₁-C₆ alkyl groups; M is a Group I cation; and x is 0 or 1. A preferred amine-containing chain extender of formula II is a monosodium salt of taurine, where, in formula II: x is 0, R₆ and R₇ are each hydrogen, R₈ is unsubstituted C₂ alkylene (ethylene), having the structure

\[ H₂N-CH₂CH₂-SO₃Na \]

Other preferred amine-containing chain extenders of formula II include diamines such as monosodium salt of N-(2-aminoethyl)-2- aminoethane sulfonic acid, where in formula II: x is 1, R₆ and R₇ are each hydrogen, R₈ and R₉ are each unsubstituted C₂ alkylene (ethylene) having the structure

\[ H₂N-CH₂CH₂-NH-CH₂CH₂-SO₃Na \]

and monosodium salt of N-(2-aminoethyl)-3-aminopropane sulfonic acid where, in formula II: x is 1, R₆ and R₇...
are each hydrogen, \( R_8 \) is unsubstituted \( C_2 \) alkylene (ethylene) and \( R_9 \) is unsubstituted \( C_3 \) alkylene (trimethylene) having the structure

\[
H_2N-\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{SO}_3\text{Na}
\]

In yet another preferred practice of the present invention, the amine-containing chain extender may be a dimer of any of the foregoing. A dimer in this regard describes the structure obtained when any of the subject chain extenders e.g. Formulae I or II, are connected with and share the terminal \( NR_6R_7 \) (formula I) or \( NH_2 \) groups (formula II). These compounds are disulfonated. Exemplifying this particular practice is the dimer of SSAMPS which has the structure:
Mixtures of any of the foregoing chain extenders may also be used.

In the practice of the invention, the amine-containing chain extender is sulfonated at least enough to supply the balance of sulfonate groups, when considered with those already provided by the sulfonated polyol as aforesaid, required to impart sufficient dispersibility to the resultant polyurethane such that an aqueous dispersion of the same eventuates that is stable over time, without agitation, without any significant phase separation or gellation occurring.

In the practice of the invention, it is preferred that the finished polyurethane product contain about 25 to about 45 meq of sulfonate groups per hundred grams of dry polyurethane product. More preferably, said dry product contains about 30 to about 40 meq sulfonate groups per hundred grams of dry product.

In keeping with the foregoing parameters, the sulfonation required of the amine-containing chain extender can be the difference between that desired for the finished polyurethane product as aforesaid, and that supplied by the chosen sulfonated polyol. For example, if the polyol employed contains 10 meq of sulfonate groups per hundred grams of polyol, then the amine-containing chain extender would be sulfonated sufficient to provide a final polyurethane product having, for example, 45 meq sulfonate groups per hundred grams of product, those in the art being aware of the necessary conversion factors in this regard.

Agitation as used herein refers to mechanical and other means known in the art, including e.g. stirring.

The practice of the invention contemplates the presence of other components common to the polyurethane arts. These include by way of example only,
comonomers, such as lower diols of 2 to 12 carbon atoms, e.g. butanediol; and cross-linking agents, e.g. silane containing cross-linking agents such as N-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane. Other chain extenders may also be present such as water and alkyl and aromatic polyols in conjunction with the amine-containing chain extender as described hereinbefore.

While flexible, the mole equivalent ratio of NCO to OH (including NH functionality should diamines be used of the reactants hereinbefore described is preferably about 0.5:1 to about 1.5:1, with about 0.8:1 to about 1.2:1 being more preferred, and about 1:1 being most preferred.

The following examples are illustrative of the present invention and not limiting thereof.
Example 1.

Preparation of polyurethane dispersion with sodium sulfonate-containing diamine chain extender (SSAMPS) without organic solvent in accordance with the present invention

RAW MATERIALS
1. For the NCO-Terminated Prepolymer:

10  IPDI (Isophorone diisocyanate)
    107.51 grams
Polyol (SS66-112)(10meq)*
    292.49 grams
*Sodium sulfonate-containing poly(hexamethylene adipate) glycol, M.W. 1,000, OH⁺ 112, containing pendant sodium sulfonate group concentration of 10 meq per hundred grams of polyester, supplied by CK Witco Corporation

2. For the Aqueous Dispersion:

NCO-terminated prepolymer
    320.00 grams
Water
    818.05 grams
Sulfonated a amine-containing Chain Extender (SSAMPS )
(aqueous 55.8%)**
    71.72 grams
**1-Propanesulfonic acid, 2-[(3-[(2-aminoethyl)amino]propionamido]-2-methyl-, monosodium salt containing sulfonate group concentration of 346 meq per hundred grams of SSAMPS.
PROCEDURE:

The polyol (polyester) and the IPDI were added to a reaction kettle. Stirring was continued with nitrogen blanket at 100°C until the theoretical isocyanate content has reached. The resulting prepolymer at a temperature of 100°C was dispersed in the mixture of water and SSAMPS at a temperature of 21°C. Stirring was continued for 4 hours. The product was a milky dispersion; solid content was about 30%. The dispersion was very stable under heat aging at 52°C (oven) for 1 month; no phase separation or gellation was found. The theoretical sodium sulfonate group concentration of the finished product was about 45 meq per hundred grams of dry product.
Comparative Example 1

Preparation of polyurethane dispersion without a sulphonated polyol and with sodium sulphonate-containing diamine chain extender (SSAMPS) without organic solvent.

RAW MATERIALS

1. For the NCO-Terminated Prepolymer:

   IPDI (Isophorone diisocyanate)  
   107.51 grams
   Polyol (Fomrez 66-112)*  
   292.49 grams

   *Poly (hexamethylene adipate) glycol, M.W.1,000, OH# 112, supplied by CK Witco Corporation

2. For the Aqueous Dispersion:

   NCO-terminated prepolymer  
   320.00 grams
   Water  
   818.05 grams
   Sulfonated Amine-containing Chain Extender SSAMPS  
   (aqueous 55.8%)**  
   71.72 grams

   **1-Propanesulfonic acid, 2-[3-[(2-aminoethyl)amino]propionamido]-2-methyl-, monosodium salt containing sulphonate group concentration of 346 meq per hundred grams of SSAMPS

PROCEDURE:
The polyol (polyester) and the IPDI were added to a reaction kettle. Stirring was continued with nitrogen blanket at 100°C until the theoretical isocyanate content was reached. The resulting prepolymer at a temperature of 100°C was dispersed in the mixture of water at a temperature of 21°C. The prepolymer could not be dispersed in water. The theoretical sodium sulfonate group concentration of the finished product would have been about 38.0 meq per hundred grams of dry product if the product were successful.
Comparative Example 2

Preparation of polyurethane dispersion without a sulfonated polyol with sodium sulfonate-containing diamine chain extender (SSAMPS) without organic solvent

**RAW MATERIALS**

1. **For the NCO-Terminated Prepolymer**

   IPDI (Isophorone diisocyanate)  
   107.51 grams  
   Polyol (Fomrez 66-112)*  
   292.49 grams  
   *Poly(hexamethylene adipate)glycol, M.W. 1,000, OH# 112, supplied by CK Witco Corporation.

2. **For the Aqueous Dispersion:**

   NCO-terminated prepolymer  
   320.00 grams  
   Water  
   818.05 grams  
   SSAMPS (aqueous 55.8%)**  
   71.72 grams  
   **1-Propanesulfonic acid, 2-[3-[(2-aminoethyl)amino]propionamido-2-methyl-, monosodium salt containing sulfonate group concentration of 346 meq per hundred grams of SSAMPS

**PROCEDURE:**

The polyol (polyester) and the IPDI were added to a reaction kettle. Stirring was continued with nitrogen blanket at 100°C until the theoretical isocyanate
content was reached. The resulting prepolymer at a temperature of 100°C was dispersed in the mixture of water and SSAMPS at a temperature of 21°C. Stirring was continued for 4 hours. The product precipitated and was discarded. The theoretical sodium sulfonate group concentration of the finished product would have been 38.0 meq per hundred grams of dry product if the product were successful.
Comparative Example 3

Preparation of polyurethane dispersion without a sulfonated polyol with sodium sulfonate-containing diamine chain extender (SSAMPS) with an organic solvent (acetone).

RAW MATERIALS

1. For the NCO-Terminated Prepolymer

IPDI (Isophorone diisocyanate)
107.51 grams

Polyol (Fomrez 66-112)*
292.49 grams

*Poly(Hexamethylene adipate)glycol, M.W. 1,000, OH#112, supplied by CK Witco Corporation

2. For the Dispersion:

NCO-terminated prepolymer
320.00 grams

Acetone
747.00 grams

Water
818.05 grams

SSAMPS (aqueous 55.8%)**
71.72 grams

**1-Propanesulfonic acid, 2-[(3-[(2-aminoethyl)amino]proionamido)-2-methyl-,monosodium salt containing sulfonate group concentration of 346 meq per hundred grams of SSAMPS

PROCEDURE:
The polyol (polyester) and the IPDI were added to a reaction kettle. Stirring was continued with nitrogen blanket at 100°C until the theoretical isocyanate content was reached. The prepolymer was transferred to a flask equipped with water-cool condenser. The acetone was introduced to the prepolymer under agitation until homogeneous acetonic solution. SSAMPS was added to the acetonic solution. The resulting polymer solution at a temperature of 38°C was dispersed in water at a temperature of 21°C. Stirring was continued for 4 hours, and the acetone was distilled off. The product was a translucent dispersion; solid content was about 30%. The dispersion was very stable under heat aging at 52°C (oven) during 1 month; no phase separation or gellation was found. The theoretical sodium sulfonate group concentration of the finished product was about 38.0 meq per hundred grams of dry product.
Comparative Example 4

Preparation of polyurethane dispersion with highly sulfonated polyol, but without a sulfonated amine-containing chain extender (SSAMPS) and without organic solvent

RAW MATERIALS

1. For the NCO-Terminated Prepolymer:

IPDI (Isophorone diisocyanate)
107.51 grams
Polyol (SS66-112) (68.3 meq)*
292.49 grams
*Sodium sulfonate-containing poly(hexamethylene adipate)glycol, M.W. 1,000, OH# 112, containing pendant sodium sulfonate group concentration of 68.3 meq per hundred grams of polyester, supplied by CK Witco Corporation.

2. For the Aqueous Dispersion:

NCO-terminated prepolymer
320.00 grams
Water
818.05 grams
Adipac dihydrazide
24.12 grams

PROCEDURE:

The polyol (polyester) and the IPDI were added to a reaction kettle. Stirring was continued with nitrogen blanket at 100°C until the theoretical isocyanate
content was reached. The resulting prepolymer at a temperature of 100°C was dispersed in the mixture of water and adipic dihydrazide at a temperature of 21°C. However, the prepolymer exhibited a very high viscosity and also was unable to be dispersed in water. The theoretical sodium sulfonate group concentration of the finished product would have been about 46 meq per hundred grams of dry product if the product were successful.
CLAIMS

What is claimed is:

1. A water-dispersible polyurethane which comprises the product obtained by contacting a polyol with a polyisocyanate under conditions effective to form an NCO-terminated prepolymer, said polyol being sulfonated sufficient to render said prepolymer dispersible in water only under conditions of agitation; and contacting said prepolymer with an amine-containing chain extender that is sulfonated sufficient to provide a water dispersible polyurethane, wherein said contacting steps occur in the absence of solubilizing amounts of an organic solvent.

2. The polyurethane of Claim 1 wherein said sulfonated polyol contains up to 40 meq of sulfonate groups per hundred grams of polyol.

3. The polyurethane of claim 2 wherein said sulfonated polyol contains about 5 to about 30 meq of sulfonate groups per hundred grams of polyol.

4. The polyurethane of Claim 3 wherein said sulfonated polyol contains about 10 to about 20 meq of sulfonate groups per hundred grams of polyol.

5. The polyester of Claim 1 wherein said sulfonated polyol is derived from a polyol selected from the group consisting of hydroxyl-terminated polyesters, polyethers and polyamides.
6. The polyurethane of Claim 1 wherein said amine-containing chain extender is selected from the group consisting of salts of aliphatic aminosulfonic acids.

7. The polyurethane of Claim 1 wherein said polyisocyanate is selected from the group consisting of diisocyanates, triisocyanates and higher isocyanates.

8. The polyurethane of Claim 1 wherein said amine-containing chain extender has formula I or II:

\[
\text{RR}_1\text{N-CH}_2\text{-CHR}_2\text{-C(O)NH-CR}_3\text{R}_4\text{-CHR}_5\text{-SO}_3\text{M} \quad (I)
\]

where \( R \) and \( R_1 \) are each independently hydrogen, \( C_1\text{-}C_8 \) alkyl or \( C_5\text{-}C_8 \) cycloalkyl which may be unsubstituted or substituted with an amino or \( C_1\text{-}C_6 \) alkylamino group with the proviso that if \( R \) is hydrogen \( R_1 \) can also be \( 4\text{-}(4\text{-aminocyclohexylmethyl})\text{-cyclohexy, 3\text{-}(3\text{-amino-n-propoxy})\text{-n-propyl or 3\text{-}(3\text{-amino-n-propyl-methylamino})\text{-n-propyl; R}_2, R_3, R_4 \text{ and R}_5 \) are each independently hydrogen or a \( C_1\text{-}C_6 \) alkyl, and \( M \) is a Group I cation;

\[
\text{R}_6\text{R}_7\text{N-R}_8\text{-}[\text{NH}-\text{R}_9\text{]x-SO}_3\text{M} \quad (II)
\]

where \( R_6 \) and \( R_7 \) are each independently hydrogen or a \( C_1\text{-}C_6 \) alkyl; \( R_8 \) and \( R_9 \) are each independently a \( C_1\text{-}C_6 \) alkylene which can be unsubstituted or substituted with one or more \( C_1\text{-}C_3 \) alkyl groups; \( M \) is a Group I cation; and \( x \) is 0 or 1.

9. The polyurethane of Claim 8 wherein said amine-containing chain extender has formula I and is 1-propanesulfonic acid, 2-[3-[2-amino ethyl]amino]propionamido]-2-methyl, monosodium salt.
10. The polyurethane of Claim 8 wherein said amine-containing chain extender has formula II and is a monosodium salt of taurine, a monosodium salt of N-(2-amino ethyl)-2-aminoethane sulfonic acid, or a monosodium salt of N-(2-amino ethyl)-3-aminopropane sulfonic acid.

11. The polyurethane of Claim 8 wherein the amine-containing chain extender of formulae I or II is in the form of a dimer.

12. The polyurethane of Claim 1 wherein said polyol is poly(hexamethylene adipate)glycol containing about 10 meq of sulfonate groups per hundred grams of resin; said polyisocyanate is isophorone diisocyanate; and said amine-containing chain extender is 1-propanesulfonic acid, 2,-[3-[(2-aminoethyl)amino]propionamido]-2-methyl-, monosodium salt.

13. A process of making an aqueous polyurethane dispersion without an organic solvent which comprises:
   (a) contacting a polyol with a polyisocyanate under conditions effective to form an NCO-terminated prepolymer, said polyol being sulfonated sufficient to render said prepolymer dispersible in water only under conditions of agitation;
   (b) dispersing said prepolymer in water with agitation;
   (c) contacting under agitation said prepolymer with an amine-containing chain extender, said chain extender being sulfonated sufficient to provide an aqueous polyurethane dispersion, wherein (a), (b) and (c) occur in the absence of solubilizing amounts of an organic solvent.
14. The process of Claim 13 wherein sulfonated polyol contains up to 40 meq of sulfonate groups per hundred grams of polyol.

15. The process of Claim 14 wherein said sulfonated polyol contains about 5 to about 30 meq of sulfonate groups per hundred grams of polyol.

16. The process of Claim 15 wherein said sulfonated polyol contains about 10 to about 20 meq sulfonate groups per hundred grams of polyol.

17. The process of Claim 13 wherein said sulfonated polyol is derived from a polyol selected from the group consisting of hydroxyl-terminated polyesters, polyethers and polyamides.

18. The process of Claim 13 wherein said amine-containing chain extender is selected from the group consisting of salts of aliphatic aminosulfonic acids.

19. The process of Claim 13 wherein said amine-containing chain extender has formula I or II:

\[ RR_1N-CH_2-CHR_2-C(O)NH-CR_3R_4-CHR_5-SO_3M \]  

(I)

where \( R \) and \( R_1 \) are each independently hydrogen, \( C_1-C_9 \) alkyl or \( C_5-C_8 \) cycloalkyl which may be unsubstituted or substituted with an amino or \( C_1-C_6 \) alkylamino group with the proviso that if \( R \) is hydrogen \( R_1 \) can also be 4-(4-aminocyclohexylmethyl)-cyclohexy, 3-(3-amino-n-propoxy)-n-propyl or 3-(3-amino-n-propyl-methylamino)-n-propyl; \( R_2, R_3, R_4 \) and \( R_5 \) are each independently hydrogen or a \( C_1-C_6 \) alkyl, and \( M \) is a Group I cation.
R₉R₇N-R₈⁻[NH-R₄]ₓ⁻SO₃M

(II)

where R₉ and R₇ are each independently hydrogen or a C₁-C₆ alkyl; R₈ and R₉ are each independently a C₁-C₆ alkylene which can be unsubstituted or substituted with one or more C₁-C₃ alkyl groups; M is a Group I cation; and x is 0 or 1.

20. The process of Chain 19 wherein said amine-containing chain extender has formula I and is 1-propanesulfonic acid, 2-[3-[(2-amino ethyl)amino] propionamido]-2-methyl, monosodium salt.

21. The process of Claim 13 wherein said amine-containing chain extender has formula II and is a monosodium salt of taurine, a monosodium salt of N-(2-aminoethyl)-2-aminoethane sulfonic acid, or a monosodium salt of N-(2-amino ethyl)-3-aminopropane sulfonic acid.

22. The process of Claim 13 wherein the amine-containing chain extenders of formulae I or II is in the form of a dimer.

23. The process of Claim 13 wherein said polyisocyanate is selected from the group consisting of diisocyanates, triisocyanates and higher isocyanates.

24. The process of Claim 13 wherein said polyol is poly(hexamethylene adipate)glycol containing about 10 meq of sulfonate groups per hundred grams of resin; said polyisocyanate is isophorone diisocyanate; and
said amine-containing chain extender is 1-propanesulfonic acid, 2-[[3-[(2-aminoethyl)amino]propionamido]-2-methyl-, monosodium salt.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/08 C08G18/46 C08G18/10

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 7 C08G

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):

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Name and mailing address of the ISA:

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Date of mailing of the international search report: 07/08/2001

Authorized officer: Angiolini, D

Form: PCT/ISA/210 (second sheet) (July 1999)
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