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(54) THIXOTROPIC POLYURETHANE COMPOSITIONS

(71) We, TAKEDA CHEMICAL INDUSTRIES LTD., No. 27, Dosho-machi 2-chome, Higashi-ku, Osaka-shi, Japan, a Company organised and existing under the

laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to thixotropic polyurethane compositions, and more particularly to compositions containing polyurethane prepolymers and specific additives capable of imparting thixotropic properties to the prepolymers.

Polyurethanes are excellent in physical properties, particularly in elasticity, weathering and abrasion resistance and have been utilized in various fields, such as elastomers, coating materials for papers or fibres, paints, sealants, flooring materials, walling materials, adhesives and synthetic leathers. For such purposes there have been generally used pasty or liquid compositions of polyurethane prepolymers having no thixotropy but fluidity. Therefore, when such compositions are applied as a paint or sealant to a vertical surface, for example, they do not allow easy brushing or spatula work, giving uneven coatings due to running thereof, and further when they are applied as an adhesive or coating material to a porous paper or fibre, for example, a difficult coating operation is required due to considerable penetration thereof.

Accordingly, it is an important problem in the art to impart thixotropy to polyurethane compositions, but as yet, there has been proposed no successful method adapted for the purpose.

The object of the invention is to provide polyurethane compositions having excellent thixotropy. A further object of the invention is to provide thixotropic polyurethane com-

positions which can be easily applied to a vertical surface or a porous material free from undesirable running or penetration.

The above and other objects of the invention will be apparent from the following description.

These objects of the invention can be accomplished by a thixotropic polyurethane composition comprising 100 parts by weight of a polyurethane prepolymer, 0.1 to 50 parts by weight of colloidal silica of an average particle size of 3 to 50 m μ and at least one ethylene glycol polymer, having an average molecular weight of 100 to 20,000 of the group consisting of polyethylene glycol, as hereinafter defined, polyethylene glycol ether, as hereinafter defined, and polyethylene glycol ester; the weight ratio of said ethylene glycol polymer to said colloidal silica being in the range of between 0.05:1 and 0.5:1.

The term polyethylene glycol used here and throughout the specification and claims is intended to mean poly(ethylene oxy ether) glycol expressed as $[\text{HO}-(\text{CH}_2\text{CH}_2-\text{O})_n\text{H}]$ and the term polyethylene glycol ether is intended to mean such poly(ethylene oxy ether) glycol wherein the terminal hydroxyl groups have been etherified. It has now been found that when said colloidal silica and polyethylene glycol or ether or ester thereof is added in combination to the polyurethane prepolymer in the specific range and ratio as above mentioned, a markedly excellent thixotropy is imparted to the prepolymer and the polyurethane composition having thixotropy can be obtained, while individual use of the colloidal silica and ethylene glycol polymer can not impart thixotropy to the prepolymer.

The polyurethane prepolymer used in the invention is liquid, pasty or solid at ambient temperature, and the preferred prepolymer is a liquid or pasty one having a 500 to 10,000 molecular weight. Such prepolymers

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are known in the art and prepared by the conventional methods, such as, by the well-known reaction of polyisocyanates with active hydrogen atom-containing compounds. Desirable ratios of NCO to active H are usually in the range of between 1.1:1 and 5.0:1, particularly between 1.5:1 and 3.0:1. Examples of the polyisocyanates are 2,4-tolylenediisocyanate, 2,6-tolylenediisocyanate, m-phenylenediisocyanate, p-phenylenediisocyanate, 1-chlorophenylene-2,4-diisocyanate, 1,5-naphthalenediisocyanate, 3,3'-bistoluene-4,4'-diisocyanate, methylene bisphenylene-4,4'-diisocyanate, tetramethylenediisocyanate, hexamethylenediisocyanate, "Papi" (trade mark, polyisocyanate of Cabot Corporation, U.S.A.) and dimers and trimers of these isocyanates and triisocyanates obtained by reacting triols such as trimethylolpropane with 3 moles of a diisocyanate.

As active hydrogen atom-containing compounds there may be preferably used those containing 2 to 5 active hydrogen atoms in the molecule thereof and having a molecular weight of 60 to 8,000. Examples are 1) Low molecular weight diols or triols, such as ethyleneglycol, propyleneglycol, 1,4-butanediol, hexamethyleneglycol, 1,4-cyclohexanediol, triisopropanolamine, trimethylolpropane and, glycerol; 2) Polyalkyleneglycols, such as polypropyleneglycol, polytetramethyleneglycol and ethyleneoxide-propyleneoxide copolymers; 3) Copolymers of alkyleneoxide (e.g. ethyleneoxide and propyleneoxide) with low molecular weight polyols (e.g. glycerine, trimethylolpropane, 1,2,6-hexanetriol, erythritol, and pentaerythritol; 4) Polyesterpolyols from polyols and polycarboxylic acids, such as reaction products of ethyleneglycol, propyleneglycol, 1,4- or 1,3-butanediol or 1,6-hexanediol with such acids as adipic acid, succinic acid, maleic acid, phthalic acid or terephthalic acid; 5) Polymers produced by the ring opening of cyclic esters, such as polycaprolactone and polybutyrolactone; 6) Esters of polyols and higher aliphatic acids, such as mono- or diricinolate of mono-, di- or triethylene glycol, mono-, di- or tricinolate of 1,2,6-hexanetriol or trimethylolpropane, mono-, di-, tri- or tetra-ricinolate of pentaerythritol or erythritol, castor oil, hydrogenated castor oil, mono- or diglyceride of castor oil acid or hydrogenated castor oil acid.

In the invention there may also be used blocked polyurethane prepolymers. The isocyanate blocking agents used are, for example, phenolic compounds such as phenol, thiophenol, chlorophenol, methyl thiophenol, ethyl phenol, ethyl thiophenol, nitrophenol, cresol, xylenol or resorcinol, alcohols such as ethanol, methanol, propanol, isopropanol, butanol, tert-butanol, tert-pentanol, tert-butanethiol or tert-hexanol or derivatives thereof such as ethylene chlorohy-

drine, ω -hydroperfluoroalcohols or 1,3-dichloro-2-propanol, aromatic amines such as diphenylamine, diphenyl naphthyl amine or xylylene, imides such as succinic acid imide or phthalic acid imide, active methylene compounds such as acetoacetic acid esters, acetyl acetone or malonic acid diesters, mercaptans such as 2-mercapto benzothiazole or tert-dodecyl mercaptan, lactams such as ϵ -caprolactam, δ -valerolactam, γ -butyrolactam or β -propyllactam, imines such as ethylene imine, urea compounds such as urea, thiourea or diethylene urea, oximes such as acetoxime, methylethyl-ketone oxime, or cyclohexanone oxime, diaryl compounds such as carbazole, phenyl naphthyl amine or N-phenyl xylylene, bisulfates and borates. Of these blocking agents, phenolic compounds and ethanol are preferable.

Conveniently the polyurethane prepolymer is used in the form of liquid prepolymer or organic solvent solution. The preferred viscosity of the liquid prepolymer or solution may be determined in accordance with the use of the final compositions, but usually those having a viscosity of 10 to 1,000,000 c.p.s., preferably 1,000 to 1,000,000 c.p.s., may be used. The viscosity is a value measured at 23°C. under 4 r.p.m. by Brookfield Viscometer. As the solvent there may be used various organic solvents, for example, esters such as ethyl acetate, butyl acetate and amyl acetate; ketones such as acetone, methylethylketone and methylisobutylketone; aromatic hydrocarbons such as toluene, benzene and xylene; ethers such as tetrahydrofuran and dioxane; alkyl amides such as N,N'-dimethylformamide and N,N'-dimethylacetamide; or dimethylsulfoxide.

The colloidal silica used in the invention has an average particle size of 3 to 50m μ , preferably 5 to 40 m μ , and is available under the trade mark of "Aerosil" (Trade Mark; colloidal silica manufactured by Degussa, West Germany) and "Carbosil" (Trade Mark; colloidal silica manufactured by Cabot Corporation, U.S.A.). While it has been known that such colloidal silica is effective for imparting thixotropy to various synthetic resin prepolymers, individual use thereof is almost ineffective in the case of polyurethane prepolymers.

According to the present invention it is essential to use the colloidal silica in combination with ethylene glycol polymers in the specific amount and ratio, whereby the final composition shows excellent thixotropy.

The ethylene glycol polymers used in the invention are polyethylene glycol, polyethylene glycol ether and polyethylene glycol ester, having a molecular weight of 100 to 20,000. The preferred polyethylene glycol ether is an aryl ether, such as diphenyl, dinaphthyl and di-o-chlorophenyl and an alkyl

ether of 1 to 18 carbon atoms, such as ethyl, iso-propyl and stearyl, and the preferred ester is a carboxylic acid ester of 2-18 carbon atoms, such as benzoate, acetate and laurate.

The amounts of the colloidal silica and ethylene glycol polymers contained in the present composition are important, and the former should be contained in the range of 0.1 to 50 weight parts, preferably 0.5 weight parts, based in 100 weight parts of the polyurethane prepolymer. The weight ratio of the ethylene glycol polymers to the colloidal silica is also significant in the invention, and the ethylene glycol polymer should be contained in 0.05 to 0.5 times, preferably 0.1 to 0.3 times the weight of the colloidal silica. When the colloidal silica and ethylene glycol polymer are used in combination in the above range of amount and ratio, the resultant polyurethane composition can display excellent thixotropy due to synergetic effect of the both compounds. If one or both compounds is used in lesser amounts a thixotropic composition can not be obtained. The use of larger amount results in gelation of the composition.

The polyurethane composition of the present invention may further contain other additives, such as fillers e.g. calcium carbonate, gypsum, talc, silica, clay, cement, magnesium carbonate, asbestos and glass wool, plasticizers e.g. dioctyl phthalate, dibutyl phthalate, tricresyl phosphite and tar, and pigments e.g. titan white and red iron oxide. The composition of the invention can be used as a one-can type composition and also a two-can type composition.

For fuller understanding of the invention Examples are given below, in which all percentages and parts are shown by weight, and the slump test was carried out in accordance with ASA (American Standard Association) A 116 1 - 1960.

Example 1

To 1,000 parts of polypropylenediol of average molecular weight of 1,000 were added 278.4 parts of 2,4-tolylenediisocyanate and 69.6 parts of 2,6-tolylenediisocyanate, and the mixture was heated at 80°C. for 2 hours in a nitrogen stream, whereby a colorless and transparent polyurethane prepolymer of amine equivalent of 720 was obtained. The molecular weight of the prepolymer was 1,440 and the viscosity was 17,500 c.p.s. at 23°C.

To 1,000 parts of the resultant prepolymer were added 60 parts of "Aerosil" (Trade Mark; colloidal silica of 5 to 40 μ average particle size manufactured by Degussa, West Germany) and 5 parts of polyethylene glycol of average molecular weight of 3,000 and the mixture was kneaded at 80°C. by a vacuum kneader to produce a composition in the form of a paste or grease.

The composition was subjected to the slump test and after one hour at 50°C. no slump was observed. The viscosity of the composition was measured at 23°C. by varying the rotation speed of the Brookfield Viscometer with the following results:

Viscosities at 23°C. (c.p.s.)

2 r.p.m.	4 r.p.m.	10 r.p.m.	20 r.p.m.
298,000	188,000	134,000	72,000

For comparison a composition of 1,000 parts of said prepolymer and 300 parts of Aerosil was prepared by the same manner as above and subjected to the same slump test, flow-down of more than 20 mm being observed.

Example 2

To a mixture of 2,400 parts of polypropylene glycol of average molecular weight of 2,000 and 300 parts of polypropylene triol of average molecular weight of 3,000 was added 252 parts of 2,4-tolylenediisocyanate and 63 parts of 2,6-tolylenediisocyanate, and the mixture was heated in a nitrogen stream at 80°C. for 2 hours, whereby was obtained a colorless and transparent polyurethane prepolymer of amine equivalent of 3,500. The prepolymer showed a viscosity of 150,000 c.p.s. at 25°C. To 100 parts of the prepolymer were added 20 parts of dioctylphthalate, 33 parts of calcium carbonate, 3 parts of titanium oxide, 6 parts of "Aerosil" (Trade Mark, same as specified in Example 1) and 0.5 part of polyethylene glycol of average molecular weight of 6,000 and the mixture was kneaded in a vacuum kneader to produce white paste. By the slump test at 70°C. in the manner same as in Example 1, it resulted in zero mm of slump.

Example 3

To 600 parts of polybutylene adipate diol of average molecular weight of 2,400 was added 125 parts of 4,4'-methylenebisphenylisocyanate and the mixture was heated in a nitrogen stream at 80°C. for 2 hours to produce a white waxy polyurethane prepolymer of amine equivalent 1,427.

To 100 parts of the prepolymer were added 30 parts of N,N'-dimethylformamide, 5 parts of "Aerosil" (Trade Mark, same as specified in Example 1) and 2 parts of polyethyleneglycol diphenylether of average molecular weight of 4,000 and the mixture was kneaded in a vacuum kneader, whereby a polyurethane composition having thixotropy was obtained.

The viscosity of the composition was measured at 23°C. by varying the rotation speed of Brookfield Viscometer with the following results.

Viscosities at 23°C. (c.p.s.)

2 r.p.m.	4 r.p.m.	10 r.p.m.	20 r.p.m.
2,350	1,750	1,010	780

Example 4

100 parts of a 75 weight % ethyl acetate

- solution of a polyurethane prepolymer prepared from trimethylolpropane and 8:2 weight ratio mixture of 2,4-tolylenediisocyanate and 2,6-tolylenediisocyanate was mixed with 6 parts of "Aerosil" (Trade Mark, same as specified in Example 1), 0.5 part of polyethylene glycol of average molecular weight of 3,000 and 50 parts of thinner to obtain the composition of the invention. To the resultant composition was added "Desmophen 1100" (Trade Mark, polyesterpolyol of Farbenfabriken Bayer, West Germany) so as to obtain a molar ratio of NCO group and OH group=about 1.2:1, and further added thinner. A vertical surface of a steel plate was coated with the resultant paint and the painted surface was compared with that painted with the same composition except that "Aerosil" and polyethylene glycol were not added, to exhibit a neat finish while the latter showed marked uneven finish due to fluidity.

Example 5

- To 3,000 parts of polypropylene triol of 3,000 average molecular weight was added 522 parts of 8:2 ratio mixture of 2,4-tolylenediisocyanate and 2,6-tolylenediisocyanate and the mixture was heated in a nitrogen stream at 80°C. for 4 hours, producing a colorless and transparent polyurethane prepolymer of 1,180 amine equivalent in the form of viscous liquid.

- From the resultant liquid prepolymer the following four sample compositions were prepared:

- Sample 1: The above liquid prepolymer to which no additive was added.

- Sample 2: The above liquid prepolymer 100 parts of which was homogeneously mixed with 3 parts of "Aerosil" (Trade Mark, same as specified in Example 1).

- Sample 3: The above liquid prepolymer 100 parts of which was homogeneously mixed with 0.3 part of polyethylene glycol of 6,000 average molecular weight.

- Sample 4: The above liquid prepolymer 100 parts of which was homogeneously mixed with 3 parts of "Aerosil" (Trade Mark) and 0.3 part of polyethylene glycol of 6,000 average molecular weight.

- The viscosities of the above four samples were measured under 2 r.p.m. and 20 r.p.m. at 23°C. by Brookfield H-type Viscometer with the following results shown in the Table below:

Sample No.	Viscosity at 23°C. (c.p.s.)		Ratio of Viscosity of 2 r.p.m. to that of 4 r.p.m.
	2 r.p.m.	20 r.p.m.	
1	9,850	9,880	0.997
2	27,200	27,000	1.00
3	12,000	12,000	0.984
4	187,000	43,500	4.50

Example 6

- To 2,000 parts of polypropylenediol of average molecular weight of 2,000 were

added 278.4 parts of 2,4-tolylenediisocyanate and 69.6 parts of 2,6-tolylenediisocyanate, and the mixture was heated at 80°C. for 8 hours in nitrogen stream, whereby a colorless and transparent polyurethane prepolymer of amine equivalent of 1,195 was obtained. To 100 parts of the resultant prepolymer were added "Aerosil" (Trade Mark, colloidal silica of 5 to 40 m μ average particle size manufactured by Degussa, West Germany) and polyethylene glycol of average molecular weight of 1,000 in various amounts shown in the table below, and the mixture was kneaded at 80°C. under vacuum to produce polyurethane compositions.

The viscosities of the compositions thus obtained are listed below:

Aerosil (weight parts)	Polyethylene Glycol (weight parts)	Viscosities at 23°C. (c.p.s.)	
		2 r.p.m.	20 r.p.m.
0	0	9,650	9,700
3	0	20,500	20,800
5	0	24,500	24,300
10	0	38,200	39,000
30	0	87,000	88,000
0	0.5	12,000	11,800
0	2	17,500	17,100
0	10	35,500	35,800
3	0.01	34,000	34,000
3	0.3	420,000	113,000
3	1.0	515,000	130,000
5	0.01	56,000	56,000
5	0.3	745,000	168,000
5	1.0	>2,000,000	1,323,000
10	0.01	43,200	44,000

It will be appreciated that it is not intended to limit the invention to the above examples only, many variations, such as might readily occur to one skilled in the art being possible without departing from the scope thereof as defined in the appended claims.

WHAT WE CLAIM IS:—

1. A thixotropic polyurethane composition comprising 100 parts by weight of a polyurethane prepolymer 0.1 to 50 parts by weight of colloidal silica of an average particle size of 3 to 50 m μ and at least one ethylene glycol polymer, having an average molecular weight of 100 to 20,000, of the group consisting of polyethylene glycol, as hereinbefore defined, polyethylene glycol ether, as hereinbefore defined, and polyethylene glycol ester; the weight ratio of said ethylene glycol polymer to said colloidal silica being in the range of between 0.05:1 and 0.5:1.

2. The thixotropic polyurethane composition according to Claim 1, in which said polyurethane prepolymer has an average molecular weight of 500 to 10,000.

3. The thixotropic polyurethane composition according to Claim 1, in which

- solution of a polyurethane prepolymer prepared from trimethylolpropane and 8:2 weight ratio mixture of 2,4-tolylenediisocyanate and 2,6-tolylenediisocyanate was mixed with 6 parts of "Aerosil" (Trade Mark, same as specified in Example 1), 0.5 part of polyethylene glycol of average molecular weight of 3,000 and 50 parts of thinner to obtain the composition of the invention. To the resultant composition was added "Desmophen 1100" (Trade Mark, polyesterpolyol of Farbenfabriken Bayer, West Germany) so as to obtain a molar ratio of NCO group and OH group=about 1.2:1, and further added thinner. A vertical surface of a steel plate was coated with the resultant paint and the painted surface was compared with that painted with the same composition except that "Aerosil" and polyethylene glycol were not added, to exhibit a neat finish while the latter showed marked uneven finish due to fluidity.

Example 5

- To 3,000 parts of polypropylene triol of 3,000 average molecular weight was added 522 parts of 8:2 ratio mixture of 2,4-tolylenediisocyanate and 2,6-tolylenediisocyanate and the mixture was heated in a nitrogen stream at 80°C. for 4 hours, producing a colorless and transparent polyurethane prepolymer of 1,180 amine equivalent in the form of viscous liquid.

- From the resultant liquid prepolymer the following four sample compositions were prepared:

- Sample 1: The above liquid prepolymer to which no additive was added.
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- Sample 4: The above liquid prepolymer 100 parts of which was homogeneously mixed with 3 parts of "Aerosil" (Trade Mark) and 0.3 part of polyethylene glycol of 6,000 average molecular weight.

- The viscosities of the above four samples were measured under 2 r.p.m. and 20 r.p.m. at 23°C. by Brookfield H-type Viscometer with the following results shown in the Table below:

Sample No.	Viscosity at 23°C. (c.p.s.)		Ratio of Viscosity of 2 r.p.m. to that of 4 r.p.m.
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4	187,000	43,500	4.50

Example 6

- To 2,000 parts of polypropylenediol of 65 average molecular weight of 2,000 were

added 278.4 parts of 2,4-tolylenediisocyanate and 69.6 parts of 2,6-tolylenediisocyanate, and the mixture was heated at 80°C. for 8 hours in nitrogen stream, whereby a colorless and transparent polyurethane prepolymer of amine equivalent of 1,195 was obtained. To 100 parts of the resultant prepolymer were added "Aerosil" (Trade Mark, colloidal silica of 5 to 40 m μ average particle size manufactured by Degussa, West Germany) and polyethylene glycol of average molecular weight of 1,000 in various amounts shown in the table below, and the mixture was kneaded at 80°C. under vacuum to produce polyurethane compositions.

The viscosities of the compositions thus obtained are listed below:

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0	0.5	12,000	11,800
0	2	17,500	17,100
0	10	35,500	35,800
3	0.01	34,000	34,000
3	0.3	420,000	113,000
3	1.0	515,000	130,000
5	0.01	56,000	56,000
5	0.3	745,000	168,000
5	1.0	>2,000,000	1,323,000
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It will be appreciated that it is not intended to limit the invention to the above examples only, many variations, such as might readily occur to one skilled in the art being possible without departing from the scope thereof as defined in the appended claims.

WHAT WE CLAIM IS:—

1. A thixotropic polyurethane composition comprising 100 parts by weight of a polyurethane prepolymer 0.1 to 50 parts by weight of colloidal silica of an average particle size of 3 to 50 m μ and at least one ethylene glycol polymer, having an average molecular weight of 100 to 20,000, of the group consisting of polyethylene glycol, as hereinbefore defined, polyethylene glycol ether, as hereinbefore defined, and polyethylene glycol ester; the weight ratio of said ethylene glycol polymer to said colloidal silica being in the range of between 0.05:1 and 0.5:1.

2. The thixotropic polyurethane composition according to Claim 1, in which said polyurethane prepolymer has an average molecular weight of 500 to 10,000.

3. The thixotropic polyurethane composition according to Claim 1, in which



said colloidal silica has an average particle size of 5 to 40 m μ .

4. The thixotropic polyurethane composition according to Claim 1, in which said colloidal silica is contained in the range of 0.5 to 20 weight parts, based on 100 weight parts of the polyurethane prepolymer.

5. The thixotropic polyurethane composition according to Claim 1, in which

said weight ratio of the polyethylene glycol polymer to the colloidal silica is in the range of between 0.1:1 and 0.3:1.

6. A thixotropic polyurethane composition according to claim 1 and substantially 15 as described herein.

For the Applicants.

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