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(54) Title: COMPOSITION FOR POLYURETHANES

(57) Abstract: A composition primarily intended for use in the manufacture of polyurethane binder formulations, especially anionic polyurethane dispersions, is disclosed. The composition comprises at least one neutralised dihydroxyfunctional monocarboxylic acid, such as 2,2-bis(hydroxymethyl)propanoic acid, neutralised with at least one amine, and in addition thereto at least one organic solvent and optionally at least one liquid diol.

COMPOSITION FOR POLYURETHANES

The present invention is relates to a composition, which primarily is intended for use in the manufacture of polyurethane binder formulations, especially anionic polyurethane dispersions. The composition comprises at least one dihydroxyfunctional monocarboxylic acid neutralised with at least one amine and at least one organic solvent and/or a liquid diol.

It is well known to produce waterborne polyurethane dispersions in substantially two different processes, namely the melt dispersion process and the acetone process. The differences between said two processes can be summarised:

① The melt dispersion process, also known as the prepolymer process, comprises processing of a polyurethane in a water miscible organic solvent being inert to isocyanate reactions at applied temperature. The polyurethane is processed until the isocyanate content is stabilised and is then neutralised and dispersed in water. The molecular weight is in a subsequent step increased by addition of a diamine or a diol chain extender. Said addition comprises reaction with the free pendant isocyanate groups of the prepolymer previously obtained. The most commonly used organic solvent is N-methylpyrrolidone. It is understood from the very beginning of the process that said organic solvent will remain in the polyurethane dispersion.

② The acetone process is substantially the process as above in the presence of a low boiling ketone, such as acetone or methylethyl ketone. The low boiling solvent is after completed processing removed at a temperature preferably not exceeding 50°C.

In both cases the synthesis of the anionic dispersion implies the presence of compounds such as one or more hydroxyfunctional carboxylic acids and neutralisation of the carboxylic group or groups using for instance an amine. The processes can be summarised in the steps of

i) preparation of the polyurethane, whereby a hydroxyfunctional carboxylic acid is built into the polyurethane chain,

ii) neutralisation of carboxyl groups emanating from said hydroxyfunctional carboxylic acid, and

iii) dispersion in water.

The hydroxyfunctional carboxylic acid is accordingly build into the polymer chain and neutralised after preparation of said polyurethane, but before dispersing the polyurethane in water, with an amine. Various processes utilising above three steps are disclosed and taught in for instance European Patent Application 0 872 502 and in the US Patents nos. 5,126,393 and 5,852,105. The most commonly used hydroxyfunctional carboxylic acid is the dihydroxyfunctional monocarboxylic acid 2,2-bis(hydroxymethyl)propanoic acid.

Frequently used dihydroxyfunctional monocarboxylic acids such as said 2,2-bis(hydroxymethyl)propanoic acid, normally have high melting points and limited solubility in the organic environment. This often creates problems and requires certain attention. The process, regardless which of the two above mentioned, requires a catalyst selected from for instance organometal salts such as organozirconium salts, tin derivatives such as dibutyltin laurate, stannous octoate, dimethyltin di(decanoate), and others, or as alternatives amino catalysts selected from for instance the group consisting of triethylene diamine, bis(2-dimethyleaminoethyl) ether, and similar compounds.

Said limited solubility can suitably be exemplified by 2,2-bis(hydroxymethyl)propionic acid exhibiting a solubility in some commonly used organic solvents at 23°C as listed below:

Solvent	**Solubility at 23°C, weight-%**
Methylisobutyl ketone	0.3
Methylethyl ketone	0.4
Ethyl acetate	0.1
Methoxypropyl acetate	1.4
N-Methylpyrrolidone	29.9

The major problem of the obtained polyurethane dispersions is the storage stability. The polyurethane dispersion often exhibits, during storage, transport and processing, a tendency to precipitate or to a certain degree form small particles as a deposit in for instance the container. This problem is mainly related to the solubility drawbacks of hydroxyfunctional carboxylic acids, which compounds therefore normally is used in form of small particles, most often not larger than 150 µm. This so called recrystallisation problem occurs at any time when the hydroxyfunctional carboxylic acid contains larger particles, which particles normally remain unreacted and in many cases must be removed by filtration. The latter gives rise to another problem, namely uncertainty regarding the exact amount of hydroxyfunctional acid built into the polyurethane chain.

The present invention quite unexpectedly eliminates or reduces above disclosed problem by utilisation of a composition comprising a neutralised dihydroxyfunctional carboxylic acid, which neutralised acid in a predetermined amount, such as 10-70% or preferably 40-65% by weight is built into the polyurethane chain. Especially the risk of recrystallisation of hydroxyfunctional carboxylic acid is eliminated or reduced. The quality of the obtained polyurethane dispersion is independent of the particle size of the used hydroxyfunctional carboxylic acid, and the reproducibility is excellent. A furthermore major advantage is that additional catalysts, such as organometal salts, tin derivatives and others as disclosed above, not are required during the process. The preparation of the polyurethane dispersion can be summarised in the steps of

i) preparation of a composition comprising a neutralised dihydroxyfunctional carboxylic acid,
i) preparation of the polyurethane whereby the neutralised dihydroxyfunctional carboxylic acid is built into the polyurethane chain,
ii) dispersion in water.

A neutralised dihydroxyfunctional carboxylic acid is accordingly build into the polymer chain. Hydroxyfunctional carboxylic acids are in known methods as disclosed in for instance said European Patent Application 0 872 502 and said US Patents nos. 5,126,393 and 5,852,105 built into the polymer chain and then neutralised. Use of the composition according to the present invention allows, contrary to known methods, manufacture of polyurethane dispersions free of organic solvents such as N-methylpyrrolidone, yields a more even distribution of the hydroxyfunctional carboxylic acid in the polymer chain and eliminates or reduces the risk of recrystallisation of hydroxyfunctional carboxylic acid.

The composition of the present invention is primarily intended for use in the manufacture of polyurethane binder formulations, especially anionic polyurethane dispersions, and comprises at least one dihydroxyfunctional monocarboxylic acid neutralised with at least one amine, and in addition thereto at least one organic solvent and/or at least one liquid diol. The molar ratio between said at least one dihydroxyfunctional monocarboxylic acid and said at least one amine is preferably found within the range of 1:0.4 to 1:1.2 (acid to amine).

Preferred embodiments of the present invention include embodiments wherein said at least one dihydroxyfunctional monocarboxylic acid is 2,2-bis(hydroxymethyl)propanoic acid, 2,2-bis(hydroxymethyl)butanoic acid, 2,2-bis(hydroxymethyl)pentanoic acid and/or 2,3-dihydroxypropanoic acid.

Preferred embodiments of the present invention, furthermore, include embodiments wherein said at least one amine is selected from the group consisting of trimethylamine, triethylamine, triisopropylamine, triisooctylamine, tricyclohexylamine, diethylamine, diethanolamine and triethanolamine.

The composition of the present invention suitably comprises at least one organic solvent, such as one, two or more organic solvents selected from one or more related or independent groups. The organic solvent included in the composition of the present invention is preferably at least one ketone, such as acetone, methylethyl ketone and/or methylisobutyl ketone; N-methylpyrrolidone and/or butyldiglycol acetate; and/or at least one dibasic ester, such as dimethylglutarate, dimethylsuccinate and/or dimethyladipate.

The liquid diol, optionally included in the composition of the present invention, is preferably monoethylene glycol, diethylene glycol, triethylene glycol, monopropylene glycol, dipropylene glycol, tripropylene glycol and/or 2-methyl-1,3-propanediol.

The composition of the present invention is, by suitable choice of solvent or solvents, such as said acetone, methylethyl ketone and/or methylisobutyl ketone, suitably used in the manufacture of anionic polyurethane dispersion for use in solvent-free anionic polyurethane formulations or, by suitable choice of solvent or solvents, such as N-methylpyrrolidone, butyldiglycol acetate and/or dibasic esters, suitably used in manufacture of solvent comprising polyurethane formulations.

The average hydroxyl functionality of the composition of the present invention may optionally be adjusted by the choice and addition of one or more diols, such as said monoethylene glycol, diethylene glycol, triethylene glycol, monopropylene glycol, dipropylene glycol, tripropylene glycol and/or 2-methyl-1,3-propanediol and/or mixtures thereof..

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilise the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever. Examples 1-8 refer to preparation of compositions according to embodiments of the present invention, whereby obtained properties are given in Table I. Examples 9 and 10 refer to polyurethane formulations prepared using a composition according to the present invention.

Example 1

In a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet, were under nitrogen blanket and in listed order 249.9 g of methylethyl ketone, 293 g of triethylamine and under efficient stirring 457.1 g of 2,2-bis(hydroxymethyl)propionic acid charged. The mixture was heated to 80°C under stirring and said nitrogen blanket until a clear solution was obtained. The solution was then filtered and a compound according to the present invention was obtained.

Obtained properties are given in Table I.

Example 2

In a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet, were under nitrogen blanket and in listed order 222 g of

N-methylpyrrolidone and 249.2 g of triethylamine charged. 528.8 g of 2,2-bis(hydroxymethyl)propionic acid was then under stirring added in small portions. The mixture was now heated to 90°C and maintained until a clear solution was obtained. The solution was then filtered and a compound according to the present invention was obtained.

Obtained properties are given in Table I.

Example 3

In a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet, were under nitrogen blanket and in listed order 103.2 g of N-methylpyrrolidone and 286.8 g of triethylamine charged. 610 g of 2,2-bis(hydroxymethyl)-propionic acid was then under stirring added in small portions. The mixture was heated to 90°C and maintained until a clear solution was obtained. The solution was then filtered and a compound according to the present invention was obtained.

Obtained properties are given in Table I.

Example 4

In a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet, were under nitrogen blanket and in listed order 88 g of acetone, 392 g of triethylamine and under efficient stirring 520 g of 2,2-bis(hydroxymethyl)propionic acid charged. The mixture was heated to 50°C under stirring and said nitrogen blanket until a clear solution was obtained. The solution was then filtered and a compound according to the present invention was obtained.

Obtained properties are given in Table I.

Example 5

In a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet, were under nitrogen blanket and in listed order 143.7 g of methylethyl ketone, 334.4 g of triethylamine and under efficient stirring 521.9 g of 2,2-bis(hydroxymethyl)propionic acid charged. The mixture was heated to 80°C under stirring and said nitrogen blanket until a clear solution was obtained. The solution was then filtered and a compound according to the present invention was obtained.

Obtained properties are given in Table I.

Example 6

In a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet, were under nitrogen blanket and in listed order 222.2 g of acetone, 249.2 g of triethylamine and under efficient stirring 528.8 g of 2,2-bis(hydroxymethyl)propionic acid charged. The mixture was heated to 50°C under stirring and said nitrogen blanket until a clear solution was obtained. The solution was then filtered and a compound according to the present invention was obtained.

Obtained properties are given in Table I.

Example 7

In a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet, were under nitrogen blanket and in listed order 222.2 g of 2-methyl-1,3-propanediol, 249.2 g of triethylamine and under efficient stirring 528.8 g of 2,2-bis(hydroxymethyl)propionic acid charged. The mixture was heated to 90°C under stirring and said nitrogen blanket until a clear solution was obtained. The solution was then filtered and a compound according to the present invention was obtained.

Obtained properties are given in Table I.

Example 8

In a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet, were under nitrogen blanket and in listed order 167 g of 2-methyl-1,3-propanediol, 211 g of triethylamine and under efficient stirring 622 g of 2,2-bis(hydroxymethyl)propionic acid charged. The mixture was heated to 90°C under stirring and said nitrogen blanket until a clear solution was obtained. The solution was then filtered and a compound according to the present invention was obtained.

Obtained properties are given in Table I.

Example 9

113 g of methylene bis(4-cyclohexylisocyanate) was charged in a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet. 37.84 g of the compound obtained in Example 7 was added under inert dry nitrogen blanket under stirring. 500 g of acetone was added and the process was allowed to continue by for 1 hour at a

temperature of 50°C. 149.4 g of a poly(neopentyl glycol) adipate having a molecular weight of about 1000 and a hydroxyl number of about 112 mg KOH/g was after said 1 hour charged. The process was allowed to continue for 7 hours to obtain a isocyanate content of about 2.6-2.8%. 3 g of ethylene diamine in 50 g water was now added and the chain extension completed. 450 g of water were added and a homogenous water dispersion was obtained. Acetone was now under vacuum removed at a temperature of 40°C and a solvent free polyurethane dispersion was obtained having a determined non-volatile content of 38.99% and a viscosity of 80 mPas at 23°C.

Example 10

54 g of N-methylpyrrolidone was charged in a reaction flask equipped with a heating system, a stirring system, a Dean-Stark separator, a cooler and nitrogen inlet. 53.63 g of isophorone diisocyanate and 23.98 g of the compound obtained in Example 3 were added under inert dry nitrogen blanket under stirring. The process was allowed to continue by for 1 hour at a temperature of 50°C followed by addition of 136.09 g poly(ε-caprolactone) having a hydroxyl number of about 90 mg KOH/g. The process was now allowed to continue over night at 50°C. The polyurethane formed was dispersed in 400 g of water and 2.62 g of ethylene diamine are was as chain extender. A polyurethane dispersion was obtained having a non-volatile content of 35 % and a viscosity of 400 mPas at 23°C.

Table I

Example	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Acid equivalent weight, g/equiv.	293	253.4	219.7	257.7	256.7	253.4	253.4	215.4
Hydroxyl equivalent weight, g/equiv.	146.6	126.7	109.8	128.8	128.4	126.7	77.9	76.9
Neutralisation degree, mole amine/mole acid	1.172	0.625	0.624	1.000	0.850	0.625	0.626	0.450

CLAIMS

1. A composition primarily intended for use in the manufacture of polyurethane binder formulations, such as anionic polyurethane dispersions **characterised in**, that said composition comprises at least one dihydroxyfunctional monocarboxylic acid neutralised with at least one amine, and in addition thereto at least one organic solvent and optionally at least one liquid diol.

2. A composition according to Claim 1 **characterised in**, that said at least one dihydroxyfunctional monocarboxylic acid is 2,2-bis(hydroxymethyl)propanoic acid, 2,2-bis(hydroxymethyl)butanoic acid, 2,2-bis(hydroxymethyl)pentanoic acid and/or 2,3-dihydroxypropanoic acid.

3. A composition according to Claim 1 or 2 **characterised in**, that said at least one amine is selected from the group consisting of trimethylamine, triethylamine, triisopropylamine, triisooctylamine, tricyclohexylamine, diethylamine, diethanolamine, triethanolamine and mixtures thereof.

4. A composition according to any of the Claims 1-3 **characterised in**, that said composition comprises two or more organic solvents.

5. A composition according to any of the Claims 1-4 **characterised in**, that said organic solvent is at least one ketone, such as acetone, methylethyl ketone and/or methylisobutyl ketone.

6. A composition according to any of the Claims 1-4 **characterised in**, that said one organic solvent is N-methylpyrrolidone and/or butyldiglycol acetate.

7. A composition according to any of the Claims 1-4 **characterised in**, that said organic solvent is at least one dibasic ester, such as dimethylglutarate, dimethylsuccinate and/or dimethyladipate.

8. A composition according to any of the Claims 1-7 **characterised in**, that said optional at least one liquid diol is monoethylene glycol, diethylene glycol, triethylene glycol, monopropylene glycol, dipropylene glycol, tripropylene glycol and/or 2-methyl-1,3-propanediol.

9. A composition according to any of the Claims 1-8 **characterised in**, a molar ratio said at least one dihydroxyfunctional monocarboxylic acid to said at least one amine of 1:0.4 to 1:1.2.

10. A composition according to any of the Claims 1-9 **characterised in**, that said composition comprises 10-70%, preferably 40-65%, by weight of said at least one dihydroxyfunctional monocarboxylic acid neutralised with said at least one amine.

11. A composition according to any of the Claims 1-10 **characterised in**, that said at least one dihydroxyfunctional monocarboxylic acid is 2,2-(dihydroxymethyl)propanoic acid and that said at least one amine is triethylamine.

12. A composition according to any of the Claims 1-10 **characterised in**, that said at least one dihydroxyfunctional monocarboxylic acid is 2,2-(dihydroxymethyl)propanoic acid, that said at least one amine is triethylamine and that said at least one optional diol is 2-methyl-1,3-propanediol.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C09J 175/04, C08G 18/34
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)

IPC7: C09J, C08G

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

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, 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.
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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01/08/00

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