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(54) Title: ASPARTATE DERIVATIVES AND PROCESS FOR THEIR PREPARATION

(57) Abrégé/Abstract:
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(54) **Title:** ASPARTATE DERIVATIVES AND PROCESS FOR THEIR PREPARATION

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ASPARTATE DERIVATIVES AND PROCESS FOR THEIR PREPARATION

BACKGROUND OF THE INVENTION

The present invention relates to novel aspartates, a process for preparing them from primary amines and maleates and to their use as reactive components for polyisocyanates in two-component polyurethane coating compositions and for preparing polyurethane prepolymers.

Two-component coating compositions which contain, as binder, a polyisocyanate component combined with one or more isocyanate-reactive components are known. They are suitable for preparing high quality coatings which are hard, elastic, abrasion resistant, solvent resistant and weather resistant.

Secondary polyamines which contain ester groups have become established in the two-component surface coating industry. They are particularly suitable, in combination with lacquer polyisocyanates, as binders in low-solvent or solvent-free, high solids coating compositions because they provide rapid curing of the coatings at low temperatures.

These secondary polyamines are polyaspartates and are described, e.g., in U.S. patents 5,126,170, 5,214,086, 5,236,741, 5,243,012, 5,364,955, 5,412,056, 5,623,045, 5,736,604, 6,183,870, 6,355,829, 6,458,293 and 6,482,333 and published European patent application 667,362. In addition, aspartates containing aldimine groups are also known (see U.S. patents 5,489,704, 5,559,204 and 5,847,195). Their use as the only isocyanate-reactive component or mixed with other isocyanate-reactive components in two-component coating compositions are also described in the above-identified patents.

The process for preparing these polyaspartates is the reaction of the corresponding primary polyamines with maleates or fumarates corresponding to the formula

$$R_3OOC\text{-}C(R_1)=C(R_2)\text{-}COOR_4$$

wherein R_1, R_2, R_3 and R_4 are identical or different organic groups, resulting in the formation of secondary polyamines. Due to stearic, structural and electronic effects, these secondary amino groups have sufficiently reduced reactivity towards isocyanate groups to be mixable with polyisocyanates in a reliable and easy manner.

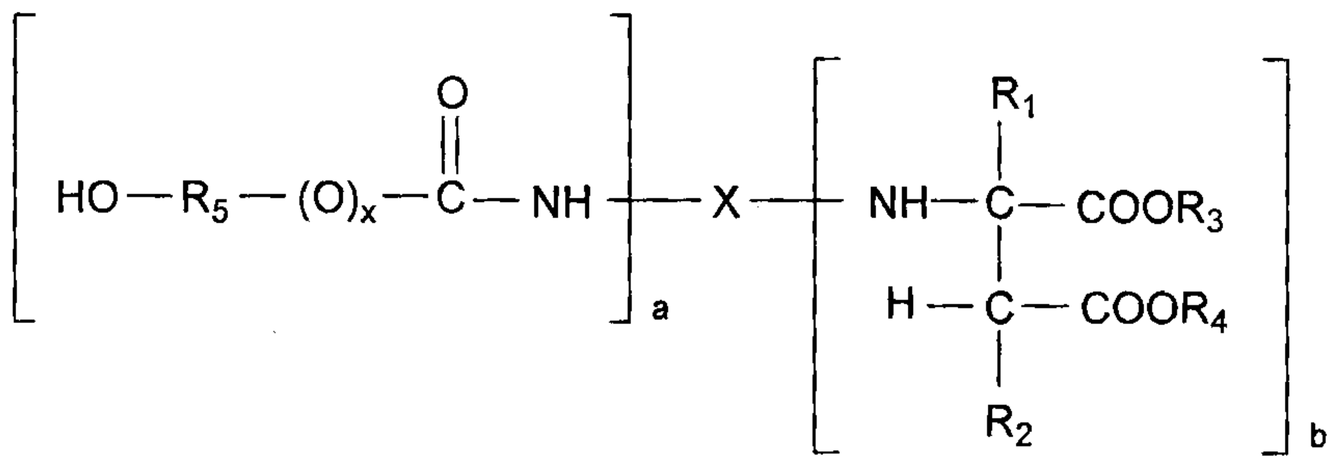
The reaction which is used to prepare polyaspartates is the addition of primary amines to the activated C-C double bond in vinyl carbonyl compounds, which has been described in the literature (see Chem. Ber. 1946, 38, 83; Houben Weyl, Meth. d. Org. Chemie, vol. 11/1, 272 (1957); Usp. Chimii 1969, 38, 1933). It has been found, however, that this reaction does not proceed to completion during the course of the actual synthesis process (e.g., 24 hours with stirring at 60°C). The actual extent of the reaction is dependent upon the type of primary polyamine. Thus, the degree of conversion (measured by the concentration of free, unconverted maleate and fumarate, into which maleate rearranges in the presence of basic catalysts) after 1 day with 1,6-hexanediamine is about 90 to 93%. The degree of conversion after 1 day with a cycloaliphatic polyamine having sterically hindered primary amino groups, i.e., 4,4'-diamino-3,3'-dimethyldicyclohexylmethane is only 77%. Complete or essentially complete conversion is achieved only after several days or, in the case of 4,4'-diamino-3,3'-dimethyldicyclohexyl-methane, only after several months.

In a typical commercial production, the reaction is run for sixteen hours when the conversion is somewhere between 75 and 95% complete depending on the amine used. The "unfinished" material is drummed and held in storage until the reaction is complete. This typically takes anywhere from two weeks to six months.

U.S. patent 5,821,326 describes the use of certain five-membered aromatic ring compounds as catalyst to accelerate the preparation of the aspartates.

DESCRIPTION OF THE INVENTION

The present invention is directed to novel aspartates of the formula:



where

X represents an m-valent organic residue obtained by removing the primary amino group or groups from a polyamine which has (cyclo)aliphatically bound amino groups and a number average molecular weight of 60 to 6000, and which may contain further functional groups that either are reactive with isocyanate groups or are inert to isocyanate groups at temperatures of up to 100°C,

R_1 and R_2 may be identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less (both are preferably hydrogen),

R_3 and R_4 may be identical or different and represent organic groups which are inert towards isocyanate groups at a temperature of 100°C or less (preferably a C_1 to C_8 and most preferably methyl or ethyl),

R_5 represents a member selected from the group consisting of C_2H_4, C_3H_6 and C_5H_{10},

a and b represent integers of from 1 to 5, provided that the sum of a and b is from 2 to 6 and that x is 1 when R_5 represents C_2H_4 or C_3H_6 and when x is 0 when R_5 represents C_5H_{10}.

The present invention also relates to a process for preparing aspartates of the above formula comprising

A) reacting at a temperature of 0 to 100°C, in solution or in the absence of a solvent and at an equivalent ratio of primary amino groups in component a) to C=C double bonds in component b) of from about 1.1:1 to about 3.0:1

a) polyamines corresponding to formula (II)

$$X[-NH_2]_m \qquad (II)$$

with

b) compounds corresponding to formula (III)

$$R_3OOC\text{-}C(R_1)=C(R_2)\text{-}COOR_4 \qquad (III)$$

wherein

X, R_1, R_2, R_3 and R_4 are as defined above and

m represents an integer of from 2 to 6, and

B) reacting the resultant product with a compound selected from the group consisting of ethylene carbonate, propylene carbonate and ε-caprolactone.

The present invention also relates to a two-component coating composition which contains, as binder,

a) a polyisocyanate component and

b) an isocyanate-reactive component containing

b1) a compound corresponding to formula (I) and

b2) optionally other isocyanate-reactive compounds,

wherein the equivalent ratio of isocyanate groups to isocyanate-reactive groups is from about 0.8:1 to about 2.0:1, and optionally, additives known in surface coatings technology.

Finally, the present invention also relates to prepolymers containing urea, urethane, allophanate and/or biuret structures, which are based on the reaction product of polyisocyanates with the aspartates of the invention, optionally in admixture with one or more isocyanate-reactive components.

The polyamines useful herein include i) high molecular weight amines having molecular weights of 400 to about 10,000, preferably 800 to about 6,000, and ii) low molecular weight amines having molecular weights below 400. The molecular weights are number average molecular weights (M_n) and are determined by end group analysis (NH number).

Examples of these polyamines are those wherein the amino groups are attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic carbon atoms.

Suitable low molecular polyamine starting compounds include ethylene diamine, 1,2- and 1,3-propane diamine, 2-methyl-1,2-propane diamine, 2,2-dimethyl-1,3-propane diamine, 1,3- and 1,4-butane diamine, 1,3- and 1,5-pentane diamine, 2-methyl-1,5-pentane diamine, 1,6-hexane diamine, 2,5-dimethyl-2,5-hexane diamine, 2,2,4-and/or 2,4,4-trimethyl-1,6-hexane diamine, 1,7-heptane diamine, 1,8-octane diamine, 1,9-nonane diamine, 1,10-decane diamine, 1,11-undecane diamine, 1,12-dodecane diamine, 1-amino-3-aminomethyl-3,5,5-trimethyl cyclohexane, 2,4- and/or 2,6-hexahydrotoluylene diamine, 2,4'- and/or 4,4'-diamino-dicyclohexylmethane, 3,3'-dialkyl-4,4'-diamino-dicyclohexyl methanes (such as 3,3'-dimethyl-4,4'-diamino-dicyclohexyl methane and 3,3'-diethyl-4,4'-diamino-dicyclohexyl methane), 1,3- and/or 1,4-cyclohexane diamine, 1,3-bis(methylamino)-cyclohexane, 1,8-p-menthane diamine, hydrazine, hydrazides of semicarbazido carboxylic acids, bis-hydrazides, bis-semi-carbazides, phenylene diamine, 2,4- and 2,6-toluylene diamine, 2,3- and 3,4-toluylene diamine, 2,4'- and/or 4,4'-diaminodiphenyl methane,higher functional polyphenylene polymethylene polyamines obtained by the aniline/formaldehyde condensation reaction, N,N,N-tris-(2-amino-ethyl)-amine, guanidine, melamine, N-(2-aminoethyl)-1,3-propane diamine, 3,3'-diamino-benzidine, polyoxypropylene amines, polyoxy-ethylene amines, 2,4-bis-(4'-aminobenzyl)-aniline and mixtures thereof.

Preferred polyamines are 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane (isophorone diamine or IPDA), bis-(4-aminocyclo-hexyl)-methane, bis-(4-amino-3-methylcyclohexyl)-methane, 1,6-diamino-hexane, 2-methyl pentamethylene diamine and ethylene diamine.

Suitable high molecular weight polyamines correspond to the polyhydroxyl compounds used to prepare the NCO prepolymers with the exception that the terminal hydroxy groups are converted to amino groups, either by amination or by reacting the hydroxy groups with a diisocyanate and subsequently hydrolyzing the terminal isocyanate group to an amino group. Preferred high molecular weight polyamines are amine-terminated polyethers such as the Jeffamine* resins available from Huntsman.

Suitable optionally substituted maleic or fumaric acid esters for use in the preparation of the aspartates are those corresponding to the formula

$$R_3OOC\text{-}C(R_1)=C(R_2)\text{-}COOR_4$$

wherein R_1, R_2, R_3 and R_4 are as previously defined. Examples include the dimethyl, diethyl and di-n-butyl and mixed alkyl esters of maleic acid and fumaric acid and the corresponding maleic or fumaric acid esters substituted by methyl in the 2- and/or 3-position. Suitable maleates or fumarates for preparing the aspartates of the present invention include dimethyl, diethyl, di-n-propyl, di-isopropyl, di-n-butyl and di-2-ethylhexyl maleates, methylethylmaleate or the corresponding fumarates.

The aspartates of the present invention are prepared by first reacting component a) with component b) at temperatures of 0 and 100°C, preferably 20 to 80°C and more preferably 20 to 60°C wherein (i) the equivalent ratio of primary amino groups in component a) to C=C double bond equivalents in component b) is from about 1.1:1 to about 3.0:1, preferably from about 1.1:1 to about 2.0:1. The reaction time may be from about 1 to about 4 hours, depending upon the type of polyamine and the

*trade-mark

desired maximum residual concentration of reactants in the reaction mixture. The resultant product is then reacted with a compound selected form the group consisting of ethylene carbonate, propylene carbonate and ε-caprolactone. This second reaction is typically conducted at a temperature of from about 50 to about 100°C, for times ranging from about 1 to about 4 hours. The ratio of reactants is chosen so that one mole of ethylene carbonate, propylene carbonate or ε-caprolactone is present for each unreacted amine group.

The process to prepare the aspartates of the present invention may be either be performed in solution or in the absence of a solvent. Solvent may also be added after the synthesis process, for example, to lower the viscosity. Suitable solvents include any organic solvents, preferably those known from surface coating technology. Examples include acetone, methyl ethyl ketone, methyl isobutyl ketone, n-butyl acetate, methoxypropyl acetate, toluene, xylene and higher aromatic solvents (such as the Solvesso* solvents form Exxon).

The aspartates prepared according to the invention may be directly used as reactive components for polyisocyanates after concluding the synthesis process.

One use of the aspartates of the present invention is to prepare coatings from two-component coating compositions containing, as binder,

a) a polyisocyanate component and

b) an isocyanate-reactive component containing

b1) the aspartates of the invention and

*trade-mark

b2) optionally other known isocyanate-reactive components.

Suitable polyisocyanate components a) are known and include the polyisocyanates known from polyurethane chemistry, e.g, low molecular weight polyisocyanates and lacquer polyisocyanates prepared from these low molecular weight polyisocyanates. Preferred are the lacquer polyisocyanates, which are known from surface coating technology. These lacquer polyisocyanates contain biuret groups, isocyanurate groups, allophanate groups, uretdione groups, carbodiimide groups and/or urethane groups and are preferably prepared from (cyclo)aliphatic polyisocyanates.

Suitable low molecular weight polyisocyanates for use in accordance with the present invention or for preparing the lacquer polyisocyanates are those having a molecular weight of 140 to 300, such as 1,4- tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), 2,2,4- and/or 2,4,4-trimethyl-hexamethylene diisocyanate, dodecamethylene diisocyanate, 2-methyl-1,5-diisocyanatopentane, 1,4-diisocyanatocyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanato-methylcyclohexane (IPDI), 2,4- and/or 4,4' diisocyanato-dicyclohexyl-methane, 1-isocyanato-1-methyl-3(4)-isocyanatomethyl-cyclohexane (IMCI), 2,4- and/or 2,6-hexahydrotoluylene diisocyanate (H_6TDI), 2,4- and/or 4,4'–diisocyanatodiphenylmethane or mixtures of these isomers with their higher homologs (which may be obtained in known manner by the phosgenation of aniline/ formaldehyde condensates), 2,4- and/or 2,6-diisocyanatotoluene, and mixtures thereof. The use of low molecular weight polyisocyanates themselves is not preferred. Also lacquer polyisocyanates prepared from aromatic polyisocyanates, such as 2,4- and/or 2,6-diisocyanatotoluene, are also less preferred. The lacquer

polyisocyanates containing urethane groups are preferably based on low molecular weight polyhydroxyl compounds having molecular weights of 62 to 300, such as ethylene glycol, propylene glycol and/or trimethylol-propane.

Preferred lacquer polyisocyanates for use as component a) are those based on 1,6-hexamethylene diisocyanate and having an NCO content of 16 to 24 wt.% and a maximum viscosity at 23°C of 10,000, preferably 3000 mPa.s.

Component b1) is selected from the aspartates of the present invention. Preferably, X represents a divalent hydrocarbon group obtained by removing the amino groups from 1-amino-3,3,5-trimethyl-5-aminomethyl-cyclohexane (IPDA), 4,4'-diaminocyclohexylmethane (HMDI), 3,3'– dimethyl-4,4'-diaminodicyclohexylmethane (Lasomin C260, BASF), hexahydro-2,4- and/or 2,6-diaminotoluene (H_6TDA), isomers of C–monomethyl-diaminodicyclohexyl-methanes, 3(4)-aminomethyl-1-methylcyclohexylamine (AMCA), hexane diamine or 2-methyl-5-pentanediamine.

Particularly preferred starting components b1) include those aspartates in which R_3 and R_4 represent C_1 to C_8 alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl or 2-ethylhexyl.

Optional starting components b2) are known compounds containing at least two isocyanate-reactive groups, including groups which react with isocyanate groups under the effect of either moisture or/and heat. Examples include hydroxy-functional polyacrylates and polyesterpolyols Mixtures of these compounds may also be used.

In the binders used according to the invention, the amounts of components a), b1) and (optionally) b2) are selected such that the equivalent ratio isocyanate groups to isocyanate-reactive groups is from about 0.8:1 to about 2.0:1, and preferably from about 0.8:1 to about 1.2:1.

The binders according to the invention are prepared by mixing the individual components either in the absence of a solvent or in the presence of the solvents which are conventionally used in polyurethane surface coating technology. Suitable solvents include ethyl acetate, butyl acetate, methoxypropyl acetate, methyl isobutyl ketone, methyl ethyl ketone, xylene, N–methylpyrrolidone, petroleum spirit, chlorobenzene, Solvesso solvent or mixtures thereof.

Preferably, the ratio by weight binder components a) and b) to solvent in the coating compositions according to the invention is from about 40:60 to about 100:0, more preferably from about 60:40 to about 90:10.

The coating compositions may also contain the known additives from surface coating technology. These include pigments, fillers, flow control agents, catalysts and anti-settling agents.

The properties of the coatings obtained from the coating compositions according to the invention may be adjusted by appropriate selection of the type and ratios of starting components a), b1) and b2).

The coating compositions may be applied to any substrate in a single layer or in several layers by known methods, e.g., by spraying, painting, immersing, flooding or by using rollers or spreaders. The coating compositions according to the invention are suitable for preparing coatings

on substrates, such as metals, plastics, wood or glass. The coating compositions are especially suitable for coating steel sheeting, which is used for the production of vehicle bodies, machines, cladding panels, barrels and containers. The substrates may be provided with suitable primer coats prior to applying the coating compositions according to the invention. Drying of the coatings may take place at a temperature of about 0 to 160°C.

The process for producing coatings using the aspartates of the present invention may also be used for the production of prepolymers containing urea, urethane, allophanate and/or biuret structures.

The aspartates of the present invention may be directly used after completion of the synthesis process because, in contrast to prior art aspartates, an approximately complete degree of conversion is achieved. As a result of the low concentration of maleates, fumarates and primary amino groups, these products are not only toxicologically and physiologically harmless, they also exhibit a reasonable, as opposed to a vigorous, reactivity towards isocyanates. Due to their low viscosity, they are a more than suitable alternative, as reactive diluents, to the environmentally polluting organic solvents previously used and may therefore be used in high quality, low-solvent or even solvent-free high solids two-component coating compositions.

All parts and percentages are by weight, unless otherwise indicated.

EXAMPLES

Example 1

A round bottom flask was fitted with stirrer, heating mantle, nitrogen inlet, thermocouple and addition funnel. 210 grams (2 eq) bis-(para-aminocyclohexyl)methane (PACM) was added to the flask at room temperature. 172 grams (1 eq) diethyl maleate was added through the addition funnel over a period of thirty minutes. The temperature of the flask rose to 35°C. The reaction was heated to 60°C and held for seven hours at which time the unsaturation number was 0.69 mg maleic acid per gram resin indicating 99% reaction. The reaction mixture was cooled to room temperature. 102 grams (1 eq) propylene carbonate was added over a half hour period. The temperature was increased to 60°C and held for one and one half hours, when the amine number was 116 (theory 116.2). The product had a 25°C viscosity of 52,000 mPa·s.

Example 2

The above procedure was repeated except that 116 grams (2 eq.) hexanediamine (HDA) was used. The amine number was 149 (theory 143.6). The product had a 25°C viscosity of 850 mPa·s.

Examples 3 and 4

Coatings were prepared at 100% solids by blending with Desmodur N-3300. (Desmodur N-3300 is a commercially available Bayer Polymers LLC trimer based on hexane diisocyanate having an NCO content of about 22%, a viscosity at 25°C of about 2500 mPa·s, and an NCO equivalent weight of about 193.) Resins were mixed with N-3300 at an NCO/(OH-NH) = 1.05. Materials were double stirred to insure proper

mixing. The materials and amounts used were as indicated in the following table.

	PACM-based hydroxy aspartate	PACM/DEM diaspartate*
Example	3	4
Aspartate form	242 g (1.0 eq)	----
Example 1		
Comparison aspart.	---	277 g (1.00 eq)
Desmodur N-3300	205 g (1.05 eq)	205 g (1.05 eq)
Work life	4-5 min.	15-20 min.
Hard-dry times	6+ hours	0.5 hours
Hardness, Shore D	52	82

* the comparison aspartate was the reaction product of one mole of PACM and two moles of diethyl maleate.

Work life end point was measured as the point the material had cured enough to lift cup easily with stir. Dry times were conducted in the constant temperature-humidity room using a six hour meter for hard dry. Hardness was done after one day cure using a Shore D probe.

Example 5

A round bottom flask was fitted with stirrer, heating mantle, nitrogen inlet, thermocouple and addition funnel. 58 grams (1.00 eq) Dytek A was

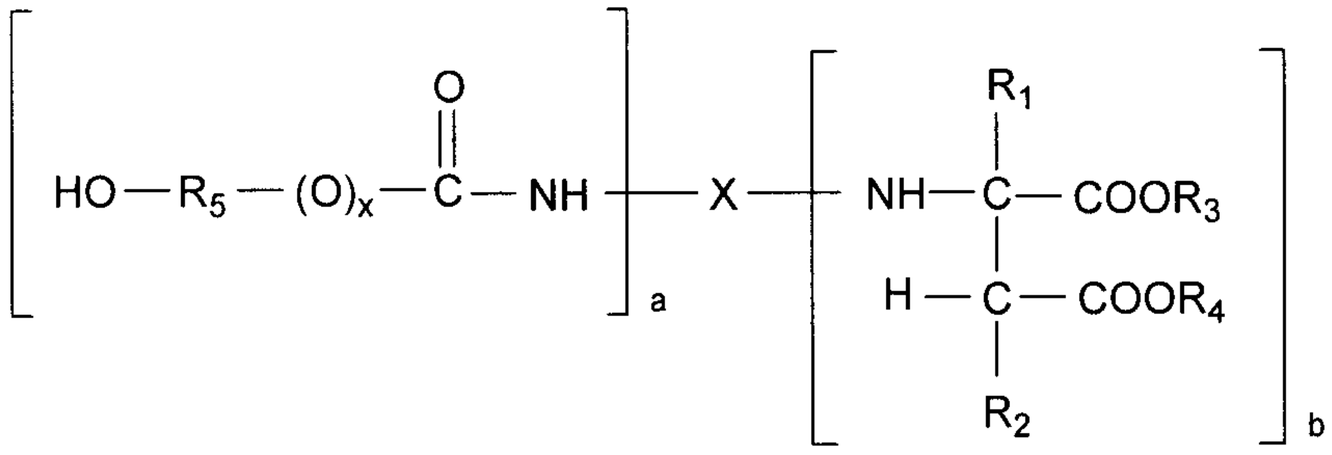
added to the flask at room temperature. 86.0 grams (0.5 eq) diethyl maleate was added all at once. The temperature of the flask rose to 35°C. The reaction was heated to 60°C and held for five and one half hours at which time the unsaturation number was 0.35 mg maleic acid per g resin indicating 99% reaction. 57.2 grams (0.5 eq) ε-caprolactone was added all at once and heated at 60°C for five days. The final unsaturation number was 0 indicating 100% reaction. The amine number was 143 (theory 139). the product had a 25°C viscosity of 300 mPa·s.

Example 6

A round bottom flask was fitted with stirrer, heating mantle, nitrogen inlet, thermocouple and addition funnel. 57.2 grams (0.5 eq) ε-caprolactone was added to the flask at room temperature. 58 grams (1.00 eq) Dytek A was added all at once. The reaction was heated to 60°C for six hours at which time the amine number was 256 mg KOH per g resin (theory 253). 86.0 grams (0.5 eq) diethyl maleate was added all at once and heated at 60°C for six and one half hours at which time the unsaturation number was 1.12 mg maleic acid per g resin indicating 96% reaction. The next day the unsaturation number was 0.58 indicating 98% reaction. The amine number was 143 (theory 139) and the product had a 25°C viscosity of 1820 mPa·s.

CLAIMS:

1. An aspartate of the formula:



where

X represents an m-valent organic residue obtained by removing the primary amino group or groups from a polyamine which has (cyclo)aliphatically bound amino groups and a number average molecular weight of 60 to 6000, and which may contain further functional groups that either are reactive with isocyanate groups or are inert to isocyanate groups at temperatures of up to 100°C,

R_1 and R_2 may be identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less,

R_3 and R_4 may be identical or different and represent organic groups which are inert towards isocyanate groups at a temperature of 100°C or less,

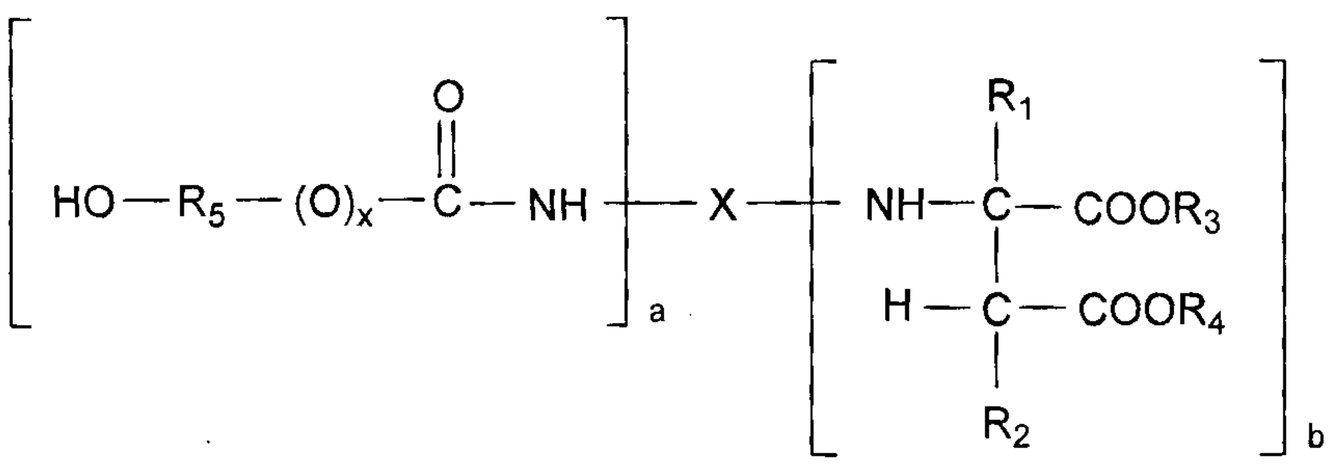
R_5 represents a member selected from the group consisting of C_2H_4, C_3H_6 and C_5H_{10},

a and b represent integers of from 1 to 5, provided that the sum of a and b is from 2 to 6,

x is 1 when R_5 represents C_2H_4 or C_3H_6 and represents 0 when R_5 represents C_5H_{10} and

m is 2-6.

2. A process for preparing an aspartate of the formula:



where

X represents an m-valent organic residue obtained by removing the primary amino group or groups from a polyamine which has (cyclo)aliphatically bound amino groups and a number average molecular weight of 60 to 6000, and which may contain further functional groups that either are reactive with isocyanate groups or are inert to isocyanate groups at temperatures of up to 100°C,

R_1 and R_2 may be identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less,

R_3 and R_4 may be identical or different and represent organic groups which are inert towards isocyanate groups at a temperature of 100°C or less,

R_5 represents a member selected from the group consisting of C_2H_4, C_3H_6 and C_5H_{10},

a and b represent integers of from 1 to 5, provided that the sum of a and b is from 2 to 6 and

x is 1 when R_5 represents C_2H_4 or C_3H_6 and represents 0 when R_5 represents C_5H_{10} comprising

A) reacting at a temperature of 0 to 100°C, in solution or in the absence of a solvent and at an equivalent ratio of primary amino groups in component a) to C=C double bonds in component b) of from about 1.1:1 to about 3.0:1

a) polyamines corresponding to formula (II)

$$X[-NH_2]_m \qquad (II)$$

with

b) compounds corresponding to formula (III)

$$R_3OOC\text{-}C(R_1)=C(R_2)\text{-}COOR_4 \qquad (III)$$

wherein

X, R_1, R_2, R_3 and R_4 are as defined above and

m represents an integer of from 2 to 6, and

B) reacting the resultant product with a compound selected from the group consisting of ethylene carbonate, propylene carbonate and ε-caprolactone.

3. A two-component coating composition which comprises, as binder,

a) a polyisocyanate component and

b) an isocyanate-reactive component containing

b1) the aspartate of Claim 1,

b2) optionally other isocyanate-reactive compounds,

wherein the equivalent ratio of isocyanate groups to isocyanate-reactive groups is from about 0.8:1 to about 2.0:1.

4. A prepolymer containing urea, urethane, allophanate and/or biuret structures comprising the reaction product of a polyisocyanate with the aspartate of Claim 1.