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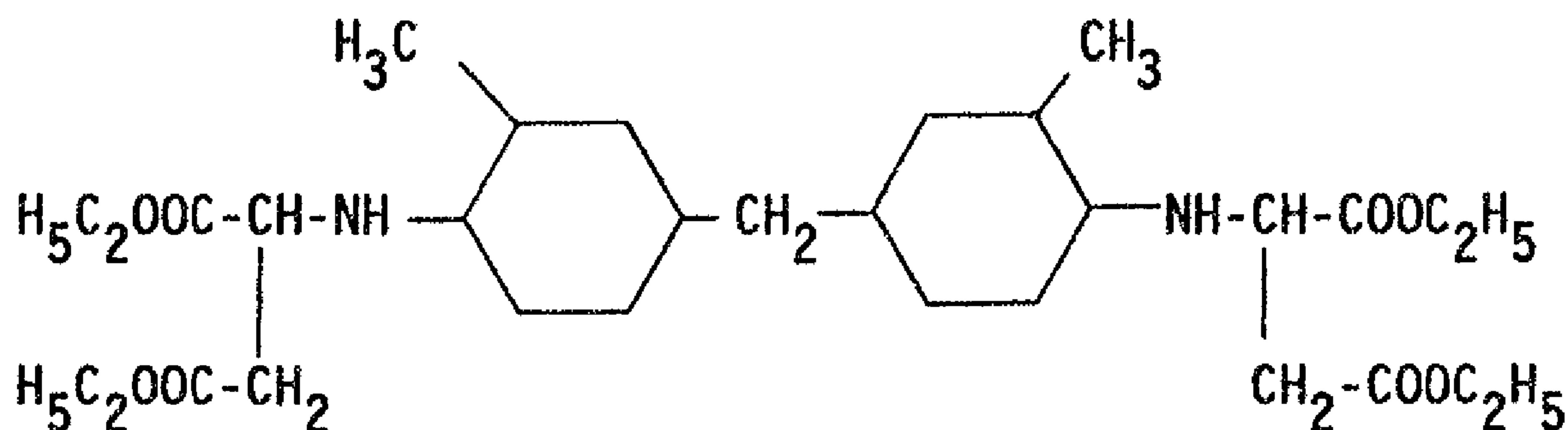
(72) Inventeurs/Inventors:
ZWIENER, CHRISTIAN, DE;
SONNTAG, MICHAEL, DE;
PEDAIN, JOSEF, DE;
SCHONFELDER, MANFRED, DE

(73) Propriétaire/Owner:
BAYER AKTIENGESELLSCHAFT, DE

(74) Agent: OGILVY RENAULT

(54) Titre : COMPOSITIONS DE REVETEMENT A DEUX CONSTITUANTS POUR VERNIS-LAQUES SERVANT A LA REPARATION DE VEHICULES AUTOMOBILES

(54) Title: TWO-COMPONENT COATING COMPOSITIONS FOR MOTOR VEHICLE REPAIR LACQUERS



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(57) Abrégé/Abstract:

The present invention relates to an improved process for repairing a motor vehicle by applying a coating composition wherein improvement is the use of a binder containing a) a polyisocyanate component and b) a mixture of organic compounds having isocyanate-reactive groups containing b1) a secondary diamine corresponding to formula I (see formula I) and b2) a polyhydroxyl component containing (i) a polyhydroxypolyacrylate or (ii) a mixture of such polyhydroxypolyacrylate with up to 95% by weight, based on the weight of (ii), of a polyester polyol, wherein components b1) and b2) are present in a weight ratio of 0.7:1 to 20:1 and components a) and b) are present in an amount which corresponds to an equivalent ratio of isocyanate groups of component a) to isocyanate-reactive groups of component b) of 0.8:1 to 1.5:1.



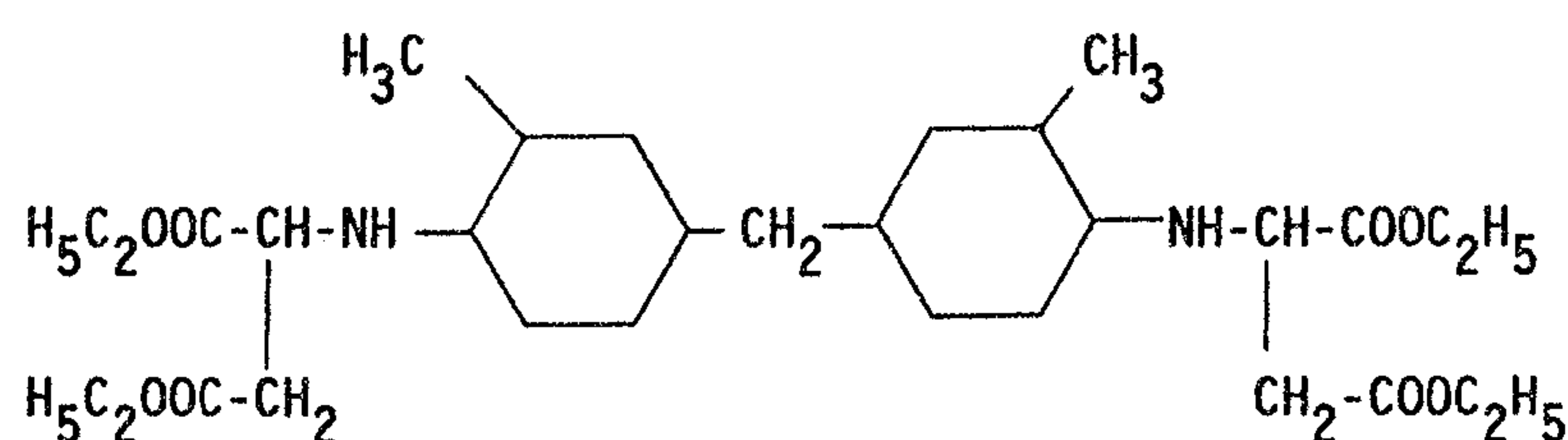
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TWO-COMPONENT COATING COMPOSITIONS
FOR MOTOR VEHICLE REPAIR LACQUERS

ABSTRACT OF THE DISCLOSURE

The present invention relates to an improved process for repairing a motor vehicle by applying a coating composition wherein improvement is the use of a binder containing

- a) a polyisocyanate component and
- b) a mixture of organic compounds having isocyanate-reactive groups containing
- b1) a secondary diamine corresponding to formula I



(I)

and

- b2) a polyhydroxyl component containing (i) a polyhydroxypolyacrylate or (ii) a mixture of such polyhydroxypolyacrylate with up to 95% by weight, based on the weight of (ii), of a polyester polyol,
- wherein components b1) and b2) are present in a weight ratio of 0.7:1 to 20:1 and components a) and b) are present in an amount which corresponds to an equivalent ratio of isocyanate groups of component a) to isocyanate-reactive groups of component b) of 0.8:1 to 1.5:1.

Mo3614
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TWO-COMPONENT COATING COMPOSITIONS
FOR MOTOR VEHICLE REPAIR LACQUERS

BACKGROUND OF THE PRESENT INVENTION

Field of the Invention

5 The present invention relates to the use of certain
two-component compositions containing a) a polyisocyanate
component and b) a component containing a mixture of organic
compounds having isocyanate-reactive groups as binder in motor
vehicle repair lacquers, in particular in top coat lacquers for
10 the repair of motor vehicles.

Description of the Prior Art

 Two-component coating compositions containing, as
binder, a polyisocyanate component in combination with an
isocyanate-reactive component, in particular a polyhydroxyl
15 component, are known. They are suitable for the production of
high quality coatings which may be adjusted to be hard,
elastic, abrasion resistant, solvent resistant and above all
resistant to weathering.

 Due to the relatively slow reaction between
20 isocyanate groups and hydroxyl groups at room temperature, the
binders for these coatings require very long drying times which
render their application uneconomical. Although curing can be
substantially increased by raising the temperature, this is
possible only to a limited extent when the coatings are applied
25 to plastics parts. Accordingly, these lacquer systems cannot
be used for repair coatings, e.g., on motor vehicles which are
already assembled.

 The systems of polyisocyanates and ketimines or
oxazolidines described in DE-OS 3,308,418 or DE-PS 2,018,233
30 harden within a relatively short time at room temperature but
these systems have several disadvantages. For example, the
isocyanate/water reaction competes with the hydrolysis of the
ketimines or oxazolidines so that, among other things, blisters
may sometimes form during the drying process. Further, the

-2-

systems decompose and release aldehydes or ketones and may therefore give rise to unpleasant odors and blisters if the coatings are relatively thick.

5 "Curable compositions" which harden at low temperatures and are suitable in particular for motor vehicle repair coatings are described in EPA-0,361,048. These compositions, however, have the disadvantages mentioned above because they also release decomposition products. In addition, they contain solvents in "the usual quantities" and, therefore, cannot be regarded as low solvent compositions.

10 In order to be able to apply two-component reactive systems by means of conventional spray guns, which are state of the art for motor vehicle repair coatings, these systems must have a certain processing time. This time is defined as the time available from the mixing of the two components until the outflow viscosity doubles.

15 It is an object of the present invention to provide a two-component coating composition for motor vehicle repair lacquer which could be applied using conventional application techniques for two-component polyurethane lacquers and would also have an outflow viscosity according to DIN 53 211 of 17 sec. at a solids content of 45 to 65 % by weight, i.e. if thinned to reach a viscosity of 17 sec. the solids content is found to be from 45 to 65 % by weight, a processing time (defined as the time from mixing of the components to doubling of the outflow time) of at least one hour, and which could be hardened at temperatures of at most 60°C after application to the substrate.

25 This object may be achieved with the binder compositions according to the present invention described below.

SUMMARY OF THE INVENTION

The present invention relates to an improved process for repairing a motor vehicle by applying a coating composition wherein improvement is the use of a binder containing

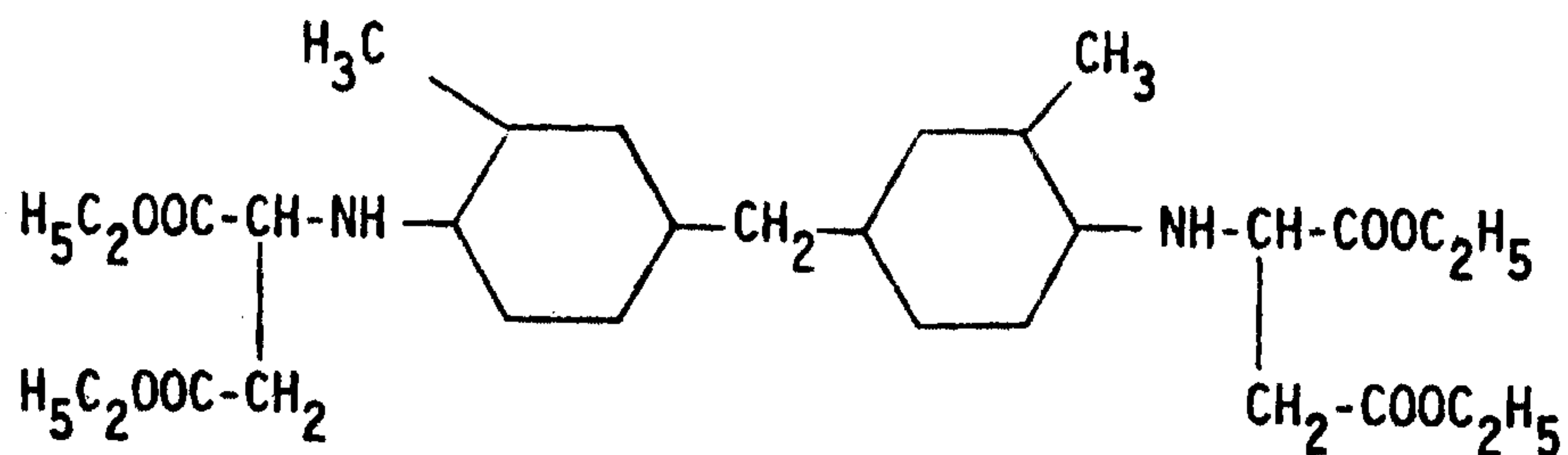
a) a polyisocyanate component and

-3-

b) a mixture of organic compounds having isocyanate-reactive groups containing

b1) a secondary diamine corresponding to formula I

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(I)

and

b2) a polyhydroxyl component containing (i) a polyhydroxypolyacrylate or (ii) a mixture of such polyhydroxypolyacrylate with up to 95% by

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weight, based on the weight of (ii), of a polyester polyol,

wherein components b1) and b2) are present in a weight ratio of 0.7:1 to 20:1 and components a) and b) are present in an amount which corresponds to an equivalent ratio of isocyanate groups of component a) to isocyanate-reactive groups of component b) of 0.8:1 to 1.5:1.

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DETAILED DESCRIPTION OF THE INVENTION

Although EP Patent Application 0 403 921 (published December 27, 1990) describes two-component binder compositions substantially corresponding to the binder compositions to be used according to the invention, apart from other two-component binder compositions, it does not teach or suggest that binder compositions of the present invention would be suitable as binders for two-component motor vehicle repair coatings.

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Suitable polyisocyanates for use in polyisocyanate component a) include any polyisocyanates known from polyurethane chemistry.

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Examples of suitable polyisocyanates include low molecular weight polyisocyanates having a molecular weight 166 to 300 such as hexamethylene diisocyanate, 2,2,4- and/or 2,4,4-trimethyl-1,6-hexamethylene diisocyanate,

Mo3614

-4-

dodecamethylene diisocyanate, 1,4-diisocyanato-cyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane (IPDI), 2,4'- and/or 4,4'-diisocyanatodicyclohexylmethane, 2,4'- and/or 4,4'-diisocyanatodiphenylmethane and mixtures of these isomers with their higher homologues which may be obtained in known manner by the phosgenation of aniline/formaldehyde condensates, 2,4-and/or 2,6-diisocyanatotoluene and mixtures of these compounds.

It is preferred, however, to use derivatives of these monomeric polyisocyanates. These derivatives include polyisocyanates containing biuret groups such as those described in US-PS 3,124,605, US-PS 3,201,372 and DE-OS 1,101,394; polyisocyanates containing isocyanurate groups such as those described in US-PS 3,001,973, DE-PS 1,022,789, 1,222,067 and 1,027,394, and DE-OS 1,929,034 and 2,004,048; polyisocyanates containing urethane groups such as those described in DE-OS 953,012, BE-PS 752,261 and US-PS 3,394,164 and 3,644,457; polyisocyanates containing carbodiimide groups such as those described in DE-PS 1,092,007, US-PS 3,152,162 and DE-OS 2,504,400, 2,537,685 and 2,552,350; and polyisocyanates containing allophanate groups such as those described in GB-PS 994,890, BE-PS 761,626 and NL-OS 7,102,524.

Particularly preferred modified polyisocyanates include N,N',N''-tris-(6-isocyanatohexyl)-biuret and mixtures thereof with higher homologues, and N,N',N''-tris-(6-isocyanatohexyl)isocyanurate and mixtures thereof with its higher homologues having more than one isocyanurate ring.

Component b1) is an ester group-containing diamine corresponding to formula I and is prepared in known manner by the reaction of 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane with maleic or fumaric acid diethylester.

The preparation of the "polyaspartic acid derivative" b1) from the aforesaid starting materials may be carried out, for example, at a temperature of 0 to 100°C, using the components in such proportions that at least one double bond,

Mo3614

preferably an olefinic double bond, is available for each primary amino group.

The reaction may be carried out solvent-free or in the presence of suitable solvents such as methanol, ethanol, propanol, dioxane or mixtures of such solvents.

Component b1) is used in the binder compositions according to the invention as a mixture with a polyhydroxyl component b2). This polyhydroxyl component b2) may contain either (i) known polyhydroxyl polyacrylates or (ii) mixtures of such polyhydroxy polyacrylates with known polyester polyols in an amount of up to 95% by weight, preferably up to 60% by weight, based on the weight of the mixture (ii).

The polyhydroxy polyacrylates (i) are hydroxyl group-containing copolymers of olefinically unsaturated compounds having a molecular weight (M_n , as determined by vapor pressure or membrane osmometry) of 800 to 50,000, preferably 1000 to 20,000 and more preferably 5000 to 10,000, and a hydroxyl group content of 0.1 to 12% by weight, preferably 1 to 10% by weight and more preferably 2 to 6% by weight. These compounds are copolymers of olefinic monomers containing hydroxyl groups with olefinic monomers free from hydroxyl groups. Examples of suitable monomers include vinyl and vinylidene monomers such as styrene, α -methyl styrene, o- and p-chlorostyrene, o-, m- and p-methylstyrene, p-tert.-butylstyrene, acrylic acid, (meth)acrylonitrile, acrylic and methacrylic acid esters having 1 to 8 carbon atoms (such as ethyl acrylate, methyl acrylate, n- or isopropyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, iso-octyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and iso-octylmethacrylate; diesters of fumaric acid, itaconic acid or maleic acid having 4 to 8 carbon atoms in the alcohol component, (meth)acrylic acid amide, vinyl esters of alkane monocarboxylic acids having 2 to 5 carbon atoms (such as vinyl acetate or vinyl propionate) and hydroxyalkyl esters of acrylic acid or methacrylic acid having

2 to 4 carbon atoms in the hydroxyalkyl residue (such as 2-hydroxyethyl-, 2-hydroxypropyl-, 4-hydroxybutyl-, trimethylolpropane mono- or pentaerythritol monoacrylate or methacrylate). Mixtures of these monomers may also be used for the preparation of the hydroxy-functional polyacrylates.

The polyester polyols, which are optionally used in admixture with polyhydroxy polyacrylates, are known from polyurethane chemistry and have a hydroxyl group content of 0.2 to 17% by weight, preferably 0.5 to 10% by weight, and may be obtained in known manner from the reaction of polybasic carboxylic acids and/or intramolecular anhydrides of polybasic carboxylic acids, optionally together with subequivalent quantities of monobasic carboxylic acids, with an excess of organic polyhydroxyl compounds, optionally together with subequivalent quantities of monohydric alcohols.

Examples of acid or acid anhydrides which are suitable for the preparation of the polyester polyols include include adipic acid, sebacic acid, phthalic acid, isophthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, maleic acid, the anhydrides of these acids and mixtures of these acids or acid anhydrides. The acid component may also contain small quantities of monobasic acids such as 2-ethylhexanoic acid.

Examples of alcohols which are suitable for the preparation of the polyester polyols include organic polyhydroxyl compounds having a molecular weight of 62 to 200, such as ethylene glycol, propylene glycol, 1,4-dihydroxybutane, 1,6-dihydroxyhexane, glycerol, trimethylolpropane and mixtures of these polyhydric alcohols. The polyol component may also contain subequivalent quantities of monohydric alcohols such as n-hexanol.

The mixtures (ii) may be obtained by mixing the individual components together, i.e., by mixing the polyhydroxy polyacrylates with the polyester polyols. Such mixtures (ii) also include mixtures obtained by preparing the polyhydroxy polyacrylates by copolymerizing the monomers exemplified above

in the polyester polyols as reaction medium. The mixtures thus obtained are present partly as graft copolymers in which the polyester polyols form the graft base.

5 In the binders used according to the invention, the ratios of components a), b1) and b2) are calculated to provide an equivalent ratio of isocyanate groups to isocyanate-reactive groups of 0.8:1 to 20:1, preferably 0.8:1 to 2:1 and more preferably 0.8:1 to 1.5:1.

10 The weight ratio of reactive components b1) and b2), based on the solids content, is 0.7:1 to 20:1, preferably 1.5:1 to 5.5:1 and more preferably 2.3:1 to 4:1.

15 The binder compositions are prepared by mixing the individual components; however, a mixture may first be prepared of reactive components b1) and b2). The binder compositions as well as the fully formulated coating compositions are generally prepared in the presence of the solvents conventionally used in coating technology, but it is an advantage of the present invention that the quantity of solvents required is substantially lower than that required for the two-component
20 polyurethane lacquers known in the art for obtaining the same processing viscosity.

Examples of suitable solvents include xylene, butyl acetate, methyl isobutyl ketone, methoxypropyl acetate, N-methylpyrrolidone, Solvesso* solvent, petroleum hydrocarbons, chlorobenzene and mixtures of these solvents.
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The weight ratio of the total quantity of binder components a), b1) and b2) to solvent is generally 45:55 to 100:0, preferably 55:45 to 65:35.

30 The coating compositions containing the binder compositions to be used according to the invention may also contain other conventional auxiliary agents and additives used in coating technology such as pigments, fillers, levelling agents, catalysts, anti-settling agents and the like.

35 The coating compositions may be applied to their substrates by known methods such as brush coating, immersion,

*trade-mark

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flooding or application with rollers or coating knives, but preferably by spraying. The coating compositions containing the binder compositions to be used according to the invention are excellent motor vehicle repair coating compositions and may be used both for the formation of interlayers or for the formation of pigmented or unpigmented topcoat lacquers.

The lacquers are generally cured at a temperature of -20 to 60°C, preferably -10 to 40°C.

All the percentages given in the following examples are percentages by weight unless otherwise indicated.

EXAMPLES

The starting materials described below are used in the examples:

Polyisocyanate component a1)

A commercial lacquer polyisocyanate obtained by the trimerization of hexamethylene diisocyanate (90% solution in butyl acetate/solvent naphtha 100 (1:1), isocyanate content of the solution: 19.4%).

Diamine component b1)

476 g of 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane (Laromin* C 260 available from BASF) were introduced into a reaction vessel together with 129 g of butyl acetate under a nitrogen atmosphere at 60°C. 688 g of diethyl maleate were added dropwise over a period of 8 hours. The mixture was then stirred for about 16 hours at 60°C under a nitrogen atmosphere and a clear, almost colorless product having a viscosity of about 100 mPa.s (23°C) and an equivalent weight of about 328 g was obtained.

Polyol component b2)

Polyol I

A 60% solution of a copolymer which has a molecular weight (M_n) of 6,500 in xylene and a hydroxyl group content of the solution of 1.6% and which was prepared from

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-9-

45.90% styrene,
29.48% butyl acrylate,
1.91% methyl methacrylate,
18.79% hydroxypropyl methacrylate,
5 0.63% acrylic acid and
3.29% t-butylperoxide.

Polyol II

10 A 65% solution in butyl acetate/xylene (ratio by weight 3:1) having a hydroxyl group content of 2.8% of a mixture of 40 parts by weight of a polyester polyol prepared from

38.84% trimethylolpropane,
28.35% phthalic acid anhydride,
9.87% adipic acid,
15 21.07% 2-ethylhexanoic acid and
1.87% maleic acid anhydride,

and 60 parts by weight of a copolymer having a molecular weight (M_n) of 3,700 and prepared from

39.63% styrene,
20 23.57% butyl acrylate,
31.42% hydroxyethyl methacrylate,
0.94% acrylic acid and
4.44% t-butyl peroctoate.

Polyol III

25 A 50% solution in butyl acetate/xylene (ratio by weight 1:1) of a copolymer which has a molecular weight (M_n) of 9000 and a hydroxyl group content of the solution of 1.0% and which was obtained from

68.02% methyl methacrylate,
30 13.81% 2-ethyl hexyl acrylate,
15.77% hydroxyethyl methacrylate,
0.99% acrylic acid
1.41% t-butyl peroxide.

Example 1

78 g of diamine b1) and 50 g of polyol I were made up into a clear lacquer with polyisocyanate a) at an equivalent ratio of NCO:(NH + OH) of 1:1 and adjusted to a solids content of 53% with methoxypropyl acetate/butyl acetate/xylene 1:1:1.

Example 2 (Comparison example to Example 1)

168 g of polyol I were made up into a clear lacquer with polyisocyanate a) at an equivalent ratio of NCO:OH of 1:1 and adjusted to a solids content of 42% with methoxypropyl acetate/butyl acetate/xylene 1:1:1.

Example 3

78 g of diamine b1) and 46 g of polyol II were made up into a clear lacquer with polyisocyanate a) at an equivalent ratio of NCO:(NH + OH) of 1:1 and adjusted to a solids content of 59% with methoxypropyl acetate/butyl acetate/xylene 1:1:1.

Example 4 (Comparison Example to Example 3)

154 g of polyol II were made up into a clear lacquer with polyisocyanate a) at an equivalent ratio of NCO:OH of 1:1 and the clear lacquer was adjusted to a solids content of 43% with methoxypropyl acetate/butyl acetate/xylene 1:1:1.

Example 5

78 g of the diamine b1) and 60 g of polyol III were made up into a clear lacquer with polyisocyanate a) at an equivalent ratio of NCO:(NH + OH) of 1:1 and adjusted to a solids content of 57% with methoxypropyl acetate/butyl acetate/xylene 1:1:1.

Example 6 (Comparison example to Example 5)

200 g of polyol III were made up into a clear lacquer with polyisocyanate a) at an equivalent ratio of NCO:OH of 1:1 and adjusted to a solids content of 33% with methoxypropyl acetate/butyl acetate/xylene 1:1:1.

The clear lacquers of Examples 1 to 6 were used to coat both steel plates which had been coated with a base lacquer and glass plates. The base lacquer was a solvent-containing composition containing a mixture of

Mo3614

-11-

cellulose acetobutyrate and a high molecular weight polyacrylate. The base lacquer was applied to the steel plates by spraying in amount sufficient to provide a dry layer thickness of about 15 μm .

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Further details are shown in the following Table.

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6
Solids content (%)	53	42	59	43	57	33
Outflow time						
DIN 53 211 (sec)	15	16	16	16	16	16
Processing time ¹⁾ (h)	4.5	>6	1.5	5	3.5	>6
Sand drying						
DIN 53 150 (h)	3.5	0.75	2.5	1.5	1.5	0.5
Touch dry						
DIN 53 150 (h)	6	>8	4.5	5.5	5.5	2.5
Pendulum hardness DIN 53 157						
Clear lacquer on base lacquer ²⁾						
After 1 d RT (sec)	120	48	70	74	115	50
After 2 d RT (sec)	143	90	76	80	120	70
After 5 d RT (sec)	158	125	90	105	130	85
Clear lacquer on glass plate ²⁾						
After 1 d RT (sec)	134	45	116	112	137	80
After 2 d RT (sec)	168	98	125	140	160	105
After 5 d RT (sec)	186	164	132	158	180	144
Resistance to premium grade gasoline						
5' after 1 d RT	2	5	0	0	1	0
5' after 2 d RT	2	5	0	0	1	0
5' after 5 d RT	0	1	0	0	0	0
Erichsen cupping						
DIN 53 156 (mm)	10.5	10.5	10.0	10.0	10.0	10.0

1) Defined as the time from mixing to doubling of the outflow time

2) Layer thickness about 50 μm

3) Assessment 0 - 5, 0 = best value
5 = poorest value

-13-

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

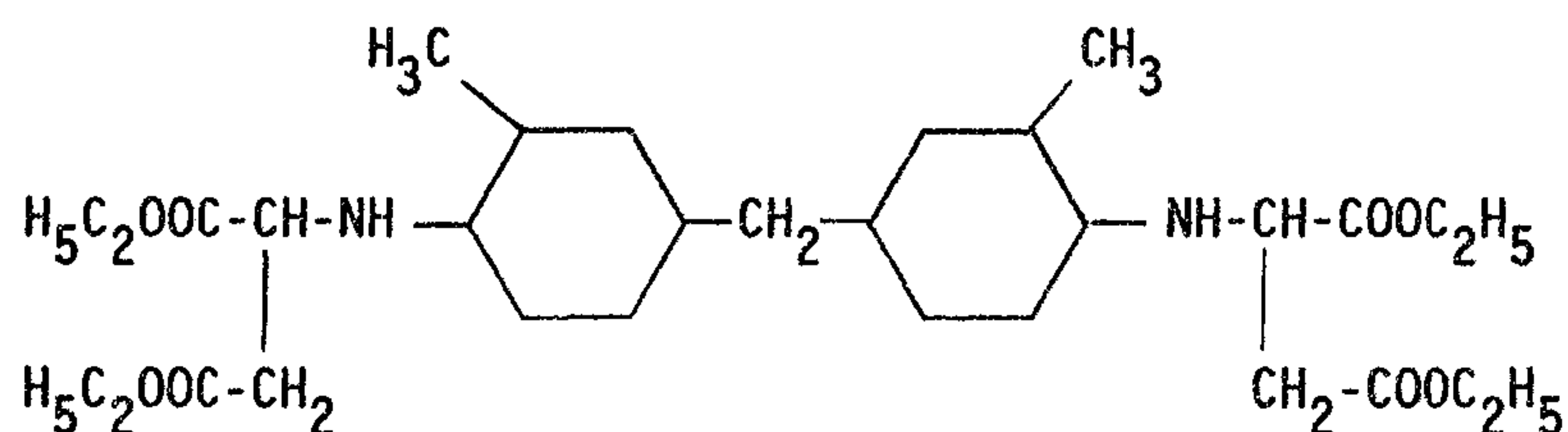
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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. In a process for repairing a motor vehicle by applying a coating composition having a binder, the improvement wherein the binder comprises

- 5 a) a polyisocyanate component and
- b) a mixture of organic compounds having isocyanate-reactive groups comprising
- b1) a secondary diamine corresponding to formula I

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(I)

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and

b2) a polyhydroxyl component comprising (i) a polyhydroxy-polyacrylate or (ii) a mixture of said polyhydroxypoly-acrylate with up to 95% by weight, based on the weight of (ii), of a polyester polyol,

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wherein components b1) and b2) are present in a weight ratio of 0.7:1 to 20:1 and components a) and b) are present in an amount which corresponds to an equivalent ratio of isocyanate groups of component a) to isocyanate-reactive groups of component b) of 0.8:1 to 20:1.

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2. The process of Claim 1 wherein component b2) comprises a copolymer which has a molecular weight (M_n) of 800 to 50,000 and a hydroxyl group content of 0.1 to 12% by weight and which is prepared from olefinically unsaturated monomers.

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3. The process of Claim 1 wherein polyisocyanate component a) comprises a member selected from the group consisting of N,N',N''-tris(6-isocyanatohexyl) -biuret, mixtures thereof with its higher homologs, N,N',N''-tris-(6-isocyanato-

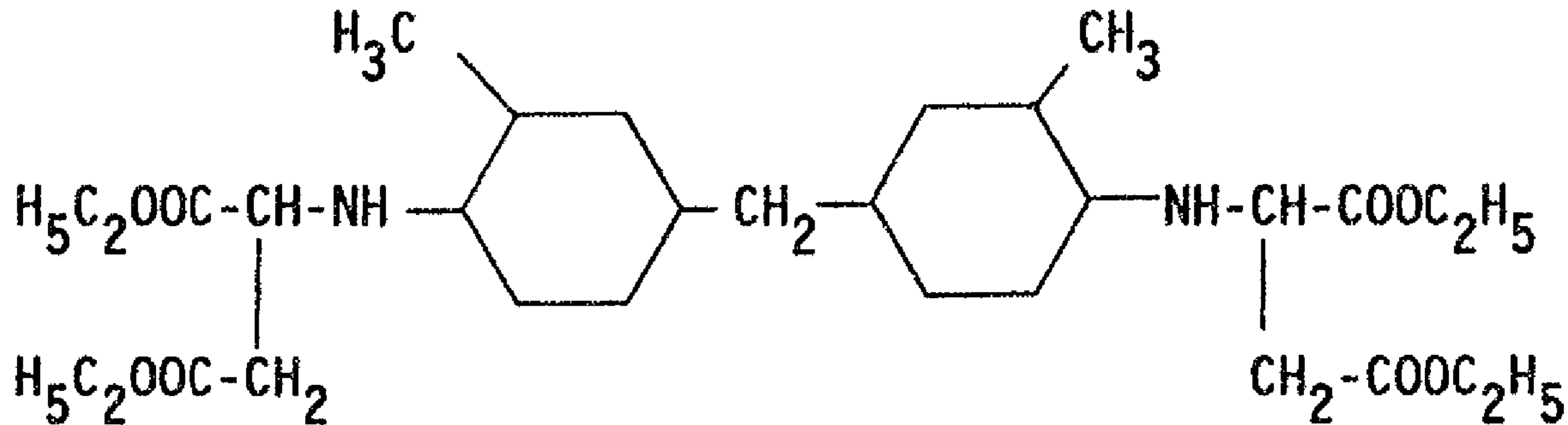
-15-

hexyl)-isocyanurate or mixtures thereof with its higher homologs having more than one isocyanurate ring.

5 4. The process of Claim 2 wherein polyisocyanate component a) comprises a member selected from the group consisting of N,N',N''-tris(6-isocyanatohexyl)-biuret, mixtures thereof with its higher homologs, N,N',N''-tris-(6-isocyanato-
hexyl)-isocyanurate and mixtures thereof with its higher homologs having more than one isocyanurate ring.

10 5. The process of Claim 1 wherein said coating composition is applied as a top coat.

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