



(51) International Patent Classification:

C07F 7/02 (2006.01) C08L 75/02 (2006.01)  
C08G 18/79 (2006.01) C07C 251/08 (2006.01)  
C08G 18/10 (2006.01) C09D 179/00 (2006.01)  
C09D 175/02 (2006.01) C08G 73/00 (2006.01)  
C08G 18/38 (2006.01)

(21) International Application Number:

PCT/US2017/049110

(22) International Filing Date:

29 August 2017 (29.08.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/380,816 29 August 2016 (29.08.2016) US

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(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM,  
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,  
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,  
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,  
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,  
KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,  
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,  
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,  
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,  
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,  
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,  
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,  
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,  
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: MULTIFUNCTIONAL POLYAMINE-BASED COMPOUNDS

(57) Abstract: Disclosed are silane-functionalized amines useful as curing agents. Examples include the reaction product of: a) aspartate modified polyamine having at least two aspartate amine groups and at least one secondary non-aspartate amino group; and b) an epoxy-functional trimethoxysilane.



WO 2018/044883 A1

## MULTIFUNCTIONAL POLYAMINE-BASED COMPOUNDS

### Background

**[0001]** Polyamines are molecules with more than one amine group. They are useful as curatives or chain extenders, in particular for epoxy or isocyanate-containing materials. For example, a polyamine may be combined with a polyisocyanate to form a polyurea. Polyureas have diverse applications in coatings, adhesives, sealants, and elastomers (commonly referred to as CASE applications). Depending on the formulation, polyureas may be designed to have a wide range of performance in terms of physical properties such as but not limited to hardness, tensile strength, elasticity or elongation, modulus, glass transition temperature, and adhesion.

**[0002]** Polyamines may also be combined with epoxy resins to form a cured epoxy polymer, also useful in CASE applications. An excess of primary polyamine may be combined with a deficiency of epoxy compound to form an adduct, which may in turn be used as an epoxy curing agent.

**[0003]** Hybrid systems comprising epoxy groups along with urethane or urea groups are also known. Although this application focuses mainly on polyurea systems, it should be appreciated that the amines disclosed herein are also useful in epoxy or hybrid systems.

**[0004]** In selecting amines for a polyurea formulation, formulators must consider and optimize multiple parameters. Among the most important are cost, physical properties and end-use performance of the finished polymer, reactivity, and safety (toxicity, flammability, etc).

**[0005]** Reactivity is one of the most critical characteristics of amine curatives and can be considered in terms of (1) pot life and (2) final cure time. Pot life relates to the length of time a user has after all ingredients are combined during which the mixture can be handled and used before it becomes too viscous or solid to handle. Pot life requirements may vary over an extremely wide range. Polyurea spray coatings or elastomers are among the fastest-growing isocyanate-based applications; a coating applied by multi-component spray systems must gel in seconds so that it doesn't run or sag when applied to non-horizontal surfaces. At the same time it must not cure too fast or the applied coating will have poor surface appearance and poor adhesion to the substrate. A different coating, applied by roller or brush, may require a much longer pot life, potentially hours. Final cure relates to the time required for the polymer to cure enough so that it can be handled or placed in service. This is particularly critical in public areas

or structures like bridges where lengthy time out of service creates significant inconvenience and expense.

[0006] As a consequence of the above, reactivity must be carefully optimized for each application. This optimization is done by careful selection of the curatives and crosslinkers used in each system. At the same time, properties and cost must be considered. New, low cost curatives and crosslinkers are always desirable to help achieve this difficult optimization.

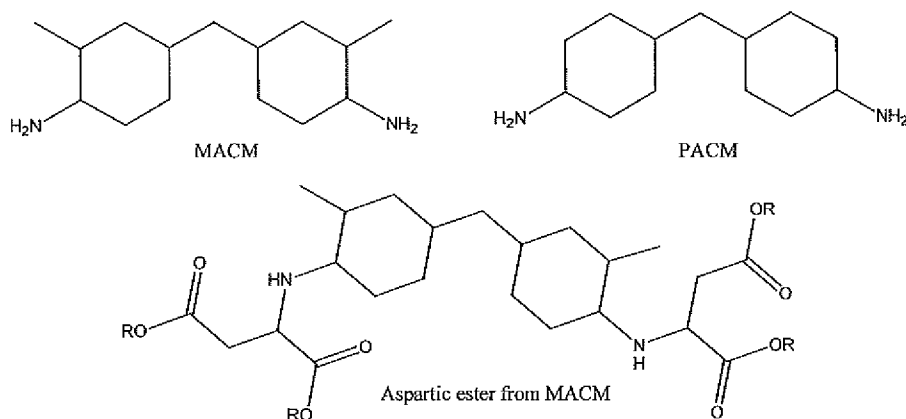
[0007] Often, the ideal reactivity profile is a “hockey stick” profile with long enough pot life for handling and yet very rapid final cure. Such a profile is very difficult to achieve. Multifunctional curatives offer one approach. For example, ketimines or aldimines have been employed as blocked amines that are unreactive toward isocyanates until exposed to water. In a coating, such blocked amines are stable and allow long pot life, but once the coating is applied the high surface area results in exposure to ambient moisture, which unblocks the amine and leads to rapid cure. As described by Hoy, Carder, and Colomb in the Journal of Paint Technology, volume 46, number 591, pages 70-81 (1974) and by Hoy and Milligan in US 3,668,183, ketimines are also useful as blocked amines to control the reaction of amines with acetoacetates to form polyenamines.

[0008] Reactivity of amines toward isocyanates can be varied over a wide range, depending on steric and electronic factors relating to the structure of the amine. For example, primary and unhindered amine groups have much higher reactivity toward isocyanate groups than secondary amine groups. Unhindered secondary amines have higher reactivity toward isocyanate groups than sterically-hindered secondary amines such as aspartic esters.

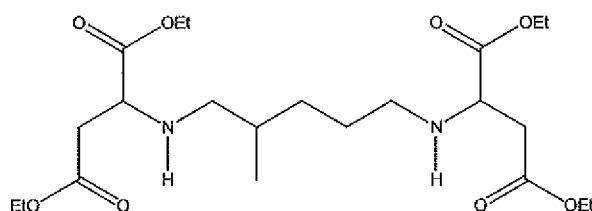
[0009] Aspartic esters and their uses in polyurea compositions are disclosed in US patent 5,126,170. They are secondary amines but have lower reactivity than simple secondary amines due to steric effects, electronic effects of the aspartic ester groups, and the possibility of intramolecular hydrogen bonding between the aspartic NH and the oxygens of the ester groups.

[0010] The most sterically hindered aspartic esters are commonly used for coatings that require long pot life such as those applied by roller and other manual techniques. Examples of more-hindered aspartic amines include aspartic esters based on PACM and MACM, illustrated below. The PACM and MACM structures have a high degree of steric hindrance due to the cyclic structure and branching on the carbon alpha to the amine group. This makes them useful

for manually-applied coatings that may be spread and applied by squeegee or roller but generally too slow for spray coatings.



[0011] Less-hindered aspartic esters such as that shown below, based on Dytek® A amine from INVISTA, are used where faster-reacting amines are desired, although still slower than typical primary or secondary aliphatic amines. They are also used in blends with slower aspartic esters or with faster aliphatic amines to fine-tune reactivity.



[0012] Spray polyurea coatings typically require faster-reacting amines to achieve the desired gel time for a spray system but reaction must be slow enough for a coating to level and adhere to the substrate. A typical spray polyurea might use a mixture of amines designed to provide appropriate reactivity; for example, a mixture of aromatic primary amines such as diethyl toluenediamine, hindered aromatic secondary amines such as 4,4'-bis(sec-butylamino) diphenylmethane, and polyether amines such as those based on propylene oxide, which have somewhat hindered primary amine groups. The mixture of amines and other curatives is typically constrained to provide the desired isocyanate index (ratio of isocyanate groups to isocyanate-reactive groups) when used in a 1:1 mix ratio with an isocyanate prepolymer so that it can be used in common spray equipment. Although these aromatic amines provide a useful reactivity profile, It may be desirable to minimize use of aromatic amines due to toxicity concerns.

**[0013]** The isocyanate side of the spray system may also be designed to adjust reactivity and properties. A wide variety of polyisocyanates are known and include: simple diisocyanates such as 1,6-hexamethylene diisocyanate (HDI) or various isomer mixtures of methylene diphenyl diisocyanate (MDI); derivatives such as HDI trimer, allophanates, or uretdiones; and an almost infinite variety of prepolymers or quasi-prepolymers. Prepolymers may be prepared from simple polyisocyanates and various polyols or polyamines. Traditional prepolymers utilize an amount of polyisocyanate sufficient to “cap” each polyol with an isocyanate, resulting in an isocyanate-terminated polyol that can be cured using various isocyanate-reactive chain extenders and curatives. Quasi-prepolymers are prepolymers containing some amount of free polyisocyanate “monomer.” Use is not restricted to any particular type of polyisocyanate. An isocyanate part and a curative part of a two-part system are often formulated to match each other so that the most common 1:1 mix ratio preferred by end users will give the desired final composition. Either or both parts may be modified to help achieve the desired mix ratio.

**[0014]** Although polyurea formulations may use raw isocyanate, it is more typical to use isocyanate-functional prepolymers as a way to adjust properties and in particular mix ratio of the isocyanate part and curative part of a two-component system. Prepolymers or quasi-prepolymers may be prepared from isocyanates in combination with polyols (urethane prepolymer) or amines (urea prepolymer).

**[0015]** Aliphatic isocyanates are known to be less reactive than aromatic isocyanates but are also much more expensive. Methylene diphenyl diisocyanate (MDI) is among the least expensive isocyanates and most widely-available isocyanates and for those reasons it is preferred for many applications where color stability on UV exposure is not critical. MDI systems with high 2,4' isomer content have been shown to have somewhat lower reactivity than systems with lower 2,4' isomer content.

**[0016]** In cases where color stability on UV exposure is critical, aliphatic isocyanates and aliphatic amines must be used. Aliphatic isocyanates react slower than aromatic systems. Primary aromatic amines such as the primary and secondary aromatic amines mentioned above may have reactivity too slow for spray systems using aliphatic isocyanates. Such aromatic amines may have reactivity lower than conventional secondary aliphatic amines by a factor of 100. In such cases, aspartic secondary amines may have useful intermediate reactivity useful alone or in blends as curatives for aliphatic isocyanates. Very hindered aspartic amines such as

those based on PACM or MACM may be too slow; in such cases less hindered aspartic amines such as those based on Dytek® A or unhindered multifunctional polyamines of the present invention may be more suitable.

**[0017]** Sealants and adhesives typically require pot life longer than spray coatings but shorter than coatings that are manually applied by brush or roller. In cases where longer pot life is desired, more hindered amines are used. Hindered multifunctional polyamines and polyimines of the present invention may be useful. It should be apparent that a wide range of reactivity and properties are needed for polyurea formulations depending on the specific application.

**[0018]** Although many different amines have been developed to provide varying properties and reactivity there is no amine that is suitable for all applications and there remains a need for alternatives that a formulator may consider to optimize reactivity, performance, and cost.

**[0019]** A wide range of epoxy resins is also known. Use is similarly not restricted to any particular type of epoxy resin.

**[0020]** Despite the wide range of isocyanate and epoxy systems available, there remains a need for new amine curatives to help formulators optimize reactivity, physical properties, cost and safety. In particular, a spray polyurea coating must be fluid enough at spray temperature to be sprayed and mixed and it must gel and cure fast enough and sufficiently so that it doesn't sag or run when applied to non-horizontal surfaces. At the same time it must remain flowable long enough to spread, form a smooth, defect-free coating, and adhere to a substrate. The cure rate must be fast but not too fast. Otherwise poor adhesion or poor surface quality or both may result. Such defects will usually result in premature coating failure.

**[0021]** Aspartic ester curatives with two aspartic secondary amines and an additional secondary amine functionality are known; see for example US 8,137,813. Such curatives are not claimed to provide enhanced adhesion and in fact use of adhesion promoters is disclosed to improve adhesion.

**[0022]** Simple aminosilanes such as 3-aminopropyl trimethoxysilane or 3-aminopropyl triethoxysilane have been disclosed as adhesion-promoting additives in polyurea systems, for example see US2006/0046068 and US 9,290,603 B2.

## Disclosure

**[0023]** The present disclosure includes the following.

Reaction product of:

- a) aspartate modified polyamine having at least two aspartate amine groups and at least one secondary non-aspartate amino group; and
- b) an epoxy-functional trimethoxysilane.

Reaction product of:

- a) aspartate modified polyamine having at least two aspartate amine groups and at least one secondary non-aspartate amino group; and
- b) 3-glycidyloxypropyl trimethoxysilane.

Reaction product of:

- a) aspartate modified triamine with a secondary non-aspartate amino group prepared from bis(hexamethylene) triamine; and
- b) 3-glycidyloxypropyl trimethoxysilane.

Reaction product of

- a) aspartate modified triamine with a secondary non-aspartate amino group prepared from diethylenetriamine and diethyl maleate; and
- b) 3-glycidyloxypropyl trimethoxysilane.

**[0024]** The disclosed reaction products are useful components of polymers including polyureas and epoxies.

**[0025]** Formulations containing the disclosed reaction products can be useful as coatings, elastomers, sealants and molded articles. For example, a molded article containing at least one of the disclosed reaction products can be useful as an automotive part. Examples of such automotive parts include window moldings, headrests, seatcovers and steering wheel covers.

**[0026]** Further disclosed are reaction products of:

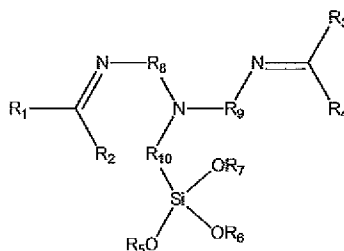
- a) ketimine or aldimine modified amine curative with at least two ketimine or aldimine groups and at least one secondary non-aspartate amino group; and
- b) 3-glycidyloxypropyl trimethoxysilane.

**[0027]** The ketimine or the aldimine can be prepared from bis(hexamethylene) triamine.

**[0028]** The bis(hexamethylene) triamine reactant can be at least 70% pure.

[0029] The above reaction products containing the ketimine or aldimine can be further reacted to produce a polyenamine.

[0030] Further disclosed is a composition having Structure A, below:



wherein R1, R2, R3, and R4 are hydrocarbyl groups that may be the same or different, where a hydrocarbyl group consists of carbon and hydrogen in linear, branched, or cyclic structure.

[0031] R1, R2, R3, and R4 of Structure A can be independently selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, t-butyl, 2-ethylhexyl and cyclohexyl. In one form of Structure A, R1 and R3 are H. Accordingly, Structure A can be an aldimine rather than a ketimine.

[0032] Both R1 and R3 of Structure A can be H and R2 and R4 can both be both tertiary hydrocarbyl groups. R2 and R4 can be t-butyl. Alternatively, R1 and R2 can link to form a cyclic structure, for example, a cyclohexyl ring.

[0033] Similarly, R3 and R4 of Structure A can link to form a cyclic structure. R8, R9, and R10 can be the same or different and can be selected from the group consisting of hydrocarbyl and ether-substituted hydrocarbyl.

R10 of Structure A can optionally contain hydroxyl functionality.

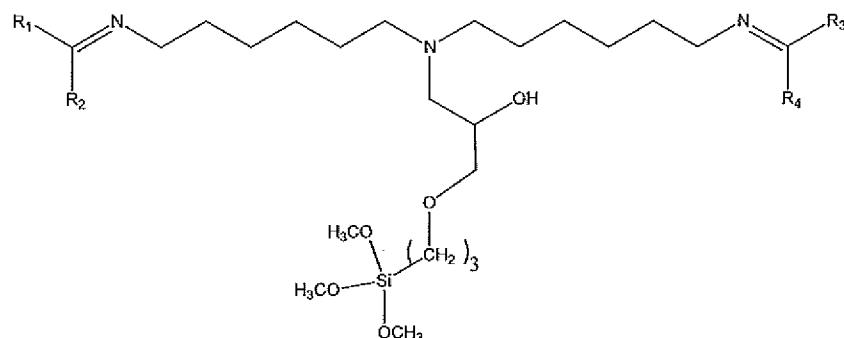
R8 and R9 can be linear aliphatic hydrocarbyl groups.

R8 and R9 can be  $-(CH_2)_n-$  groups, wherein  $n$  is  $\geq 2$  and  $\leq 20$ , for example  $\geq 4$  and  $\leq 12$ .

R8 and R9 can both be hexamethylene groups.

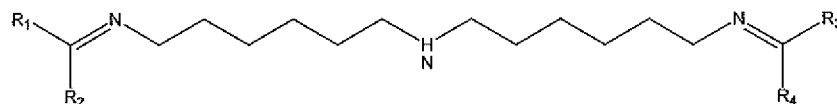
R10 can be a hydroxyl-containing ether-substituted hydrocarbyl link derived from an epoxysilane.

[0034] Further disclosed is a composition having Structure B as shown below:



[0035] Structure B can be prepared by first reaction of bis(hexamethylene)triamine with the aldehydes or ketones  $R_1C(O)R_2$  and  $R_3C(O)R_4$ , where  $R_1$  through  $R_4$  are as described above, with removal of water formed by the reaction, to form a bis(aldimine) or bis(ketimine).

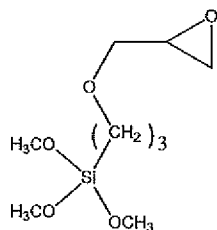
[0036] The bis(aldimine) or bis(ketimine) can have the structure:



[0037] The reaction products described above can be subjected to a purification step.

[0038] The compositions of Structure B can optionally be prepared by reacting Structure B as described with 3-glycidyloxypropyl trimethoxysilane.

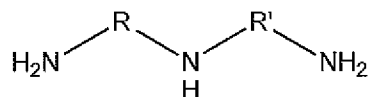
[0039] Disclosed is a composition prepared by reacting Structure B with reactant having the structure:



[0040] Disclosed are novel multifunctional compositions prepared from triamines, dialkyl maleate or fumarate, and epoxy-silanes. The multifunctional compositions incorporates into one molecule (1) two secondary amine groups with reactivity suitable for polyurea compositions, (2) at least one secondary hydroxyl group with lower reactivity toward isocyanates, (3) at least one moisture-curable alkoxy silane group, and (4) at least one tertiary amine group. Incorporating the novel composition as part of a polyurea formulation provides

multiple advantages including (1) enhanced ability to control and optimize reactivity of the polyurea system through blending with other curatives, (2) rapid formation of polyurea linkages for high initial strength, (3) slower cure of secondary hydroxyl for higher ultimate strength, (4) increased crosslink density for improved physical properties (tensile strength, impact performance), (5) improved adhesion, and (5) non-migratory amine catalysis of polyurethane-forming reactions.

**[0041]** Any suitable triamine can be used. A triamine will be understood as typically having the general formula



wherein each R and R' is the same or different and is a hydrocarbyl group.

**[0042]** Hydrocarbyl groups comprise only the elements of carbon and hydrogen and may be linear, branched, or cyclic, aliphatic or aromatic. Examples of triamines that may be used include but are not limited to: diethylenetriamine, 2-methyl-diethylenetriamine, 3-methyl-diethylenetriamine, 2,2,6,6-tetramethyl diethylenetriamine, N-(2-aminoethyl)-1,3-propanediamine, N-(4-aminobutyl)-1,5-pentanediamine, N-(3-aminopropyl)-1,8-octanediamine, N-(8-aminooctyl)-1,8-octanediamine, N-(3-aminopropyl)-1,6-hexanediamine, N-(4-aminobutyl)-1,4-butanediamine, N-(6-aminohexyl)-1,6-hexanediamine, N-(3-aminopropyl)-1,3-propanediamine, N-(2-aminoethyl)-1,2-benzenediamine, N-(2-aminoethyl)-1,3-benzenediamine, N-(2-aminoethyl)-1,4-benzenediamine, N-(4-aminophenyl)-1,2-benzenediamine, N-(4-aminophenyl)-1,4-benzenediamine, and N-(4-aminocyclohexyl)-1,4-cyclohexanediamine.

**[0043]** Aliphatic dialkylene triamines are particularly suitable, such as diethylenetriamine, dipropylenetriamine, and especially bis(hexamethylene)triamine available from INVISTA as Dytex® BHMT amine.

**[0044]** Any dialkyl maleate and/or dialkyl fumarate can be used. Examples of suitable dialkyl maleates and fumarates include but are not limited to esters of maleic acid and fumaric acid with monoalcohols such as dimethyl, diethyl, di-n-propyl, di-isopropyl, di-n-butyl, di-sec-butyl, di-tert-butyl, di-isobutyl, di-penyl, di-t-amyl, di-hexyl, di-cyclohexyl and di-2-ethylhexyl maleates or the corresponding fumarates. In certain embodiments, dialkyl maleates or dialkyl fumarates with two different alkyl groups, and/or mixtures of dialkyl maleates and dialkyl fumarates can be used. The alkyl groups of dialkyl maleate and/or dialkyl fumarate may

comprise additional functional groups such as hydroxyl groups, such as the reaction product of maleic anhydride, an alcohol, and an epoxy, the reaction produce of maleic anhydride with a glycol such as ethylene glycol and an alcohol, the reaction product of maleic acid or fumaric acid with an alcohol and an epoxy, or the reaction product of maleic acid or fumaric acid with an epoxy. Suitable alcohols include but are not limited to methanol, ethanol, propanol, isopropanol, butanol, isobutanol, sec-butanol, tert-butanol, various isomeric pentanols, various isomeric hexanols, cyclohexanol, 2-ethylhexanol, and the like. Suitable epoxies include but are not limited to ethylene oxide, propylene oxide, 1,2-epoxybutane, and glycidyl neodecanoate (an example of which is CARDURA E10P, Hexion Speciality Chemicals, Inc.).

**[0045]** Suitable epoxy-silanes include but are not limited to 3-glycidyloxypropyl trimethoxysilane (e.g. Silquest® A-187 silane from Momentive) and beta(3,4-epoxycyclohexyl)ethyl trimethoxysilane (e.g. Silquest® A-186 from Momentive). Other epoxy-functional trimethoxy silanes may be used. Trialkoxysilanes other than trimethoxy may also be used but typically are slower to moisture cure than trimethoxysilanes and are less preferred.

**[0046]** The novel multifunctional polyamine compositions are formed by first reaction of a triamine with a dialkyl maleate or fumarate to form an aspartic ester derivative as is known in the art (US 8,137,813 B2). The aspartic ester derivative is then allowed to react with an epoxy-silane to form the inventive composition.

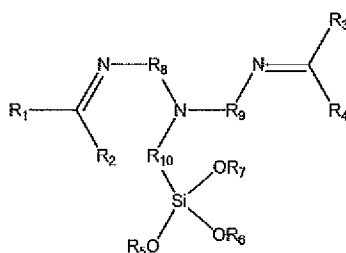
**[0047]** Polyaldimines and polyketimines are useful in formulating polyurea or polyenamine polymers. For example, a polyketimine or polyaldimine may be regarded as a blocked primary amine and can be used as a latent primary amine curative in a polyurea coating or adhesive; see, for example, US 2009/0017311. Ketimines or aldimines with no active hydrogen are particularly preferred as blocked amines in isocyanate systems since they are unable to form the enamine tautomer and therefore do not contain active hydrogen. When a coating formulation containing such a ketimine or aldimines and isocyanate is spread on a surface, the surface area is increased dramatically and absorption of water from the environment occurs, leading to hydrolysis of the ketimine and release of the original primary amine which then reacts rapidly with isocyanate to form polyurea.

**[0048]** Polyketimines and polyaldimines are also useful in formulating polyenamine polymers useful as coatings or adhesives. The fundamental polyenamine chemistry is described in US 3,668,183 but the area continues to be developed and improved. A recent patent, US

9,359,471, describes novel foam compositions based on the same fundamental chemistry. Polyketimines and polyaldimines as disclosed are useful in such systems. As described above, hydrolysis releases primary amine and a volatile ketone or aldehyde that diffuses and evaporates from the curing coating. The primary amine then is free to react rapidly with beta-keto esters such as polyacetoacetate monomers to form polyenamine.

**[0049]** The disclosure provides for improved silane-functionalized polyaldimines and polyketimines that improve adhesion and properties of derived polyenamines. Benefits of using silane-functionalized polyketimine or polyaldimine of the disclosure include the masked primary amine, which will moderate cure of the final polyenamine, and the moisture-curable siloxane side chain which will improve adhesion of the polyenamine, increase crosslinking, and improve flexibility and toughness, such as impact resistance.

**[0050]** The general structure below illustrates silane-functionalized aldimines and ketimines of the disclosure:

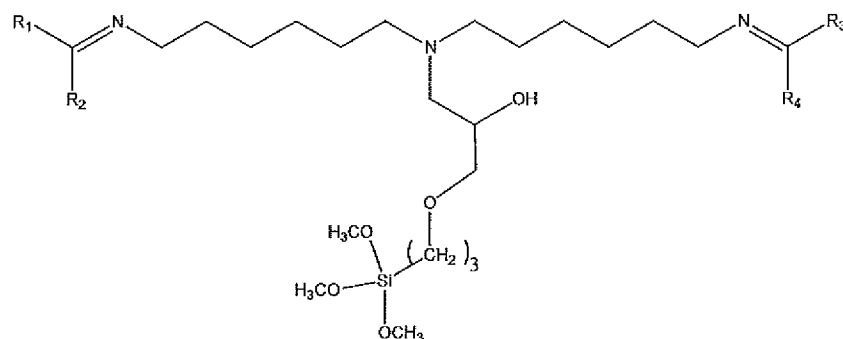


**[0051]** In the above structure, R1, R2, R3, and R4 are hydrocarbyl groups that may be the same or different, where a hydrocarbyl group is one comprising only the elements of carbon and hydrogen that may be linear, branched, or cyclic. They may independently be methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, t-butyl, 2-ethylhexyl, cyclohexyl, etc. Either or both of R1 and R3 may be H, in which case the structure is an aldimine rather than a ketimine.

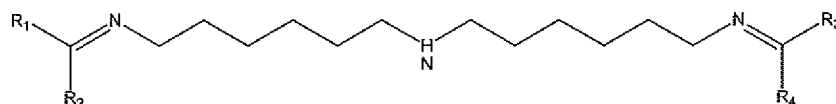
Aldimines where both R1 and R3 are H and where R2 and R4 are both tertiary hydrocarbyl groups such as t-butyl are of particular interest in that they do not contain active hydrogen and, as stated above, are inert toward isocyanate. R1 and R2 may be linked together to form a cyclic structure such as a cyclohexyl ring. The same is true of R3 and R4. R8, R9, and R10 are linking groups that may be the same or different and are hydrocarbyl or ether-substituted hydrocarbyl. In addition, R10 may contain hydroxyl functionality. Structures wherein R8 and R9 are linear aliphatic hydrocarbyl groups are of particular interest, i.e.  $-(CH_2)_n-$  groups. In this case n is

typically in the range of 2 to 20, more preferably in the range 4 to 12. Structures where R8 and R9 are both hexamethylene groups are of particular interest.

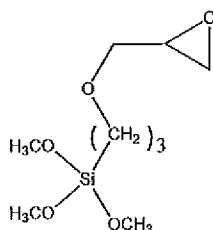
**[0052]** Structures wherein R10 is a hydroxyl-containing ether-substituted hydrocarbyl link derived from an epoxysilane are of particular interest since they typically contain a secondary hydroxyl reactive toward isocyanates and ultimately provide increased crosslinking without significantly reducing pot life of a formulation. Specifically, the structures below are of particular interest.



**[0053]** The structures above may be prepared by first reaction of bis(hexamethylene)triamine with the aldehydes or ketones R1C(O)R2 and R3C(O)R4, where R1 through R4 are as described above, with removal of water formed by the reaction, to form a bis(aldimine) or bis(ketimine) illustrated below.



**[0054]** This intermediate may be purified if desired, but purification is not required. This intermediate is then combined with 3-glycidyloxypropyl trimethoxysilane, shown below, to give the final product.



#### Example 1

**[0055]** First, an aspartate modified amine curative with a secondary non-aspartate amino group is prepared from dipropylene triamine as described in US 8,137,813 B2, Example A.

Then, when the reaction is complete, 4129 g of 3-glycidyloxypropyl trimethoxysilane is added and the reaction mixture is stirred at 50°C for 3 hours. The product is found to have total amine content of 4.29 meq/g and tertiary amine content of 1.43 meq/g. The difference between total amine and tertiary amine, 2.86 meq/g, represents reactive amine hydrogen. The reactive amine equivalent weight is thus 349.5 g.

#### Example 2

**[0056]** First, an aspartate modified amine curative with a secondary non-aspartate amino group is prepared from bis(hexamethylene) triamine as described in US 8,137,813 B2, Example B. Then, when the reaction is complete, 189 g of 3-glycidyloxypropyl trimethoxysilane is added and the reaction mixture is stirred at 50°C for 3 hours. The product is found to have total amine content of 2.40 meq/g and tertiary amine content of 0.80 meq/g. The difference between total amine and tertiary amine, 2.56 meq/g, represents reactive amine hydrogen. The reactive amine equivalent weight is thus 390.7 g.

#### Example 3

**[0057]** First, an aspartate modified amine curative with a secondary non-aspartate amino group is prepared from 600 g diethylenetriamine and 1953 g diethyl maleate following the general procedure described in US 8,137,813 B2. Then, when the reaction is complete, 1375 g of 3-glycidyloxypropyl trimethoxysilane is added and the reaction mixture is stirred at 50°C for 3 hours. The product is found to have total amine content of 4.44 meq/g and tertiary amine content of 1.48 meq/g. The difference between total amine and tertiary amine, 2.96 meq/g, represents reactive amine hydrogen. The reactive amine equivalent weight is thus 337.6 g.

#### Comparative example 4

**[0058]** An aspartate modified amine curative with a secondary non-aspartate amino group is prepared from bis(hexamethylene) triamine as described in US 8,137,813 B2. Total amine content is found to be 5.50 meq/g and the amine equivalent weight is 181.7

Examples 5 through 8

**[0059]** Polyureas are prepared at NCO index 1.1 using the formulations given in

**[0060]** Table 1. Each formulation is prepared for a conventional 1:1 mix ratio. In all cases the prepolymer is formed from 2000 molecular weight polypropylene glycol diol (PGP 2000 from Carpenter) and Isonate® 143L modified MDI from Dow. To obtain the desired 1:1 mix ratios, the proportions of polyol and isocyanate used to prepare the quasi-prepolymer part of each formulation is modified slightly to match the curative compositions. A diethyl aspartic ester prepared from INVISTA Dytek® A amine and diethyl maleate is used as the base component of the curative part in every case; commercial products are available from Covestro (Desmophen® NH-1220), Pflaumer Brothers (Teraspartic® 230 ), and others. The inventive amine curatives and comparative example 4 are tested at a 10% substitution rate.

Table 1. Polyurea formulations (amounts given in parts by weight).

| Example                     | 5        | 6        | 7        | 8        |
|-----------------------------|----------|----------|----------|----------|
| BHMT aspartic (Comp Ex 4)   |          |          |          | 10       |
| Dytek Et aspartic           | 100      | 90       | 90       | 90       |
| BHMT aspartic silane (Ex 2) |          | 10       |          |          |
| DETA aspartic silane (Ex 3) |          |          | 10       |          |
| Total curative              | 100      | 100      | 100      | 100      |
| Curative equiv wt           | 230.2808 | 240.1409 | 237.8415 | 224.2842 |
| Isonate 143L MDI            | 76.15    | 73.58    | 74.16    | 77.83    |
| Polypropylene glycol diol   | 23.85    | 26.42    | 25.84    | 22.17    |
| Total prepolymer            | 100      | 100      | 100      | 100      |
| Prepolymer %NCO             | 20.07%   | 19.25%   | 19.43%   | 20.61%   |
| Prepolymer equiv wt         | 209.35   | 218.31   | 216.22   | 203.89   |
| NCO index                   | 1.1      | 1.1      | 1.1      | 1.1      |
| Impact test (1 = best)      | 4        | 1        | 3        | 2        |
| Adhesion test (1 = best)    | 4        | 1        | 2        | 3        |

**[0061]** In each of examples 5 through 8, the prepolymer and curative are charged to opposite sides of a double-barrel syringe. The syringe is fitted with a 20-element static mixer tip.

Two smooth-edged, 1/4" thick glass plates are positioned flat on a PTFE sheet with their edges held apart 1/8" using ceramic tile spacers. The syringe plunger is depressed and a bead of polyurea is quickly applied to slightly overfill the gap between the glass plates. Excess polyurea is immediately squeegeed away, flush with the top of the glass, using a PTFE spatula. The polyurea ingredients remaining in the syringe are quickly expelled onto a PTFE sheet and allowed to cure in a mass for impact testing.

[0062] Test specimens are aged for 1 week at 70°C and 50% relative humidity before testing. An adhesion test is performed by clamping one glass plate onto a flat surface and raising the outer edge of the second glass plate so that the 1/8" seam of polyurea acts as a hinge. The angle between the glass plates when adhesive or cohesive failure or cracking occurs is taken as a measure of adhesive performance and the four examples ranked in order based on that angle. An impact test is performed using the hardened mass of polyurea from the PTFE sheet. The mass is placed on a steel anvil and a 16-oz hammer is allowed to fall onto the polyurea from various heights until the force of the impact cracks or otherwise visibly damages the polyurea. The examples are ranked using height as an indicator of impact performance.

[0063] It can be seen from the results in

[0064] Table 1 that the inventive aminosilanes from DETA (example 7) and from BHMT (example 6) both provide improved performance over simple aspartic esters (example 5) in terms of impact performance and adhesion. Further, the more preferred aminosilane from BHMT (example 6) provides improved performance over a less preferred aminosilane from DETA (example 7).

#### Example 9

[0065] A mixture of 500 g bis(hexamethylene)triamine and 550 g cyclohexanone (a slight excess) is stirred and heated to reflux. Water of reaction and cyclohexanone distill from the reaction mixture. Additional cyclohexanone is added and heating continued until water evolution ceases. Pressure is then reduced to 20 mm Hg and heating is continued to remove residual cyclohexanone. The reaction mixture is cooled to 50°, then 549 g of 3-glycidylpropyl trimethoxysilane is added. The mixture is held at 50°C for 3 hours to complete reaction. The product is found to have 1.57 meq/g tertiary amine and (after hydrolysis) 4.72 meq/g total amine.

The primary amine content (revealed by hydrolysis) is thus the difference between these two values, 3.15 meq/g and the amine equivalent weight is 318 g.

#### Comparative example 10

[0066] A mixture of 500 g 1,6-hexanediamine and 1000 g cyclohexanone (a slight excess) is stirred and heated to reflux. Water and cyclohexanone distill from the reaction mixture. Additional cyclohexanone is added until water evolution ceases. Pressure is then reduced to 20 mm Hg and heating is continued to remove residual cyclohexanone. The product is a bis(ketimine) of hexamethylenediamine but does not contain silane functionality of the present invention.

#### Example 11

[0067] The inventive composition of example 9 is evaluated as a coating using a cross-cut adhesion test. For purposes of comparison, it is tested in a mixture comprising 10% composition of example 9 and 90% composition of example 10 for comparison to 100% comparative example 10.

[0068] A coating is prepared as follows: First, a mixture of ketimines is prepared comprising 10% composition of example 9 and 90% composition of comparative example 10. Next, a coating mixture is prepared comprising this polyketimine mixture and trimethylolpropane trisacetoacetate, containing equal equivalents of ketimine groups and acetoacetate groups. Then, a coating is applied to a clean, bare sheet of glass using a 5-mil drawdown bar. The coating is allowed to cure for 24 hours at room temperature, then baked for 10 minutes in a forced-draft oven at 150°C to ensure removal of ketone released by the cure.

[0069] Adhesion is evaluated by the cross-cut adhesion test and rated as 4 on a scale of 1-5 where 5 is perfect and 1 is worst. Adhesion is improved compared to Comparative example 12 below.

#### Comparative example 12

[0070] The composition of comparative example 10 is evaluated as a coating using a cross-cut adhesion test.

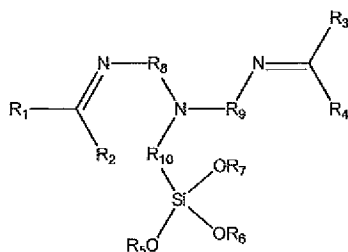
[0071] A coating is prepared as in example 11 except using 100% ketimine of comparative example 10: First, a coating mixture is prepared comprising the polyketimine of example 10 and trimethylolpropane trisacetoacetate, containing equal equivalents of ketimine groups and acetoacetate groups. Then, a coating is applied to a clean, bare metal aluminum panel using a 5-mil drawdown bar. The coating is allowed to cure for 24 hours at room temperature, then baked for 10 minutes in a forced-draft oven at 150°C to ensure removal of ketone released by the cure.

[0072] Adhesion is evaluated by the cross-cut adhesion test and rated as 2 on a scale of 1-5 where 5 is perfect and 1 is worst.

What is claimed is:

1. The reaction product of:
  - a) aspartate modified polyamine having at least two aspartate amine groups and at least one secondary non-aspartate amino group; and
  - b) an epoxy-functional trimethoxysilane.
2. The reaction product of:
  - a) aspartate modified polyamine having at least two aspartate amine groups and at least one secondary non-aspartate amino group; and
  - b) 3-glycidyloxypropyl trimethoxysilane.
3. The reaction product of:
  - a) aspartate modified triamine with a secondary non-aspartate amino group prepared from bis(hexamethylene) triamine; and
  - b) 3-glycidyloxypropyl trimethoxysilane.
4. The reaction product of:
  - a) aspartate modified triamine with a secondary non-aspartate amino group prepared from diethylenetriamine and diethyl maleate; and
  - b) 3-glycidyloxypropyl trimethoxysilane.
5. Polyurea comprising at least one of the reaction products of claims 1 to 4.
6. Epoxy comprising at least one of the reaction products of claims 1 to 4.
7. Coating comprising the composition of at least one of claims 5 and 6.
8. Elastomer comprising the composition of at least one of claims 5 and 6.
9. Sealant comprising the composition of at least one of claims 5 and 6.

10. Article comprising the composition of at least one of claims 5 and 6.
11. Automotive part comprising any one of claims 1 to 10.
12. The reaction product of:
  - a) ketimine or aldimine modified amine curative with at least two ketimine or aldimine groups and at least one secondary non-aspartate amino group; and
  - b) 3-glycidyloxypropyl trimethoxysilane.
13. The reaction product of claim 12 wherein the ketimine or the aldimine is prepared from bis(hexamethylene) triamine.
14. The reaction product of claim 13 wherein the bis(hexamethylene) triamine reactant is at least 70% pure.
15. Polyenamine comprising at least one reaction product of claims 12, 13 or 14.
16. Composition having the structure:

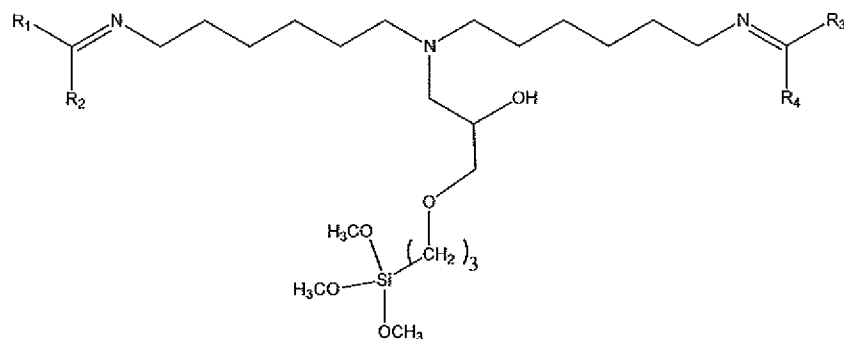


wherein R1, R2, R3, and R4 are hydrocarbyl groups that may be the same or different, where a hydrocarbyl group consists of carbon and hydrogen in linear, branched, or cyclic structure.

17. The composition of claim 16 wherein R1, R2, R3, and R4 are independently selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, t-butyl, 2-ethylhexyl and cyclohexyl.

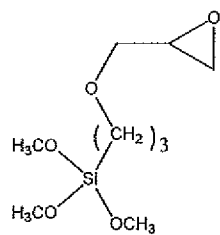
18. The composition of claim 17 wherein at least one of R1 and R3 is H, in which case the structure is an aldimine rather than a ketimine.
19. The composition of claim 18 wherein both R1 and R3 are H and wherein R2 and R4 are both tertiary hydrocarbyl groups.
20. The composition of claim 19 wherein R2 and R4 are t-butyl.
21. The composition of any one of claims 16 to 20 wherein R1 and R2 link to form a cyclic structure.
22. The composition of claim 21 wherein the cyclic structure is a cyclohexyl ring.
23. The composition of any one of claims 16 to 20 wherein R3 and R4 link to form a cyclic structure.
24. The composition of any one of claims 16 to 20 wherein R8, R9, and R10 are the same or different and selected from the group consisting of hydrocarbyl and ether-substituted hydrocarbyl.
25. The composition of any one of claims 16 to 20 wherein R10 contains hydroxyl functionality.
26. The composition of any one of claims 16 to 20 wherein R8 and R9 are linear aliphatic hydrocarbyl groups.
27. The composition of claim 26 wherein R8 and R9 are  $-(CH_2)_n-$  groups.
28. The composition of claim 27 wherein n is  $\geq 2$  and  $\leq 20$ .
29. The composition of claim 28 wherein n is  $\geq 4$  and  $\leq 12$ .

30. The composition of any one of claims 16 to 20 wherein R8 and R9 are both hexamethylene groups.
31. The composition of claim 30 wherein R10 is a hydroxyl-containing ether-substituted hydrocarbyl link derived from an epoxysilane.
32. Composition having the structure:



33. Composition prepared by first reaction of bis(hexamethylene)triamine with the aldehydes or ketones R1C(O)R2 and R3C(O)R4, where R1 through R4 are as described above, with removal of water formed by the reaction, to form a bis(aldimine) or bis(ketimine).
34. Composition of claim 33 wherein the bis(aldimine) or bis(ketimine) has the structure:
- 
35. Composition of claim 33 or 34 that has been subjected to a purification step.
36. Composition prepared by reacting product of at any one of claims 33 to 35 with 3-glycidyloxypropyl trimethoxysilane.

37. Composition prepared by reacting product of any one of claims 33 to 35 with reactant having the structure:



## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2017/049110

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C07F7/02 C08G18/79 C08G18/10 C09D175/02 C08G18/38  
C08L75/02 C07C251/08 C09D179/00 C08G73/00

ADD.

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)

C07F C08G C09D C08L C07C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.



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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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

Date of the actual completion of the international search

19 October 2017

Date of mailing of the international search report

07/11/2017

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Authorized officer

Lanz, Sandra

## INTERNATIONAL SEARCH REPORT

International application No  
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Information on patent family members

International application No

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