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⑤④ **One-package, heat-curable compositions suitable for use as sealants, solid coatings and moldings.**

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DE-A-2 346 213
DE-B-1 694 237
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GB-A-1 200 718
US-A-3 721 647
US-A-4 065 410

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Description

This invention relates broadly to compositions containing two or more reactive components which must not co-react until raised to above 100°C (212°F), and which then must co-react rapidly. These compositions have utility in various fields, including the field of sealant compositions, the field of high solids coatings, and the field of reaction injection molding.

In the field of sealant compositions the invention relates, inter alia, to one-package heat-curable compositions useful for sealing insulating glass.

The term "insulated glass" broadly refers to a structure comprising panes of glass, the faces of which are in spaced relationship, thereby providing between the glass panes a space which imparts insulating properties to the structure. In its most widely used form, 2 parallel panes of glass are positioned in spaced relationship by metallic spacers positioned around the perimeters of the panes, and indented a short distance from the edges of the panes, thereby forming a U-shaped channel in which the legs of the U comprise the interior surface edges of the panes and the base of the U comprises a side of the spacer. Typically, the spacer is a hollow member filled with a water-absorbent material, for example, a molecular sieve, to keep the enclosed air space between the glass panes dry. In such a structure, the aforementioned U-shaped channel is filled with a sealant, generally a polymeric composition, which must have a combination of properties for satisfactory use.

The sealant must have a very low water vapor transmission (WVT) rate so that moisture is prevented from entering the dry space between the panes of glass. The presence of moisture in the space tends to reduce the insulating value thereof. Moisture in the space can also condense on the panes of glass and create visibility or aesthetic problems. If the sealant does not have a satisfactory low WVT rate, the capacity of the water-absorbent material in the hollow spacer will be exceeded, and moisture will find its way into the space.

The sealant should form an excellent bond with glass which is not degraded over long periods of time under normal conditions of use, which generally include exposure to sunlight, moisture, and large changes in temperature.

Furthermore, the sealant itself should not be a source of material which enters the space between the panes of glass. Should one or more constituents comprising the sealant volatilize into the space, fogging, often referred to as "chemical fogging" of the glass panes, may result.

Temperature variation will tend to cause contraction and expansion of the insulated glass structure. Therefore, the sealant should have an elongation of at least 100%, and preferably an elongation of at least 200%.

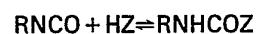
The sealant should also resist degradation due to contact with conventional caulks and putties.

Sealant compositions may be classified either as "two-package" or "one-package" formulations. The two-package sealants store their reactants in separate packages which are mixed together immediately prior to application, thereby avoiding premature cure problems. However, in some applications, the premixing requirements is a decided commercial disadvantage which "one-package" sealant formulations have attempted to overcome.

One-package sealant formulations store all their reactants in a single package. Such a formulation must be indefinitely stable at room temperature or in the absence of moisture or air. These sealants should not cure during "hot storage" at 30°C (100°F). These reactants will be "activated", or begin to cure, upon exposure to a more elevated temperature, 100–200°C, (212–392°F), or ambient moisture or air. The ideal sealant formulation will continue to cure upon removal of the activation.

"Blocking" of reactive functional groups with an inert derivative during organic synthesis is a well known synthetic tool. Once the desired synthetic transformation has been achieved the blocking agent is liberated, thereby regenerating the original reactive functional group. Removal of the blocking agent may be achieved by chemical reaction, and often by thermal dissociation at elevated temperature.

A "blocked isocyanate" is a compound which contains no free isocyanate groups, but which, though relatively inert at room temperature, will react at elevated temperatures in a manner which is similar to that of a free isocyanate. The formation of such compounds from isocyanates may be illustrated by the equation.



The blocking agents (HZ) should have threshold dissociation temperatures of 80–130°C (176–234°F), thereby ensuring total blockage of the isocyanate groups at ambient temperature and total dissociation at typical extrusion temperatures. Typical blocking agents include such compounds as phenols and thiols, tertiary alcohols, secondary aromatic amines, sodium bisulfite, imides, and 1,3-dicarbonyl compounds.

One example of a conventional one-package sealant formulation system employs an isocyanate-terminated polymer and a curing agent, typically an alcohol or amine. Premature reaction between the isocyanate-terminated polymer and the curing agent is prevented by blocking the isocyanate groups with a thermal dissociation blocking agent.

One unblocked, the free isocyanate will react with the curing agent. However, the rate of reaction is often unacceptably slow for commercial application. Addition of a Lewis acid catalyst, such as a tin salt, may greatly increase the reaction rate. However, coordination of the Lewis acid with the carbonyl group of the blocked isocyanate often allows direct attack of the curing agent

on the blocked terminal, resulting in room temperature cure. Certain curing agents, such as aliphatic or aromatic di- or polyamines do react rapidly with the isocyanate. However, these compounds are sufficiently basic to attack the blocked isocyanate terminal, thereby resulting in room temperature cure over several hours.

N. Seeger, "Synthetic Elastomeric Isocyanate Modified Polymers and Method for their Preparation", U.S. Patent No. 2 801 990 (August 6, 1957), discloses the substituted area reaction products of a polyisocyanate and an elastomeric diisocyanate-modified polyester or polyesteramide. The polyisocyanate reactivity is controlled by blocking at least one but not all the isocyanate groups with a thermal dissociation blocking agent. The number of isocyanate groups which are blocked may be controlled by adjusting the molecular proportions of polyisocyanate and blocking agent employed to block the polyisocyanate.

G. Bowser, "Multiple Glazed Unit", U.S. Patent No. 3 791 910 (February 12, 1974), discloses a two-package insulating glass sealant formulation composed of butyl rubber, polyisobutylene, polybutene, silica pigment with hydroxy groups, lead dioxide, and paraquinone dioxime. A two-package formulation is required because the composition will cure slowly at room temperature. The sealant will attain a substantially full cure in about two weeks.

V. McGinnis et al, "Compositions Containing Carbamothioate Curing Agents and their Uses", U.S. Patent No. 4 246 369 (January 20, 1981), discloses temperature-sensitive carbamothioic acid esters. At temperatures from 100 to 250°C (212 to 482°F) these compounds dissociate into free isocyanates and free thiols. The carbamothioate curing agents are employed in conjunction with a compound "A" which is reactive with isocyanate and a compound "B" which is reactive with thiol.

E. de Cleur et al, "Pulverulent Coating Compositions", U.S. Patent No. 4 248 978 (February 3, 1981), discloses a stable pulverulent coating composition which consists of a monomer which has reactive hydroxyl, carboxyl, mercapto, amino, amide, urethane, urea, or thiourea groups and a blocked polyisocyanate compound having at least one uretone imine group per molecule.

US-A 3 721 647 discloses a one-package, three-component heat-curable methane polymer casting composition comprising a urethane prepolymer the isocyanate terminals of which have been blocked with a high molecular weight, solid non-volatile, substituted phenol, a curative amount of a diamine curing agent and a stabilizing amount of an organic acidic material.

The applicants' inventive concept is to block all the reactive groups in a formulation. In this way all the reactive compounds may be formulated in one package and stored for long periods of time without appreciable interaction. Blockage of all reactants allows the use of more highly reactive compounds than is currently possible in formulations which block only one component.

From one aspect, the present invention pro-

vides a one-package heat-curable composition, comprising:

A. the reaction product, at a temperature below about 100°C (212°F) of an isocyanate-terminated prepolymer and an isocyanate blocking agent; and

B. a curing agent for said reaction product; characterised in that the curing agent comprises the reaction product, at a temperature below about 100°C (212°F), of a C₁ to C₂₀ alkyl or alkoxy polyamine curing agent and a polyamine blocking agent, all the amine groups of the polyamine being blocked.

From another aspect, the invention provides a one-package heat-curable composition, comprising:

A. the reaction product, at a temperature below about 100°C (212°F), of an amine-terminated, prepolymer and an amine blocking agent wherein all the amine groups of the prepolymer are blocked; and

B. a curing agent for said reaction product; characterised in that the curing agent comprises the reaction product, at a temperature below about 100°C (212°F), of a polyisocyanate curing agent and a polyisocyanate blocking agent.

Three applications of the invention are in the fields of one-package insulating glass sealant compositions, high solids coatings (both powder and wire), and reaction injection molding (RIM) of thermosetting resins. The remainder of this disclosure will illustrate the applicant's invention as applied to one-package insulating glass sealant compositions.

As applied to insulating glass sealant compositions, the applicant's inventive concept is to block both the prepolymer and the curing agent allows use of highly reactive curing agents which, when unblocked at elevated temperature, react rapidly with the free prepolymer. Blockage of the prepolymer ensures room temperature stability by rendering the prepolymer non-reactive not only to the free curing agent but also to moisture and other potential sources of instability.

A specific embodiment of the invention may be illustrated by describing its application to a one-package insulating glass sealant composition in which the prepolymer has an isocyanate group at each end, and is cured with a diamine compound. In order to achieve rapid cure times the use of strongly basic amine curing agents is desirable. However, these strongly basic curing agents can attack blocked isocyanate terminals at room temperature, thereby precluding their use in conventional one-package insulating glass sealant compositions. Blockage of the diamine curing agent allows use of strongly basic amines which, when unblocked at elevated temperatures, react rapidly with the free isocyanate. Blockage of the isocyanate-terminated prepolymer avoids moisture sensitivity and potential instability of the free isocyanate-terminated prepolymer.

The present invention also pertains to one-package sealant compositions in which the

prepolymer is terminated with amine groups and the curing agent is a polyisocyanate. For example, the amine-terminated prepolymers may be selected from amine-terminated polysulfides [see E. Fettes, "Polysulfide Polymer Reaction and Product", U.S. Patent No. 2 606 173 (August 5, 1952), and also E. Bertozzi, "Amino-Functional Phenol Containing Polysulfide Polymers and their Reaction Products with Polyepoxides", U.S. Patent No. 3 335 201 (August 8, 1967)] and amine-terminated polyoxyethylene polymers (commercially available from Jefferson Chemical Company, Inc., 3336 Richmond Avenue, P.O. Box 53300, Houston, Texas 77052, under the trademark Jeffamine® ED). The amine blocking agent may be selected from sodium bisulfite, sodium bisulfate, p-toluene sulfonic acid, sulfamic acid, and mixtures thereof, or from cis-9-octadecenoic acid, n-octadecanoic acid, isostearic acid, decanoic acid, hexanoic acid, and mixtures thereof. The polyisocyanate curing agent may be selected from ethylene diisocyanate, hexamethylene diisocyanate, p-phenylene diisocyanate, 4,4'-diphenyl-enemethane diisocyanate, and cyclohexylene-1,4-diisocyanate and the polyisocyanate blocking agent from n-dodecanethiol and phenol. All that is required is that both reactants be blocked.

The isocyanate-terminated prepolymer should provide the cured sealant composition with the physical properties discussed above: low water vapor transmission, excellent glass adhesion, low volatility, and terminated vinylic polymers, especially thioether-modified vinylic polymers.

Suitable isocyanate-terminated vinylic polymers may be prepared from hydroxyl-terminated polybutadiene and hydroxyl-terminated polyisoprene. These prepolymers may themselves be prepared by free radical addition polymerization of their respective monomers, 1,3-butadiene and 2-methyl-1,3-butadiene. Hydroxyl-terminated polybutadiene is commercially available under the trademark Arco R45M from the Arco Chemical Company, 1500 Market Street, Philadelphia, Pennsylvania 19101, U.S.A. The hydroxyl-terminated prepolymer is reacted with a diisocyanate to form the isocyanate-terminated prepolymer. A one to one molar ratio of hydroxyl to diisocyanate is required to ensure that the prepolymer is only "capped" with an isocyanate group on each end, rather than forming a polyurethane composed of many isocyanate and vinyl prepolymer segments.

Suitable diisocyanates for use in the preparation of the isocyanate-terminated prepolymer include ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, toluene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, isophorone diisocyanate, and 4,4'-diphenylene methane diisocyanate.

The isocyanate blocking agent should produce essentially irreversible blocking at room temperature, with a threshold dissociation temperature of at least 80°C (176°F) and preferably over 100°C

(212°F). The following isocyanate blocking agents may be employed in the practice of the invention:

- 5 1. Tertiary alcohols such as tertiary butyl alcohol, tertiary amyl alcohol, dimethyl ethinyl carbinol, dimethyl phenyl carbinol, methyl diphenyl carbinol, triphenyl carbinol, 1-nitro tertiary butyl carbinol, 1-chloro tertiary butyl carbinol, and triphenyl silanol;
- 10 2. Secondary aromatic amines which contain only one group having a hydrogen reactive with an isocyanate group, such as the diaryl compounds, including diphenyl amine, o-ditoyl amine, m-ditoyl amine, p-ditoyl amine, N-phenyl toluidine, N-phenyl exylidine, phenyl alpha naphthyl amine, phenyl beta naphthyl amine, carbazole, and the nuclear substituted aromatic compounds such as 2,2'-dinitro diphenyl amine and 2,2'-dichloro diphenyl amine;
- 15 3. Mercaptans such as 2-mercaptobenzothiazole, 2-mercapto thiazole, ethyl 2-mercapto thiazole, dimethyl 2-mercapto thiazole, beta naphthyl mercaptan, alpha naphthyl mercaptan, phenyl 2-mercapto thiazole, 2-mercapto 5-chloro-benzothiazole, methanethiol, ethanethiol, propane-
- 20 4. Lactams such as epsilon-caprolactam, delta-valerolactam, gamma-butyrolactam, and beta-propiolactam;
- 25 5. Imides such as carbimide, succinimide, phthalimide, naphthalimide, and glutarimide;
- 30 6. Monohydric phenols in which the hydroxyl group is the only group containing hydrogen reactive with the isocyanate group, such as phenol, the cresols, the xylenols, the trimethyl phenols, the ethyl phenols, the propyl phenols, the chloro phenols, the nitro phenols, the thymols, the carvacrols, mono alpha phenyl ethyl phenol, di alpha phenyl ethyl phenol, tri alpha phenyl ethyl phenol, and tertiary butyl phenol;
- 35 7. Compounds containing enolizable hydrogen such as aceto-acetic ester, diethyl malonate, ethyl n-butyl malonate, ethyl benzyl malonate, acetyl acetone, acetonyl acetone, benzimidazole, and 1-phenyl-3-methyl 5-pyrazolon.
- 40 8. Ketoximes including methyl ethyl ketoxime and acetophenone ketoxime.
- 45
- 50

The mercaptans are preferred as the polysocyanate blocking agent due to cost and toxicity considerations.

The polyamine curing agent must be sufficiently basic so as to rapidly cure the free isocyanate at temperatures above 130°C (234°F). The polyamine curing agent may be alkyl or alkoxy of from 1 to 20 carbon atoms. Effective polyamine curing agents include ethylene diamine, hexamethylene diamine, and bis(p-amino-cyclo-hexyl)methane. Ethylene diamine is preferred due to cost considerations.

A "blocked amine" is a compound which contains no free amino groups, but which, though relatively inert at room temperature, will react at

elevated temperatures in a manner which is similar to that of a free amine. The formation of such compounds from amines may be illustrated by the equation



The polyamine blocking agent should produce essentially irreversible blocking at room temperature, with a threshold dissociation temperature above 100°C (212°F). The polyamine blocking agent should possess low volatility to prevent bubbling or frothing during cure. Alkyl or aryl mono or polycarboxylic acids of from one to 30 carbon atoms may be employed as the polyamine blocking agent. Monocarboxylic acids are preferred since they allow one to one stoichiometry. Saturated carboxylic acids are further preferred due to their superior thermal stability. Effective polyamine blocking agents include stearic and oleic acids.

Inorganic acids may also be employed as the polyamine blocking agent. Suitable inorganic acids include sodium bisulfite, sodium bisulfate, p-toluene sulfonic acid, and sulfamic acid.

Combinations of two or more polyamine blocking agents may be employed to achieve optimum insulating glass composition characteristics or to lower the cost of the polyamine blocking agent.

Conventional additives may be incorporated into the insulating glass sealant formulation to achieve optimum sealant performance. Typically, such additives include plasticizers, glass adhesion promoters, antioxidants, reinforcing fillers, dyes, and pigments.

Suitable plasticizers include low volatility phthalates and low volatility chlorinated hydrocarbon polymers. Suitable phthalates include benzyl phthalate and alkyl benzyl phthalates. Chlorinated hydrocarbon plasticizers suitable for use are paraffins or -olefins containing from 16 to 20 carbon atoms which are chlorinated to a final chlorine content of from 52 to 58 weight percent chlorine, and blends thereof. These plasticizers may be included in the sealant formulation in an amount ranging from zero to thirty percent by weight based upon the total composition weight.

Suitable glass adhesion promoters are the organo-alkoxysilanes such as gamma-glycidoxypentyl trimethoxysilane, gamma-aminopropyl triethoxysilane, n-bis (beta-hydroxyethyl) gamma-aminopropyl triethoxysilane, and N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane. They may be incorporated in the sealant formulation in an amount ranging from 0.5 to four percent by weight based on the total composition weight. Gamma mercaptopropyltrimethoxysilane is commercially available as A-189 from the Union Carbide Co.

Reinforcing fillers include carbon black, silica, talc, titanium dioxide, zinc sulfide, calcium silicate, calcium carbonate, calcium oxide, and hydrated aluminum. A neutral or acidic filler is preferred so as to eliminate any possibility of premature deblocking. These fillers may be in-

corporated into the sealant formulation in an amount ranging from twenty to seventy percent by weight based upon the total composition weight.

The examples which follow are intended to illustrate the practice and advantage of the applicants' invention, and are not intended to limit the scope of the invention in any way. All percentages are measured by total weight of the composition unless otherwise stated.

Example I

Blocking of an isocyanate-terminated prepolymer with n-dodecanethiol

339.5 grams of isocyanate-terminated polybutadiene, which had previously been partially saturated (5 mole percent) with n-dodecanethiol, were heated under nitrogen at 95°C (203°F) and mixed with 54.8 grams of n-dodecanethiol and one gram of triethylamine catalyst. After 18 hours of heating, chemical and infrared analysis of the reaction product indicated no isocyanate groups were present.

The dodecanethiol-blocked prepolymer prepared above was denominated prepolymer "A".

Example II

Blocking of an isocyanate-terminated prepolymer with phenol

59.4 grams of isocyanate-terminated polybutadiene, which had previously been partially saturated (5 mole percent) with n-dodecanethiol, were heated under nitrogen at 70°C (185°F) and mixed with 3.1 grams of phenol. After eleven hours of heating, chemical and infrared analysis of the reaction product indicated that no isocyanate groups were present.

The phenol blocked prepolymer prepared above was denominated prepolymer "B".

Example III (Reference)

Formulation of a conventional one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and a non-blocked diol curing agent

80.02 grams of prepolymer "A" were thoroughly mixed in a plastic beaker with 11.41 grams of a diol derivative of ricinoleic acid (Cis-12-hydroxyoctadec-9-enoic acid) known under the trademark Polycin 53, which is commercially available from CasChem, Inc., Bayonne, NJ 07002, U.S.A. The composition so prepared was divided into six samples.

Cure of the first sample required 23 hours at 150°C (302°F), which is much too slow for commercial application.

Dibutyltindiacetate (DBTDA), a cure accelerator, was added to three samples in an amount corresponding to 0.4%, 2%, and 5% by weight, respectively. The three samples were then heated to 150°C (302°F). The 0.4% DBTDA sample required 24 hours to cure. The 2% DBTDA sample required about 2 hours to cure, while the 5% DBTDA sample required about an hour.

Dibutyltindiacetate was added to the remain-

195°C (383°F). One sample cured in about thirteen minutes, but displayed foaming and bubbles in the cured sealant. The other sample cured in about twenty three minutes without exhibiting any swelling or bubbles.

Example IV (Reference)

Formulation of a conventional one-package heat-curable composition employing a phenol-blocked prepolymer and a non-blocked diol curing agent

7.19 grams of prepolymer "B" were thoroughly mixed with 0.79 grams of Polycin 53 in a plastic beaker. The composition was placed in a two inch square sheet mold and heated to 145°C (293°F). The composition required 8 hours to cure. The cured composition had a Shore A hardness of 25 and an elongation of 120.

7.75 grams of prepolymer "B", 0.85 grams of Polycin 53, and an amount of dibutylindiacetate (DBTDA) cure accelerator corresponding to 0.2 weight percent were thoroughly mixed. The composition was placed in a two inch square sheet mold and heated to 145°C (293°F). Cure required thirty minutes. The cured composition had a Shore A hardness of 30, but poor elongation (approximately 70%).

Example V (Reference)

Formulation of a conventional one-package heat-curable composition employing phenol-blocked prepolymer and non-blocked hexamethylene diamine as the curing agent

5.61 grams of prepolymer "B" were thoroughly mixed in a plastic beaker with 0.56 grams of xyl-

ene to decrease viscosity. Then 0.170 grams of hexamethylene diamine were added to the reaction mixture, which cured the prepolymer immediately.

Example VI (Reference)

Formulation of a conventional one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and non-blocked hexamethylene diamine as the curing agent

25.69 grams of prepolymer "A" and 1.02 grams of hexamethylene diamine were thoroughly mixed in a plastic beaker. A sample required twelve minutes to cure at 150°C (302°F) and displayed a Shore A hardness of 65.

A sample maintained at room temperature cured within two hours.

Example VII (Reference)

Formulation of a conventional one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and non-blocked amine-terminated polysulfide as the curing agent

74.8 grams of prepolymer "A" and 126.3 grams of amine-terminated liquid polysulfide were mixed in a plastic beaker, forming a white suspension. A sample heated to 150°C (302°F) cured on the sealant surface only. A sample heated to 195°C (383°F) cured in approximately one hour.

Table I summarizes the various deficiencies of conventional one-package heat-curable compositions, as represented by Reference Examples III through VII:

Table I

Example	Isocyanate blocking agent	Curing agent	Room temp. stability	Time to cure
III A	N-Dodecanethiol	Polycin 53	good	23 hrs at 302°F
III B	N-Dodecanethiol	Polycin 53/0.4% DBTDA		24 hrs at 302°F
III C	N-Dodecanethiol	Polycin 53/2% DBTDA		2 hrs at 302°F
III D	N-Dodecanethiol	Polycin 53/5% DBTDA		1 hr at 302°F
III E	N-Dodecanethiol	Polycin 53/5% DBTDA		13 min at 383°F
III F	N-Dodecanethiol	Polycin 53/5% DBTDA		23 min at 383°F
IV A	Phenol	Polycin 53	good	8 hrs at 293°F
IV B	Phenol	Polycin 53/0.2% DBTDA	good	30 min at 293°F
V	Phenol	Hexamethylene diamine	immed. cure	-
VI	N-Dodecanethiol	Hexamethylene diamine	2 hours	12 min at 302°F
VII	N-Dodecanethiol	Amine terminated sulfide	good	1 hr at 383°F

Example VIII

Formulation of a one-package heat-curable composition employing n-dodecanethiol blocked prepolymer and hexamethylene diamine blocked with oleic acid

25.65 grams of Prepolymer "A" were thoroughly mixed with 4.97 grams of oleic acid (cis-9-octadecenoic acid) in a plastic beaker. 1.02 grams of hexamethylene diamine, previously liquified by heating to 70°C (158°F), were added to the plastic beaker. The mixture was thoroughly and rapidly mixed. A white color signalled the formation of the blocked diamine, hexamethylene diammonium dioleate.

A sample heated to 150°C (302°F) required less than ten minutes to cure. The cured composition had a Shore A hardness of about 30, and displayed no foaming during cure.

An uncured sample displayed promising "hot storage" stability by remaining in the uncured state for over three weeks at 38°C (100°F).

Example IX

Formulation of a one-package heat-curable composition employing n-dodecanethiol blocked prepolymer and hexamethylene diamine blocked with stearic acid

23.01 grams of prepolymer "A" were warmed and poured into a plastic beaker. 4.53 grams (corresponding to 10% excess) of hot liquified stearic acid (n-octadecanoic acid) were added to the beaker. The mixture was stirred vigorously while heating to dissolve the stearic acid.

0.86 gram of warm liquified hexamethylene diamine was added to the beaker, and the mixture vigorously stirred. A milky suspension signalled the formation of the blocked diamine, hexamethylene diammonium distearate.

A sample heated to 150°C (302°F) required 8 minutes to cure. The cured composition had a Shore A hardness of 45, a minimal non-offensive odor, and showed no foaming.

An uncured sample displayed good "hot storage" stability. It remained uncured after six weeks at 30°C (100°F).

Example X

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and hexamethylene diamine blocked with isostearic acid

34.48 grams of prepolymer "A" were thoroughly mixed with 6.63 grams (a five percent excess) of isostearic acid in a plastic beaker. Isostearic acid is a mixture of C₁₇H₃₅COOH saturated acids, primarily of the methyl-branched series. The reaction mixture was warmed to facilitate solution. 1.28 grams of warm, liquified hexamethylene diamine were added to the reaction mixture which was then mixed thoroughly. A milky suspension signalled the formation of the blocked diamine salts.

A sample heated to 150°C (302°F) required 8 minutes to cure. The cured composition had a Shore A hardness of 25, and a minimal mild non-offensive odor.

A cured sample placed in a 150°C (302°F) oven for 24 hours to evaluate its thermal stability was darker and displayed some brittleness but was still fairly elastic.

An uncured sample was heated to 30°C (100°F) for 1 month. It remained uncured.

Example XI

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and hexamethylene diamine blocked with hexanoic acid

20.75 grams of prepolymer "A" were thoroughly mixed with 1.65 grams of hexanoic acid in a

plastic beaker. 0.82 grams of liquified hexamethylene diamine were added to the beaker and thoroughly mixed. A white suspension signalled the formation of the blocked diamine, hexamethylene diammonium dihexanoate.

A sample heated to 150°C (302°F) required fifteen minutes to cure. The cured composition had a Shore A hardness of 35, but gave off a disagreeable odor.

A cured sample placed in a 150°C (302°F) oven for 24 hours to evaluate its thermal stability was slightly darker but had retained its elasticity.

Example XII

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and hexamethylene diamine blocked with decanoic acid

25.64 grams of prepolymer "A" were mixed with 3.03 grams of warmed, liquified decanoic acid in a plastic beaker. 1.02 grams of warmed, liquified hexamethylene diamine were added to the reaction mixture, which was then thoroughly mixed. A milky suspension signalled the formation of the blocked diamine, hexamethylene diammonium didecanoate.

A sample heated to 150°C (302°F) required 8 minutes to cure. The cured composition had a Shore A hardness of 30. Neither the uncured nor the cured samples gave off a disagreeable odor.

A cured sample was placed in a 150°C (302°F) oven for 24 hours to evaluate thermal stability. The sample had darkened but retained its elasticity.

Example XIII

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and hexamethylene diamine blocked with carbamic acid

23.16 grams of prepolymer "A" were mixed with 1.89 grams of hexamethylenediaminedicarbamate, commercially available from E.I. duPont de Nemours & Co., Wilmington, Delaware 19898, U.S.A. under the trademark Diak 1.

A sample heated to 150°C (302°F) required 10 minutes to cure and displayed severe foaming.

Table II summarizes the rapid cure times and good "hot storage" stability of heat curable compositions in which both reactants are thermally blocked, as represented by Examples VIII through XIII in which the hexamethylene diamine blocking agent is varied:

Table II

Example	Diamine blocking agent	Cure time at 302°F	Hot storage	Remarks
VIII	Oleic acid	Less than 10 mins	1 week	
IX	Stearic acid	8 mins	3 weeks	
X	Isostearic acid	8 mins	4 weeks	
XI	Hexanoic acid	15 mins	-	disagreeable odor
XII	Decanoic acid	8 mins	-	
XIII	Carbamic acid	10 mins	-	severe foaming

In the following Examples XIV through XVI ethylene diamine is substituted for hexamethylene diamine as the curing agent, and various amine blocking agents are evaluated.

Example XIV

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and ethylene diamine blocked with isostearic acid

6.29 grams, a five percent excess, of isostearic acid (a complex mixture of isomers of stearic acid, primarily of the methyl branched series, that are mutually soluble and virtually inseparable) were thoroughly mixed with 32.74 grams of warmed, liquified prepolymer "A" in a plastic beaker. 0.63 grams of ethylene diamine were added to the reaction mixture, which was then thoroughly mixed. A milky suspension signalled the formation of the blocked diamine salts.

A sample heated to 150°C (302°F) required 8 minutes to cure. The cured sample had a Shore A hardness of 23.

An uncured sample displayed superior "hot storage" stability. It remained uncured and stable for over four weeks at 38°C (100°F).

A cured sample was placed in a 150°C (302°F) oven to evaluate thermal stability. The sample had darkened, but was still flexible, after 24 hours of exposure.

Example XV

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and ethylene diamine blocked with octanoic acid

34.43 grams of prepolymer "A" were thoroughly mixed with 3.35 grams (a five percent excess) of octanoic acid in a plastic beaker. 0.67 grams of

ethylene diamine were added to the reaction mixture, which was then thoroughly mixed. A milky suspension signalled the formation of the blocked diamine salt, ethylene diammonium octanoate.

A sample heated to 150°C (302°F) required 8 minutes to cure. The cured sample had a Shore A hardness of 30, and exhibited a disagreeable odor which may have been due to suspected impurities in the commercial octanoic acid.

A cured sample was placed in a 150°C (302°F) oven for 24 hours to evaluate its thermal stability. The sample darkened and became brittle. This poor thermal stability may be due to suspected impurities in the commercial sample of octanoic acid employed in this Example.

Example XVI

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and ethylene diamine blocked with acetic acid

39.98 grams of prepolymer "A" were thoroughly mixed with 1.62 grams (a five percent excess) of acetic acid in a plastic beaker. 0.77 grams of ethylene diamine were added to the reaction mixture; which was again thoroughly mixed.

A sample heated to 150°C (302°F) required 10 minutes to cure. The cured sample had a Shore A of 30, and elongation of about 100, but exhibited a disagreeable odor.

A cured sample was placed in a 150°C (302°F) oven for 24 hours to evaluate its thermal stability. The sample retained its elasticity.

An uncured sample maintained at 38°C (100°F) remained uncured for over three weeks.

Table III summarizes the results obtained in Examples XIV through XVI using ethylene diamine as the polyamine curing agent:

Table III

Example	Diamine blocking agent	Cure time at 302°F	Hot storage	Remarks
XIV	Isostearic acid	8 mins	4 weeks	
XV	Octanoic	8 mins		disagreeable odor
XVI	Acetic acid	10 mins	over 3 weeks	disagreeable odor

The following Example XVII evaluates a third diamine curing agent, while Examples XVIII and XIX evaluate a combination of two diamine blocking agents.

Example XVII

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and bis-(aminocyclohexyl) methane blocked with isostearic acid

32.17 grams of prepolymer "A" were thoroughly mixed with 6.18 grams (a five percent excess) of isostearic acid in a plastic beaker. 2.17 grams of bis-(p-aminocyclohexyl) methane were added to the reaction mixture which was again thoroughly mixed. A milky suspension signalled the formation of the blocked diamine salts.

A sample heated to 150°C (302°F) required 8 minutes to cure. The cured composition had a Shore A hardness of 22, and exhibited a mild odor.

An uncured sample heated to 38°C (100°F) remained uncured for about ten days.

A cured sample was placed in a 150°C (302°F) oven to evaluate thermal stability. The sample had darkened, but was still flexible after 24 hours of exposure.

Example XVIII

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and ethylene diamine blocked with a combination of isostearic acid and decanoic acid

7.84 grams of decanoic acid were liquified and

mixed with 1.57 grams of isostearic acid, thereby producing a room temperature liquid comprising 89 mole percent decanoic acid and 11 mole percent isostearic acid. There was some minor crystallization of the decanoic acid after the solution stood overnight. This solution was labelled "combination blocking agent I".

38.75 grams of prepolymer "A" were mixed with 4.81 grams (a five percent excess) of the combination blocking agent I in a plastic beaker. 0.75 grams of ethylene diamine were added to the reaction mixture, which was again mixed thoroughly. A milky suspension signalled the formation of the blocked diamine salts.

A sample heated to 150°C (302°F) required 8 minutes to cure. The cured composition had a Shore A hardness of 22, but gave off a slightly disagreeable odor.

A cured sample placed in a 150°C (302°F) oven for 24 hours to evaluate its thermal stability darkened but retained its flexibility.

An uncured sample was heated to 38°C (100°F) for six weeks. It remained uncured.

Example XIX

Formulation of a one-package heat-curable composition employing n-dodecanethiol-blocked prepolymer and ethylene diamine blocked with a combination of isostearic acid and decanoic acid

7.68 grams of warmed, liquified decanoic acid were mixed with 2.30 grams of isostearic acid, thereby producing a room temperature liquid comprising 84.6 mole percent decanoic acid and 15.4 mole percent isostearic acid. After standing for two days there was no crystallization of the decanoic acid. This solution was labelled "combination blocking agent II".

34.26 grams of prepolymer "A" were mixed with 4.37 grams (a five percent excess) of combination blocking agent II in a plastic beaker. 0.66 gram of ethylene diamine was added to the reaction mixture, which was again thoroughly mixed. A milky suspension signalled the formation of the blocked diamine salts.

A sample heated to 150°C (302°F) required 8 minutes to cure. The cured composition had a Shore A hardness of 30 and a minimal amount of disagreeable odor.

A cured sample placed in a 150°C (302°F) oven for 24 hours to evaluate its thermal stability darkened but retained its elasticity.

Claims

1. A one-package heat-curable composition, comprising:

A. the reaction product, at a temperature below about 100°C (212°F), of an isocyanate-terminated prepolymer and an isocyanate blocking agent; and

B. a curing agent for said reaction product; characterised in that the curing agent comprises the reaction product, at a temperature below about 100°C (212°F) of a C₁ to C₂₀ alkyl or alkoxy polyamine curing agent and a polyamine blocking

agent, all the amine groups of the polyamine being blocked by conversion to quaternary ammonium groups having a threshold dissociation temperature above 100°C, the blocking being substantially irreversible at room temperature.

2. The composition of claim 1, characterised in that the isocyanate-terminated prepolymer is a polybutadiene or a polysulfide.

3. The composition of claim 1 or 2, characterised in that the isocyanate blocking agent is selected from n-dodecanethiol and phenol.

4. The composition of claim 1, 2 or 3, characterised in that the polyamine curing agent is selected from ethylene diamine, hexamethylene diamine, and bis(p-aminocyclohexyl) methane.

5. The composition of any of claims 1 to 4, characterised in that the polyamine blocking agent is selected from sodium bisulfite, sodium bisulfate, p-toluene sulfonic acid, sulfamic acid, and mixtures thereof or from cis-9-octadecenoic acid, n-octadecanoic acid, isostearic acid, decanoic acid, hexanoic acid, ethanoic acid, and mixtures thereof.

6. A one-package heat-curable composition, comprising:

A. the reaction product, at a temperature below about 100°C (212°F) of an amine-terminated prepolymer and an amine blocking agent wherein all the amine groups of the polyamine are blocked by conversion to quaternary ammonium groups having a threshold dissociation temperature above 100°C, the blocking being substantially irreversible at room temperature; and

B. a curing agent for said reaction product; characterised in that the curing agent comprises the reaction product, at a temperature below about 100°C (212°F), of a polyisocyanate curing agent and a polyisocyanate blocking agent.

7. The composition of claim 6, characterised in that the amine blocking agent is selected from sodium bisulfite, sodium bisulfate, p-toluene sulfonic acid, sulfamic acid, and mixtures thereof, or from cis-9-octadecenoic acid, n-octadecanoic acid, isostearic acid, decanoic acid, hexanoic acid, and mixtures thereof.

8. The composition of claim 6 or 7, characterised in that the polyisocyanate curing agent is selected from ethylene diisocyanate, hexamethylene diisocyanate, p-phenylene diisocyanate, 4,4'-diphenylenemethane, diisocyanate, and cyclohexylene-1,4-diisocyanate.

9. The composition of claim 6, 7 or 8, characterised in that the polyisocyanate blocking agent is selected from n-dodecanethiol and phenol.

Patentansprüche

1. In einer Verpackung abpackbare, durch Wärme härtbare Mischung, bestehend aus:

A. einem bei einer Temperatur unterhalb von etwa 100°C (212°F) gebildeten Reaktionsprodukt aus einem Vorpolymerisat mit endständigen Isocyanat-Gruppen und einer Isocyanat blockierenden Verbindung; und

B. einem Härtemittel für das Reaktionsprodukt, dadurch gekennzeichnet, dass das Härtemittel aus dem bei einer Temperatur unterhalb von etwa 100°C (212°F) gebildeten Reaktionsprodukt eines 1-20 C-Atome enthaltenden Alkyl- oder Alkoxympolyaminhärter und einer Polyamine blockierenden Verbindung besteht, und sämtliche Amino-Gruppen des Polyamins durch Umsetzung in quaternäre, eine Grenzspaltungstemperatur von über 100°C aufweisende Ammonium-Gruppen blockiert sind, wobei die Blockierung im wesentlichen unwiderruflich bei Raumtemperatur ist.

2. Mischung nach Anspruch 1, dadurch gekennzeichnet, dass das Vorpolymerisat mit den endständigen Isocyanat-Gruppen ein Polybutadien oder ein Polysulfidharz ist.

3. Mischung nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass die Isocyanat blockierende Verbindung n-Dodecanthiol oder Phenol ist.

4. Mischung nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, dass der Polyaminhärter aus Ethylendiamin, Hexamethylendiamin oder bis-p-Aminocyclohexylmethan besteht.

5. Mischung nach einem der Ansprüche 1-4, dadurch gekennzeichnet, dass die Polyamine blockierende Verbindung aus Natriumhydrogensulfid, Natriumhydrogensulfat, p-Toluolsulfosäure, Amidoschwefelsäure oder Mischungen dieser Verbindungen besteht, oder cis-9-Octadecensäure, n-Octadecensäure, Isostearinsäure, Caprinsäure, Capronsäure, Essigsäure oder eine Mischung dieser Verbindungen ist.

6. In einer Verpackung abpackbare, durch Wärme härtbare Mischung, bestehend aus:

A. einem bei einer Temperatur unterhalb von etwa 100°C (212°F) gebildeten Reaktionsprodukt aus einem Vorpolymerisat mit endständigen Aminogruppen und einer Amine blockierenden Verbindung, bei dem sämtliche Amino-Gruppen des Vorpolymerisates durch Umsetzung in quaternäre, eine Grenzspaltungstemperatur von über 100°C aufweisende Ammonium-Gruppen blockiert sind, wobei die Blockierung im wesentlichen unwiderruflich bei Raumtemperatur ist, und

B. einem Härtemittel für das Reaktionsprodukt, dadurch gekennzeichnet, dass das Härtemittel aus dem bei einer Temperatur unterhalb von etwa 100°C (212°F) gebildeten Reaktionsprodukt eines Polyisocyanathärter und einer Polyisocyanate blockierenden Verbindung besteht.

7. Mischung nach Anspruch 1, dadurch gekennzeichnet, dass die Amine blockierende Verbindung Natriumhydrogensulfid, Natriumhydrogensulfat, p-Toluolsulfosäure, Amidoschwefelsäure oder eine Mischung dieser Verbindungen ist, oder aus cis-9-Octadecensäure, n-Octadecensäure, Isostearinsäure, Caprinsäure, Capronsäure oder Mischungen dieser Verbindungen besteht.

8. Mischung nach Anspruch 6 oder 7, dadurch gekennzeichnet, dass der Polyisocyanat-Härter Ethylendiisocyanat, Hexamethylendiisocyanat, p-Phenylendiisocyanat, 4,4'-diphenylmethan,

Diisocyanat oder Cyclohexylen-1,4-diisocyanat ist.

9. Mischung nach Anspruch 6, 7 und 8, dadurch gekennzeichnet, dass die Polyisocyanate blockierende Verbindung n-Dodecanthiol oder Phenol ist.

Revendications

1. Composition en un seul conditionnement, polymérisable à chaud contenant:

A. le produit de la réaction, à température inférieure à 100°C environ, d'un prépolymère à groupement terminal isocyanate et d'un agent de blocage d'isocyanate et

B. un agent de polymérisation pour ledit produit de réaction, caractérisé par le fait que l'agent de polymérisation contient le produit de réaction, à une température inférieure à 100°C environ d'un agent de polymérisation polyamine alkyle ou alcoxy présentant de un à vingt atomes de carbone, et un agent de blocage polyamine, tous les groupes amines de la polyamine étant bloqués par conversion en groupes d'ammonium quaternaires ayant une limite de la température de dissociation au-dessus de 100°C, ce blocage étant essentiellement irréversible à la température normale d'intérieur.

2. Composition selon la revendication 1, caractérisée par le fait que le prépolymère à groupement terminal isocyanate est un polybutadiène ou un polysulfure.

3. Composition selon revendications 1 ou 2, caractérisée par le fait que l'agent de blocage isocyanate est choisi parmi les n-dodecanéthiols et les phénols.

4. Composition selon les revendications 1, 2 ou 3, caractérisée par le fait que l'agent de polymérisation est choisi parmi les diamines d'éthylène, les diamines d'hexaméthylène et le méthane bis(p-aminocyclohexyle).

5. Composition selon l'une des revendications 1 à 4, caractérisée par le fait que l'agent de blocage polyamine est choisi parmi les bisulfites de sodium, acides sulfoniques o-toluène, acides sulfamiques et leurs mélanges, ou parmi les acides cis-9-octadécénoïques, n-octadécénoïque, isostéarique, décanoïque, hexanoïque, éthanoïque et leurs mélanges.

6. Composition en un seul conditionnement, polymérisable à chaud comprenant:

A. le produit de réaction, à une température inférieure à 100°C environ d'un prépolymère à groupement terminal amine et d'un agent de blocage amine, dans lequel tous les groupes amines de la polyamine sont bloqués par conversion en groupes d'ammonium quaternaires ayant une limite de la température de dissociation au-dessus de 100°C, ce blocage étant essentiellement irréversible à la température normale d'intérieur, et

B. un agent de polymérisation pour ledit produit de réaction, caractérisée par le fait que l'agent de polymérisation contient le produit de réaction, à une température inférieure à 100°C

environ, d'un agent de polymérisation polyisocyanate et d'un agent de blocage polyisocyanate.

7. Composition selon la revendication 6, caractérisée par le fait que l'agent de blocage amine est choisi parmi le bisulfite de sodium, bisulfate de sodium, l'acide sulfonique p-toluène, l'acide sulfamique et leurs mélanges, ou parmi l'acide cis-9-octadécénoïque, l'acide n-octadécanoïque, l'acide isostéarique, l'acide décanoïque, hexanoïque et leurs mélanges.

8. Composition selon les revendications 6 ou 7, caractérisée par le fait que l'agent de polymérisation polyisocyanate est choisi parmi les diisocyanates d'éthylène, d'hexaméthylène, de p-phénylène, de 4,4'-diphénylène-méthane, et cyclohexylène-1,4.

9. Composition selon les revendications 6, 7 ou 8, caractérisée par le fait que l'agent de blocage est choisi parmi les n-dodecanéthiols et les phénols.

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