Description

BACKGROUND OF THE INVENTION

This invention relates to a novel organoboron complex initiator system and an acrylic adhesive composition containing this initiator. More particularly this invention involves a two-part initiator system comprising in one-part a stable organoboron amine complex and in the second part an organic acid destabilizer or activator. This initiator system is especially useful in elastomeric acrylic adhesive compositions.

Adhesive compositions including acrylic adhesives such as solutions of elastomeric polymers in soluble polymerizable acrylic or methacrylic monomers are well known in the art. These compositions which are especially known for their toughening properties generally include a redox system which comprises a catalyst or initiator, an accelerator and an activator to initiate cure, as well as other additives such as adhesion promoters, chelators, cross-linking agents, thickeners and plasticizers. Two-part acrylic adhesives where an activator is added as a separate second component are widely used and are known for curing speed as well as toughness. The catalyst or initiator typically used in these adhesives are free-radical initiators of the organic peroxy or hydroperoxy type, perester or peracid type.

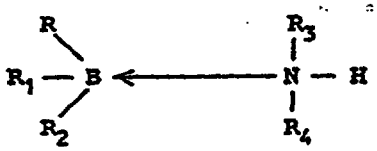
Many known adhesive systems, such as the epoxies, require a thermal cure to obtain desirable properties, while others that do not, usually require prolonged cure times. In comparison, the adhesive composition with organoboron amine complex initiator of this invention cures at room temperature and reaches high tensile strength in a short period of time. Additionally, the adhesive composition of this invention has shown exceptional stability on ageing while exhibiting both high tensile strength and high peel strength.

SUMMARY OF THE INVENTION

This invention involves a novel two-part organoboron amine complex initiating system useful in elastomeric acrylic adhesives compositions to provide better and faster room temperature curing thereof.

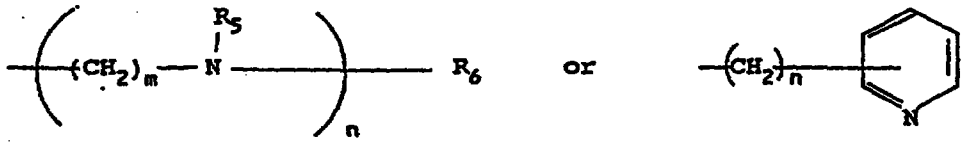
The organoboron initiating system of this invention is a two-part system comprising:

A) a stabilized organoboron amine complex of the formula:



(I)

where R, R_1 and R_2 are alkyl of 1 to 10 carbon atoms or phenyl, R_3 and R_4 are hydrogen or alkyl of 1 to 10 carbon atoms, or



where R_5 and R_6 are hydrogen or alkyl of 1 to 10 carbon atoms, m is 2 to 10 and n is 1 to 6, and

B) an organic acid activator having the formula:

R - COOH

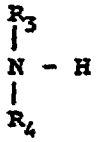
where R is hydrogen, alkyl or alkenyl of 1 to 8 carbon atoms, or aryl having 6 to 10 carbon atoms.

DETAILED DESCRIPTION OF THE INVENTION

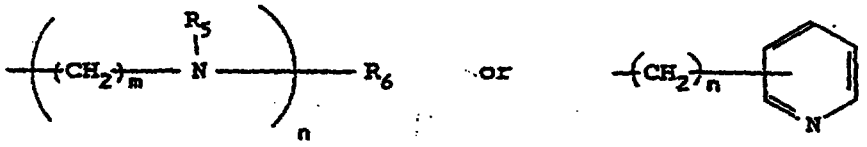
The stabilized organoboron amine complex of the structure (I) which comprises one part of the initiator of this invention is made by combining an organoboron compound with a primary or secondary amine or polyamine containing primary or secondary amines. The organoboron compound has the formula:

where R, R_1 and R_2 are alkyl of 1 to 10 carbon atoms or phenyl, preferably alkyl of 1 to 4 carbons. In this formula, the alkyl groups may be straight or branch chained and the phenyl group may contain substituents such as alkyl, alkoxy or halogen. Illustrative compounds of this type include, e.g., trimethylboron, triethylboron, tri-n-butylboron, tri-sec-butylboron and tri-isobutylboron.

The amine which is used in forming the organoboron amine complex (I) may be any primary or secondary amine or polyamine containing a primary or secondary amino, or ammonia and having the following formula:



where R_3 and R_4 are hydrogen or alkyl of 1 to 10 carbon atoms, or



where R_5 and R_6 are hydrogen or alkyl of 1 to 10 carbon atoms, m is 2 to 10, and n is 1 to 6. The alkyl groups in this formula may be straight or branch chained. Preferably, the R groups noted in the amino will he hydrogen or alkyl of 1 to 4 carbon atoms, m will be 2 to 6 and more preferably 2 to 3 and n will be 1 to 2. Illustrative compounds of this type include, e.g., n-octylamine, 1,6-diaminohexane, diethylamine, dibutylamine, diethylene triamine, dipropylene diamino, ammonia, 1,3-propylenediamine and 1,2-propylenodiamine.

The stabilized amino complex can be prepared by combining a solution of the organoboron with the amino under an inert atmosphere with cooling as needed.

The activator used as the second part or component of the initiator system will be a compound which will destabilize or liberate the free organoboron compound by removing the amino group and thereby allow it to initiate the polymerization process. This activator is an organic acid having the formula:

R - COOH

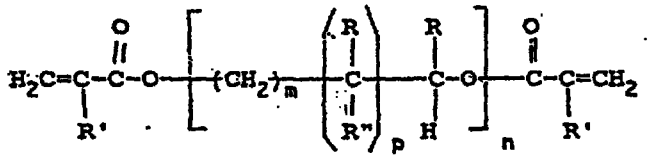
where R is H, alkyl or alkenyl of 1 to 8 and preferably 1 to 4 carbon atoms, or aryl of 6 to 10, preferably 6 to 8 carbon atoms. It is further understood that the alkyl or alkenyl group of this organic acid may be straight or branch chained and the aryl may contain substituents such as alkyl, alkoxy or halogen. Illustrative examples of compounds of this type include: acrylic acid, methacrylic acid, benzoic acid, and p-methoxybenzoic acid.

Generally the initiator system of this invention will comprise the organoboron amino complex and an effective destabilizing amount of the organic acid activator. More particularly from about 0.1:1 to 200:1 parts by weight of acid to amine complex and preferably from about 1:1 to 24:1 parts by weight of acid to amine complex may be used.

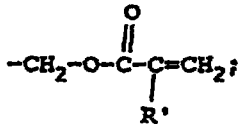
The organoboron initiator of this invention is particularly useful in acrylic adhesive compositions and especially solutions of elastomeric or rubber polymers in compatible polymerizable acrylic monomers.

The polymerizable acrylic monomer may be monofunctional, polyfunctional or a combination thereof.

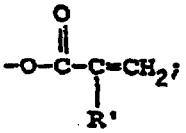
One class of polymerizable monomers useful in the present compositions correspond to the general formula:



wherein R is selected from the group consisting of hydrogen methyl, ethyl, $-CH_2OH$ and



R' is selected from the group consisting of hydrogen, chlorine, methyl and ethyl;
R" is selected from the group consisting of hydrogen, hydroxy, and

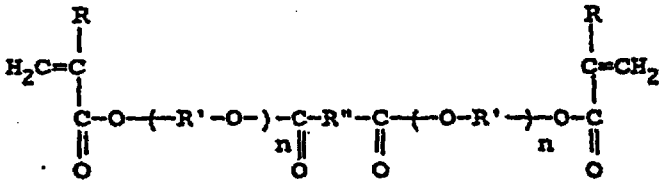


m is an integer equal to at least 1, e.g., from 1 to 8 or higher and preferably from 1 to 4 inclusive;
n is an integer equal to at least 1, e.g., from 1 to 20 or more; and
p is one of the following: 0 or 1.

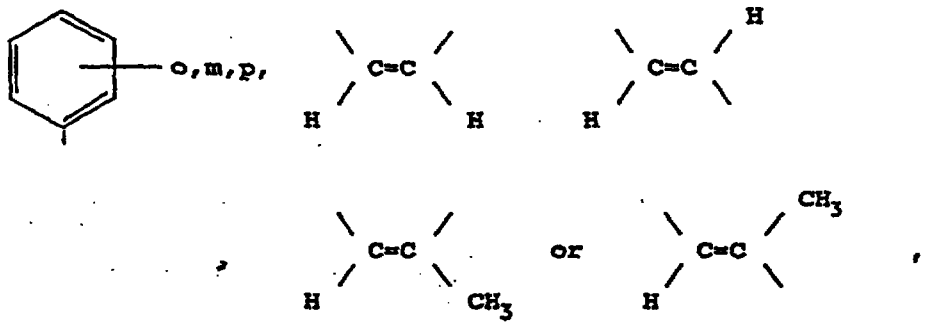
Monomers useful in this invention and which come within the above general formula include, for example, ethylene glycol dimethacrylate, ethylene glycol diacrylate, polyethylene glycol diacrylate, tetraethylene glycol dimethacrylate, diglycerol diacrylate, diethylene glycol dimethacrylate, pentaerythritol triacrylate, trimethylolpropane trimethacrylate, and other polyether diacrylates and dimethacrylates.

The above class of monomers is in essence described in U.S. Pat. No. 3,043,820 issued July 10, 1962 (to R. H. Krieble).

A second class of polymerizable monomers useful in the present compositions correspond to the general formula:



wherein R represents hydrogen, chlorine, methyl or ethyl; R' represents alkylene with 2-6 carbon atoms; and, R" represents $(CH_2)_m$ in which m is an integer of from 0 to 8, or

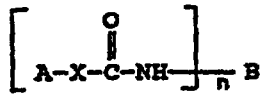


and n represents an integer of from 1 to 4.

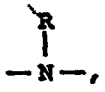
Typical monomers of this class include, for example, dimethacrylate of bis(ethylene glycol) adipate, dimethacrylate of bis(ethylene glycol) maleate, dimethacrylate of bis(diethylene glycol) phthalate, dimethacrylate of bis(tetraethylene glycol) phthalate, dimethacrylate of bis(tetraethylene glycol) sebacate, dimethacrylates of bis(tetraethylene glycol) maleate, and the diacrylates and chloroacrylates corresponding to said dimethacrylates, and the like.

The above class of monomers is in essence described in U.S. Pat. No. 3,457,212 issued July 22, 1969 (Sumitomo Chemical Company, Ltd.)

Also useful herein are monomers which are isocyanate-hydroxyacrylate or isocyanate-aminoacrylate reaction products which may be characterized as acrylate terminated polyurethanes and polyureides or polyureas. These monomers correspond to the general formula:



wherein X is selected from the group consisting of -O- and



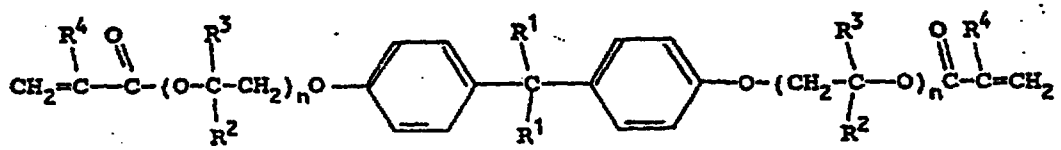
and

R is a member selected from the group consisting of hydrogen and lower alkyl of 1 to 7 carbon atoms; A represents the organic residue of an active hydrogen containing acrylic ester wherein the active hydrogen has been removed, the ester being hydroxy or amino substituted on the alkyl portion thereof and the methyl, ethyl and chlorine homologs thereof; n is an integer from 1 to 6 inclusive; and B is a mono- or polyvalent organic radical selected from the group consisting of alkyl, alkylene, alkenyl, cycloalkyl, cycloalkylene, aryl, aralkyl, alkaryl, poly(oxyalkylene), poly(carboalkoxyalkylene), and heterocyclic radicals both substituted and unsubstituted.

Typical monomers of this class include the reaction product of mono- or polyisocyanate, for example, toluene diisocyanate, with an acrylate ester containing a hydroxy or amino group in the non-acrylate portion thereof, for example, hydroxyethyl methacrylate.

The above class of monomers is in essence described in U.S. Pat. No. 3,425,988 issued February 4, 1969 (Loctite Corporation).

Another class of monomers useful in the present application are the mono-and polyacrylate and methacrylate esters of bisphenol type compounds. These monomers may be described by the formula:



where R^1 is methyl, ethyl, carboxyalkyl or hydrogen; R^2 is hydrogen, methyl or ethyl; R^3 is hydrogen, methyl or hydroxyl; R^4 is hydrogen, chlorine, methyl or ethyl; and n is an integer having a value of 0 to 8.

Representative monomers of the above-described class include: dimethacrylate and diacrylate esters of 4,4'-bis-hydroxyethoxy-bisphenol A; dimethacrylate and diacrylate esters of bisphenol A; etc. These monomers are essentially described in Japanese Patent Publication No. 70-15640 (to Toho Chemical Manuf. Ltd.).

In addition to the monomers already described, other useful monomers are monofunctional acrylate and methacrylate esters and the substituted derivatives thereof such as hydroxy, amide, cyano, chloro, and silane derivatives. Such monomers include, for example, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isobornyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, butyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, decylmethacrylate, dodecyl methacrylate, cyclohexyl methacrylate, tert-butyl methacrylate, acrylamide, N-methylolacrylamide, diacetone acrylamide, N-tert-butyl acrylamide, N-tert-octyl acrylamide, N-butoxyacrylamide, gamma-methacryloxypropyl trimethoxysilane, 2-cyanoethyl acrylate, 3-cyanopropyl acrylate, tetrahydrofurfuryl methacrylate, tetrahydrofurfuryl chloroacrylate, glycidyl acrylate, glycidyl methacrylate, and the like.

The monomers useful herein are seen to be polymerizable monomers having one or more acrylic or substituted acrylic groups as a common, unifying characteristic, and for convenience may be generically termed acrylic monomers.

The elastomer or rubber polymers may be any of the typically available synthetic rubbers that are soluble in the monomer such as those based on polyisoprenes, polybutadienes, polyolefins, polyurethane, polyesters, etc. Examples of elastomeric materials include homopolymers such as polybutadiene, polyisoprene and polyisobutylene; diene type copolymers such as butadiene/styrene copolymer, butadiene/acrylonitrile copolymer, butadiene/methyl methacrylate copolymer and butadiene/alkyl acrylate copolymer; ethylene/vinyl acetate copolymers; ethylene/alkyl acrylate copolymers (1-8 carbons in the alkyl group), rubbery polyalkyl acrylates or copolymers thereof; polyurethane; chlorinated polyethylenes; and EPDM (ethylene/propylene/diene terpolymers).

The elastomers of these structures may contain a functional group at one or both ends or within a particular segment or repeating unit of the copolymer. Among the suitable functional groups are vinyl, epoxy, carboxyalkyl, and mercapto groups. Other functional groups may be employed as deemed useful as determined by routine experimentation.

One preferred group of elastomers are the block copolymers. Several such block copolymers are manufactured by Shell Chemical Company under the tradename Kraton and by Firestone under the tradename Stereon. In particular, Stereon 840A, a poly(styrene-b-butadiene-b-styrene) block copolymer, has been found to be especially useful in the instant adhesive composition. Other preferred block copolymers of this type are available under the tradename Solprene 416, manufactured by Phillips Petroleum Co.

The monomer solution containing the elastomer or rubbery polymer is commonly prepared by dissolving the elastomer in the monomer, which may be in the form of a syrup. In some cases, the monomer solution may be prepared by extracting a rubbery polymer from a latex of the rubbery polymer in water, as used for suspension polymerization, and then dissolving in the monomer.

The amount of the acrylic monomer to be used in this invention may vary somewhat depending on the specific properties desired but generally about 10 to 90% by weight of the composition and preferably about 15 to 80% by weight is used. Adjustment within these ranges are easily made within the skill of the art. The elastomer is generally present in amounts of about 5 to 80% by weight and preferably about 20 to 60% by weight of the composition.

The second part of the initiator which contains the acid activator, preferably may also contain a peroxy or hydroperoxy component having the formula:

R-OOH

where R is hydrogen, alkyl of 1 to 10 preferably 4 to 10 carbon atoms or aryl or alkaryl of 6 to 14, preferably 6 to 10 carbon atoms. Illustrative compounds of this type are t-butyl hydroperoxide and cumene hydroperoxide. Typically these hydroperoxy compounds which aid in the initiation of polymerization are used in the initiator system in amounts of about 0.2:1 to 100:1 and preferably from about 0.4:1 to 20:1 parts by weight of hydroperoxy to amine complex.

The organoboron amine complex used in an adhesive composition in accordance with this invention generally comprises from about 0.1 to 5% by weight of the total composition and preferably from about 0.5 to 2.5% and the organic acid activator comprises from about 0.5 to 20%, preferably from about 1 to 12%

by weight of the total composition. When a hydroperoxy compound is used in the adhesive composition, it generally comprises from about 0.2 to 10% by weight of the total composition and preferably from about 0.5 to 2%.

Other additives useful in elastomeric acrylic adhesives of this type, such as adhesion promoters, chelators, cross-linking agents, inhibitors, activators such as N,N-dimethyltoluidine as well as thickeners, plasticizers and diluents may also be used in the adhesive compositions of this invention.

The organoboron initiator system as described above comprises a two component system. When used in the acrylic rubber compositions of this invention generally the two parts are mixed in equal quantities of the monomer-polymer solution, but this may vary at the discretion of the user. That is, the stabilized organoboron compound is added to a solution of the elastomer or rubber polymer dissolved in the polymerizable acrylic monomer and the organo acid activator and optional hydroperoxy compound are added as a second part which also may be in a solution of the rubber polymer in acrylic monomer.

Adhesive compositions of this invention are particularly useful in structural and semi-structural applications such as speaker magnets, metal-metal bonding (automotive) glass-metal bonding, glass-glass bonding, circuit board component bonding, selected plastic to metal, glass, wood, etc. and electric motor magnets.

In the following examples, which are merely illustrative of the embodiments of this invention, all parts and percentages are given by weight and all temperatures are in degrees Celsius unless otherwise noted.

EXAMPLE I

Preparation of Organoboron Amine Complexes

Into a 3-neck flask containing a stirrer, condenser, thermometer and a nitrogen purge, 11.1 g (0.15 m, 50% excess) of 1,3-propylene diamine was added and the nitrogen purge continued while 100 ml of 1 molar solution (0.1 m) of tributylboron in tetrahydrofuran was further added. A mild exotherm developed and the temperature was kept below about 40 °C by cooling as necessary. When the addition was complete, the mixture was stirred for about 0.5 hour and transferred to a bottle previously flushed with nitrogen. This amine complex is identified below as initiator XII as well as other amine complexes prepared in a similar manner using the amines and amounts indicated.

AMINE	AMOUNT	INITIATOR NO.
ethylene diamine	6.0 g (0.10m)	I
ethylene diamine	9.0 g (0.15 m)	II
ethylene diamine	12.0 g (0.20 m)	III
1,2-propylene diamine	11.1 g (0.15 m)	IV
n-octylamine	19.4 g (0.15 m)	V
1,6-diaminohexane	17.4 g (0.15 m)	VI
diethylenetriamine	10.3 g (0.10 m)	VII
1,3-propylene diamine[1]	7.4 g (0.10 m)	VIII
4-aminomethylpyridine	10.8 g (0.10 m)	IX
3-aminomethylpyridine	10.8 g (0.10 m)	X
diethylamine	10.95 g (0.15 m)	XI
1,3-propylene diamine	11.1 g (0.15 m)	XII

[1] 1 molar solution of triethylboron in tetrahydrofuran used

EXAMPLE II

Preparation of Adhesive Composition

An adhesive formulation was prepared consisting of two parts that were mixed just prior to use. The first part contained the monomer-polymer syrup and the stabilized organoboron amine complex initiator from Example I. The second part contained a similar monomer-polymer syrup and an acid activator or reagent that destabilized the organoboron amino complex liberating the free organoboron. When mixed with the first part polymerization was initiated. The two adhesive composition parts were:

Part I	
Stereon 840A (styrene-butadiene block copolymer)	30 parts
Isobornyl methacrylate	70 parts
Organoboron amine initiator No. 12[1]	4 parts

[1] 1 molar solution in tetrahydrofuran

Part II	
Stereon 840A	30 parts
Isobornyl methacrylate	61 parts
Methacrylic acid	5 parts
Cumene hydroperoxide (CHP)	4 parts

Approximately equal portions of Parts I and II were mixed and applied to steel plates and allowed to cure. Tensile shear strength measurement on the adhesive bond was made according to the ASTM standard method D1002-72(1973) and found to be 2000 psi.

Additional adhesive formulations were prepared in a similar manner using the components as identified below along with the resulting tensile strength determined is described above for the formed adhesive bond.

RUBBER (%)	INITIATOR (%)	% ACID[1]	% CHP[2]	BOND TENSILE STRENGTH PSI
Stereon 840a (20)	XII (0.5)	10	0.1	1875
Stereon 840a (25)	VIII (0.5)	1	1	1550
Kraton 1107 (20)[3]	II (0.5)	10	1	1850
Kraton 1107 (20)	II (0.25)	10	1	1350
Kraton 1107 (20)	II (1.0)	10	1	2100
Hycar 4051 (10)[4]	IV (0.5)	10	1	1200
Kraton 1122 (25)[5]	VI (0.5)	1	1	1500
Stereon 840A (20)	I (0.5)	0.5	1.7	1500
	also contains 13% octyl acrylate			
Stereon 840A (30)	VIII (0.5)	10	1	2700
	monomer was tetrahydrofurfuryl methacrylate			

[1] methacrylic acid
[2] cumene hydroperoxide
[3] styrene-isoprene
[4] polyacrylic rubber polymer
[5] styrene-isoprene

EXAMPLE III

Similar adhesive formulations were prepared as in Example II using an amine complex of 1,3 propylene diamine and triethyl boron as the initiator (initiator No. VIII). The formulations contained two-parts as in Example II that were mixed just prior to use and had the following compositions:

Part I

Sample No.	Initiator	Rubber[1]	Monomer A	Monomer B	Monomer C
3A-I	2 parts	25 parts	60 parts (IBOMA)	15 parts (OMA)	—
3B-I	2 parts	25 parts	60 parts (IBOMA)	15 parts (OMA)	—
3C-I	2 parts	25 parts	60 parts (IBOMA)	15 parts (ODA)	—
3D-I	2 parts	25 parts	60 parts (IBOMA)	15 parts (HDDA)	—
3E-I	2 parts	25 parts	60 parts (IBOMA)	15 parts (HDDMA)	—
3F-I	2 parts	30 parts	—	—	70 parts (THFMA)
3G-I	2 parts	30 parts	—	—	70 parts (THFMA)
3H-I	2 parts	30 parts	—	—	70 parts (THFMA)
3I-I	2 parts	30 parts	—	—	70 parts (THFMA)
3J-I	2 parts	30 parts	55 parts (IBOMA)	—	15 parts (HPMA)

[1] Stereon 840A
IBOMA - isobornyl methacrylate
OMA - 2-ethylhexyl methacrylate
ODA - n-octylacrylate/n-decylacrylate mixture
HDDA - 1,6-hexanediol diacrylate
HDDMA - 1,6-hexanediol dimethacrylate
THFMA - tetrahydrofurfryl methacrylate
HPMA - 2-hydroxypropyl methacrylate
MAA - methacrylic acid
CHP - cumene hydroperoxide

Part II

Sample No.	Rubber[1]	Monomer A	Monomer B	Acid	CHP
3A-II	25 parts	50 parts (THFMA)	15 parts (OMA)	10 parts (MAA)	—
3B-II	25 parts	50 parts (IBOMA)	15 parts (OMA)	10 parts (MAA)	—
3C-II	25 parts	50 parts (THFMA)	15 parts (ODA)	10 parts (MAA)	—
3D-II	25 parts	50 parts (THFMA)	15 parts (HDDA)	10 parts (MAA)	—
3E-II	25 parts	50 parts (THFMA)	15 parts (HDDMA)	10 parts (MAA)	—
3F-II	30 parts	60 parts (THFMA)	—	10 parts (MAA)	0.125 parts
3G-II	30 parts	60 parts (THFMA)	—	10 parts (MAA)	0.250 parts
3H-II	30 parts	60 parts THFMA)	—	10 parts (MAA)	0.5 parts
3I-II	30 parts	60 parts (THFMA)	—	10 parts (MAA)	1 part
3J-II	30 parts	55 parts (THFMA)	15 parts (HPMA)	1 part (MAA)	—

[1] Stereon 840A
IBOMA - isobornyl methacrylate
OMA - 2-ethylhexyl methacrylate
ODA - n-octylacrylate/n-decylacrylate mixture
HDDA - 1,6-hexanediol diacrylate
HDDMA - 1,6-hexanediol dimethacrylate
THFMA - tetrahydrofurfryl methacrylate
HPMA - 2-hydroxypropyl methacrylate
MAA - methacrylic acid
CHP - cumene hydroperoxide

Approximately equal portions of Parts I and II were applied to steel plates and allowed to cure at room temperature. The bonds were evaluated for tensile shear strength using ASTM standard method D1002-72 (1973) in pounds/inch^2(psi) and for T-peel using ASTM standard method D1876-72 in pounds/linear inch (pli). These results are shown below (where, eg., 3A is 3AI + 3AII).

Adhesive Sample No.	Tensile Shear (psi)	T-Peel (pli)
3A	2500	20
3B	1700	8
3C	2400	14
3D	2700	6
3E	2900	5
3F	1875	--
3G	2600	--
3H	2000	--
3I	2600	--
3J	1800	4

Claims

1. A curable two-part adhesive composition wherein one-part comprises a polymerizable acrylic monomer and an effective amount of a stabilized organoboron amine complex initiator of the formula:

* C L M S *

Part II

Sample No.	Rubber[1]	Monomer A	Monomer B	Acid	CHP
3A-II	25 parts	50 parts (THFMA)	15 parts (OMA)	10 parts (MAA)	—
3B-II	25 parts	50 parts (IBOMA)	15 parts (OMA)	10 parts (MAA)	—
3C-II	25 parts	50 parts (THFMA)	15 parts (ODA)	10 parts (MAA)	—
3D-II	25 parts	50 parts (THFMA)	15 parts (HDDA)	10 parts (MAA)	—
3E-II	25 parts	50 parts (THFMA)	15 parts (HDDMA)	10 parts (MAA)	—
3F-II	30 parts	60 parts (THFMA)	—	10 parts (MAA)	0.125 parts
3G-II	30 parts	60 parts (THFMA)	—	10 parts (MAA)	0.250 parts
3H-II	30 parts	60 parts THFMA)	—	10 parts (MAA)	0.5 parts
3I-II	30 parts	60 parts (THFMA)	—	10 parts (MAA)	1 part
3J-II	30 parts	55 parts (THFMA)	15 parts (HPMA)	1 part (MAA)	—

[1] Stereon 840A
IBOMA - isobornyl methacrylate
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THFMA - tetrahydrofurfryl methacrylate
HPMA - 2-hydroxypropyl methacrylate
MAA - methacrylic acid
CHP - cumene hydroperoxide

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Adhesive Sample No.	Tensile Shear (psi)	T-Peel (pli)
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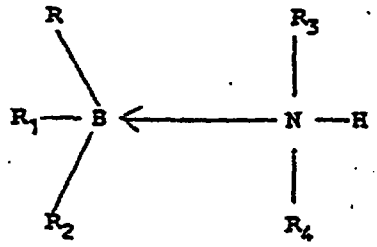
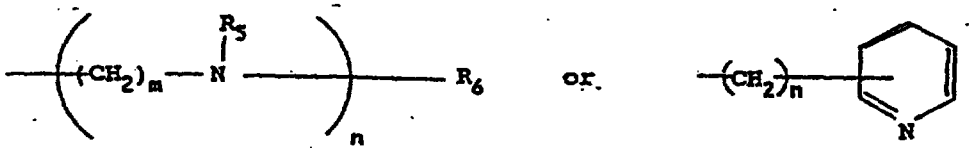
3B	1700	8
3C	2400	14
3D	2700	6
3E	2900	5
3F	1875	--
3G	2600	--
3H	2000	--
3I	2600	--
3J	1800	4

Claims

1. A curable two-part adhesive composition wherein one-part comprises a polymerizable acrylic monomer and an effective amount of a stabilized organoboron amine complex initiator of the formula:



where R, R_1 and R_2 are alkyl of 1 to 10 carbon atoms or phenyl, R_3 and R_4 are hydrogen or alkyl of 1 to 10 carbon atoms, or



where R_5 and R_6 are hydrogen or alkyl of 1 to 10 carbon atoms, m is 2 to 10 and n is 1 to 6; and the second part contains an effective destabilizing amount of an organic acid activator having the formula:

R - COOH

where R is H, alkyl or alkenyl of 1 to 8 carbons or aryl of 6 to 14 carbon atoms.

2. The composition of Claim 1 wherein in the organoboron amine complex R, R_1 and R_2 are alkyl of 1 to 4 carbons, R_3, R_4 and R_5 are hydrogen or alkyl of 1 to 4 carbons, R_6 is hydrogen, m is 2 to 6 and n is 1 to 2 and in the organic acid activator the R group is an alkyl or alkenyl group of 1 to 4 carbons or an aryl of 6 to 8 carbons.

3. The composition of Claims 1 or 2 wherein from about 0.1:1 to 200:1 parts by weight of acid to amine complex are used.

4. The adhesive composition of Claim 3 wherein the first part of the composition containing the acrylic monomer further comprises a rubber polymer and wherein the second part of the initiator system also contain a hydroperoxy compound.

5. The adhesive composition of Claim 4 wherein the second part containing an organic acid activator further comprises a polymerizable acrylic monomer with a rubber polymer dissolved therein

6. The composition of Claim 5 wherein from about 0.1 to 5% by weight of the organoboron amine complex and from about 0.5 to 20% by weight of the organic acid activator based on the total weight of the composition are used.

7. The composition of Claims 4 or 5 wherein the second part further contains a hydroperoxy compound having the formula R-OOH, where R is hydrogen, alkyl of 1 to 10 carbon atoms or aryl or alkaryl of 6 to 14 carbon atoms wherein from about 10 to 90% by weight of the acrylic monomer and from about 5 to 80% by weight of the rubber polymer based on the total weight of the composition are used.

8. The composition of Claim 7 wherein the acrylic monomer is an alkyl acrylate or methacrylate and the rubber polymer is a polymer, copolymer or block copolymer of polybutadiene, polyisoprene, polyisobutylene, butadiene/styrene, butadiene/acrylonitrile and butadiene/alkyl acrylate.

9. A two-part initiator composition comprising:

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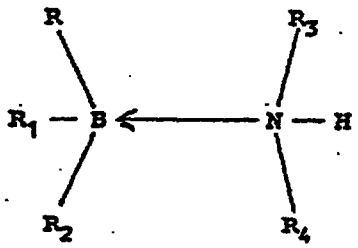
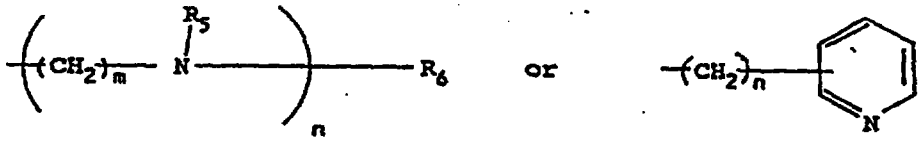
A) a stabilized organoboron amine complex of the formula:



where R, R_1 and R_2 are alkyl of 1 to 10 carbon atoms or phenyl, R_3 and R_4 are hydrogen or alkyl of 1 to 10 carbon atoms, or



where R_5 and R_6 are hydrogen or alkyl of 1 to 10 carbon atoms, m is 2 to 10 and n is 1 to 6, and B) an effective destabilizing amount of an organic acid activator having the formula:

R - COOH

where R is H, alkyl or alkenyl of 1 to 8 carbon atoms or aryl of 6 to 10 carbon atoms.

10. The composition of Claim 9 wherein in the organoboron amine complex, R, R_1 and R_2 are alkyl of 1 to 4 carbons, R_3, R_4 and R_5 are hydrogen or alkyl of 1 to 4 carbon atoms, R_6 is hydrogen, m is 2 to 6 and n is 1 to 2 and wherein the R group of the organic acid of Part B is an alkyl or alkenyl group of 1 to 4 carbons or an aryl of 6 to 8 carbons.

11. The composition of Claims 9 or 10 wherein from about 0.1:1 to 200:1 parts by weight acid to amine complex are used.

12. The composition of Claim 11 wherein the second part B) also contains a hydroperoxy compound.

13. The composition of Claim 12 wherein the hydroperoxy compound has the formula R-OOH, where R is hydrogen, alkyl of 1 to 10 carbon atoms or aryl or alkaryl of 6 to 14 carbon and wherein the complex is a combination of tributyl boron and ethylene diamine or propylene diamine.

14. A method of bonding facing surfaces which comprises interposing between said surfaces the curable adhesive composition of Claim 1 or 5, placing the surfaces in an abutting relationship and permitting the adhesive to cure.

Patentansprüche

1. Härtbare Zwei-Komponenten-Klebstoffzusammensetzung, worin eine Komponente ein polymerisierbares acrylisches Monomer und eine wirksame Menge eines stabilisierten Organobor-Amin-Komplex-Initiators der Formel

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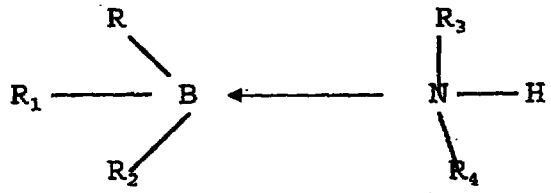
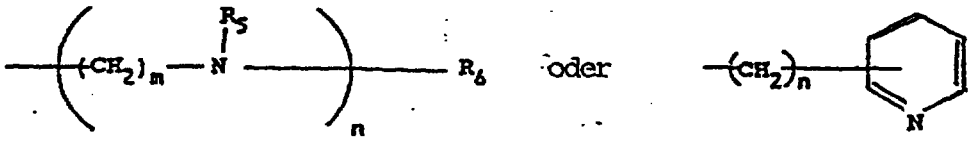


umfaßt, worin R, R_1 und R_2 Alkyl mit 1 bis 10 Kohlenstoffatomen oder Phenyl, R_3 und R_4 Wasserstoff oder Alkyl mit 1 bis 10 Kohlenstoffatomen oder



sind, worin R_5 und R_6 Wasserstoff oder Alkyl mit 1 bis 10 Kohlenstoffatomen sind, m 2 bis 10 ist und n 1 bis 6 ist; und die zweite Komponente eine wirksam destabilisierende Menge eines organisch sauren Aktivator mit der Formel

R—COOH

enthält, worin R H, Alkyl oder Alkenyl mit 1 bis 8 Kohlenstoffatomen oder Acryl mit 6 bis 14 Kohlenstoffatomen ist.

2. Zusammensetzung nach Anspruch 1, worin in dem Organobor-Amin-Komplex R, R_1 und R_2 Alkyl mit 1 bis 4 Kohlenstoffatomen sind, R_3, R_4 und R_5 Wasserstoff oder Alkyl mit 1 bis 4 Kohlenstoffatomen sind, R_6 Wasserstoff ist, m 2 bis 6 ist und n 1 bis 2 ist, und in dem organisch sauren Aktivator die Gruppe R eine Alkyl- oder Alkenylgruppe mit 1 bis 4 Kohlenstoffatomen oder eine Arylgruppe mit 6 bis 8 Kohlenstoffatomen ist.

3. Zusammensetzung nach Anspruch 1 oder 2, worin etwa 0,1:1 bis 200:1 Gewichtsanteile Säure auf Amin-Komplex verwendet werden.

4. Klebstoffzusammensetzung nach Anpsruch 3, worin die erste Komponente der Zusammensetzung, die das acrylische Monomer enthält, darüber hinaus ein Kautschuk-Polymer umfaßt, und worin die zweite Komponente des Initiatorsystems auch eine Hydroperoxyverbindung enthält.

5. Klebstoffzusammensetzung nach Anspruch 4, worin die zweite Komponente, die einen organisch sauren Aktivator enthält, darüber hinaus ein polymerisierbares acrylisches Monomer mit einem darin gelösten Kautschuk-Polymer umfaßt.

6. Zusammensetzung nach Anspruch 5, worin etwa 0,1 bis 5 Gew.-% des Organobor-Amin-Komplexes und etwa 0,5 bis 20 Gew.-% des organisch sauren Aktivators, bezogen auf das Gesamtgewicht der Zusammensetzung, verwendet werden.

7. Zusammensetzung nach Anspruch 4 oder 5, worin die zweite Komponente darüber hinaus eine Hydroperoxyverbindung mit der Formel R-OOH enthält, worin R gleich Wasserstoff, Alkyl mit 1 bis 10 Kohlenstoffatomen oder Aryl oder Alkaryl mit 6 bis 14 Kohlenstoffatomen ist, und worin etwa 10 bis 90 Gew.-% des acrylischen Monomers und etwa 5 bis 80 Gew.-% des Kautschuk-Polymers, bezogen auf das Gesamtgewicht der Zusammensetzung verwendet, werden.

8. Zusammensetzung nach Anspruch 7, worin das acrylische Monomer ein Alkylacrylat oder -methacrylat und das Kautschuk-Polymer ein Polymer, Copolymer oder Blockcopolymer von Polybutadien, Polyisopren, Polyisobutylen, Butadien/Styrol, Butadien/Acrylnitril und Butadien/Alkylacrylat ist.

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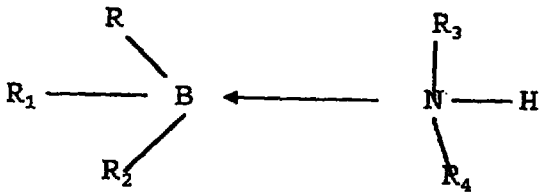
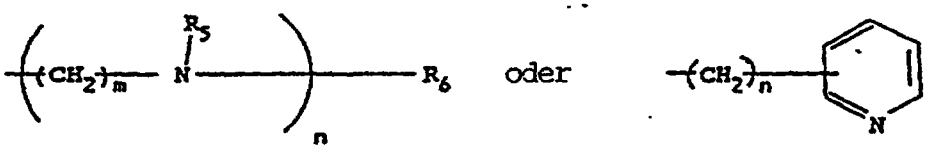
9. Zwei-Komponenten-Initiator-Zusammensetzung, umfassend:
A) einen stabilisierten Organobor-Amin-Komplex der Formel



worin R, R_1 und R_2 Alkyl mit 1 bis 10 Kohlenstoffatomen oder Phenyl sind, R_3 und R_4 Wasserstoff oder Alkyl mit 1 bis 10 Kohlenstoffatomen oder



sind, worin R_5 und R_6 Wasserstoff oder Alkyl mit 1 bis 10 Kohlenstoffatomen sind, m 2 bis 10 ist und n 1 bis 6 ist, und
B) eine wirksam destabilisierende Menge eines organisch sauren Aktivators mit der Formel

R—COOH

worin R H, Alkyl oder Akenyl mit 1 bis 8 Kohlenstoffatomen oder Aryl mit 6 bis 10 Kohlenstoffatomen ist.

10. Zusammensetzung nach Anspruch 9, worin im Organobor-Amin-Komplex R, R_1 und R_2 Alkyl mit 1 bis 4 Kohlenstoffatomen sind, R_3, R_4 und R_5 Wasserstoff oder Alkyl mit 1 bis 4 Kohlenstoffatomen sind, R_6 Wasserstoff ist, m 2 bis 6 ist und n 1 bis 2 ist, und worin der Rest R der organischen Säure der Komponente B eine Alkyl- oder Alkenylgruppe mit 1 bis 4 Kohlenstoffatomen oder ein Arylrest mit 6 bis 8 Kohlenstoffatomen ist.

11. Zusammensetzung nach Anspruch 9 oder 10, worin etwa 0,1:1 bis 200:1 Gewichtsanteile Säure zu Aminkomplex verwendet werden.

12. Zusammensetzung nach Anspruch 11, worin die zweite Komponente B) darüber hinaus eine Hydroperoxyverbindung enthält.

13. Zusammensetzung nach Anspruch 12, worin die Hydroperoxyverbindung die Formel R-OOH hat, worin R Wasserstoff, Alkyl mit 1 bis 10 Kohlenstoffatomen oder Aryl oder Alkaryl mit 6 bis 14 Kohlenstoffatomen ist, und worin der Komplex eine Kombination von Tributylboran und Ethylendiamin oder Propylendiamin ist.

14. Verfahren zum Verbinden einander gegenüberliegende Oberflächen, welches das Einbringen der härtbaren Klebstoffzusammensetzung nach Anspruch 1 oder 5 zwischen die Oberflächen, das Auf-Stoß-Bringen der Oberflächen und das Aushärtenlassen des Klebstoffs umfaßt.

Revendications

1. Composition d'adhésif durcissable en deux parties, dans laquelle une partie comprend un monomère acrylique polymérisable et une quantité efficace d'un initiateur, consistant en un complexe stabilisé d'un composé organique de bore et d'une amine, de formule :

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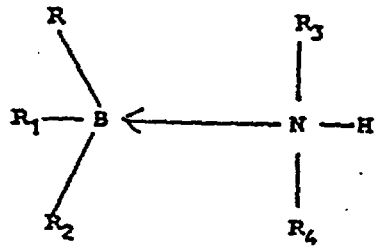
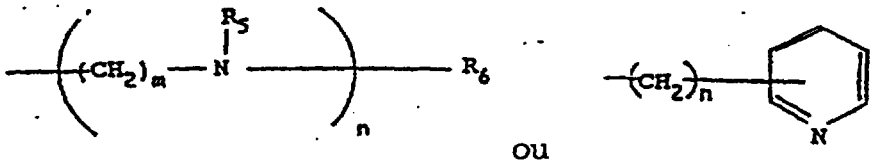


dans laquelle R, R_1 et R_2 représentent des groupes alkyle ayant 1 à 10 atomes de carbone ou phényle, R_3 et R_4 représentent l'hydrogène ou des groupes alkyle ayant 1 à 10 atomes de carbone, ou des groupes



dans lesquels R_5 et R_6 représentent l'hydrogène ou des groupes alkyle ayant 1 à 10 atomes de carbone, m a une valeur de 2 à 10 et n a une valeur de 1 à 6 ; et la seconde partie contient une quantité déstabilisante efficace d'un activateur consistant en un acide organique de formule

R - COOH

dans laquelle R représente H, un groupe alkyle ou alcényle ayant 1 à 8 atomes de carbone ou aryle ayant 6 à 14 atomes de carbone.

2. Composition suivant la revendication 1, dans laquelle, dans le complexe de composé organique de bore et d'amine, R, R_1 et R_2 représentent des groupes alkyle ayant 1 à 4 atomes de carbone, R_3, R_4 et R_5 représentent l'hydrogène ou des groupes alkyle ayant 1 à 4 atomes de carbone, R_6 représente l'hydrogène, m à une valeur de 2 à 6 et n a une valeur de 1 à 2 et, dans l'activateur consistant en un acide organique, le groupe R est un groupe alkyle ou alcényle ayant 1 à 4 atomes de carbone ou un groupe aryle ayant 6 à 8 atomes de carbone.

3. Composition suivant la revendication 1 ou 2 dans laquelle un rapport d'environ 0,1:1 à 200:1 parties en poids de l'acide au complexe d'amine est utilise.

4. Composition d'adhésif suivant la revendication 3, dans laquelle la première partie contenant le monomère acrylique comprend en outre un polymère du type caoutchouc et dans laquelle la seconde partie de l'initiateur contient également un composé à fonction hydroperoxy.

5. Composition d'adhésif suivant la revendication 4, dans laquelle la seconde partie contenant un activateur consistant en un acide organique comprend en outre un monomère acrylique polymérisable dans lequel est dissous un polymère du type caoutchouc.

6. Composition suivant la revendication 5, dans laquelle une quantité d'environ 0,1 à 5 % en poids du complexe de compose organique de bore et d'amine et une quantité d'environ 0,5 à 20 % en poids de l'activateur consistant en un acide organique, sur la base du poids total de la composition, sont utilisées.

7. Composition suivant la revendication 4 ou 5, dans laquelle la seconde partie contient en outre un composé à fonction hydroperoxy répondant à la formule R-OOH, dans laquelle R représente l'hydrogène, un groupe alkyle ayant 1 à 10 atomes de carbone ou un groupe aryle ou alkaryle ayant 6 à 14 atomes de carbone, et dans laquelle une quantité d'environ 10 à 90 % en poids du monomère acrylique et une quantité d'environ 5 à 80 % en poids du polymère du type caoutchouc, sur la base du

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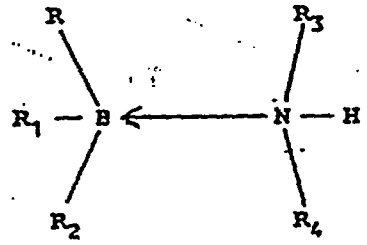
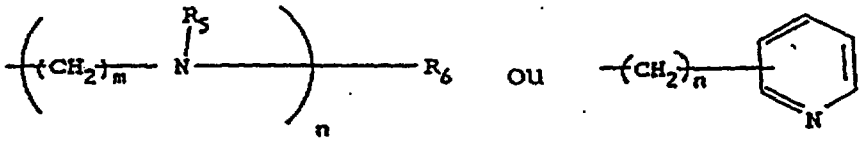
poids total de la composition, sont utilisées.

8. Composition suivant la revendication 7, dans laquelle le monomère acrylique est un acrylate ou méthacrylate alkyle et le polymère du type caoutchouc est un polymère, un copolymère ou un copolymère séquencé de polybutadiène, polyisoprène, polyisobutylène, butadiène/styrène, butadiène/acrylonitrile ou butadiène/acrylate d'alkyle.

9. Composition d'initiateur en deux parties comprenant :
A) un complexe stabilisé d'un composé organique de bore et d'une amine, de formule :



dans laquelle R, R_1 et R_2 représentent des groupes alkyle ayant 1 à 10 atomes de carbone, ou phényle, R_3 et R_4 représentent l'hydrogène ou des groupes alkyle ayant 1 à 10 atomes de carbone, ou des groupes



dans lesquels R_5 et R_6 représentent l'hydrogène ou des groupes alkyle ayant 1 à 10 atomes de carbone, m a une valeur de 2 à 10 et n a une valeur de 1 à 6, et
B) une quantité déstabilisante efficace d'un activateur consistant en un acide organique de formule

R - COOH

dans laquelle R représente H, un groupe alkyle ou alcényle ayant 1 à 8 atomes de carbone ou aryle ayant 6 à 10 atomes de carbone.

10. Composition suivant la revendication 9, dans laquelle, dans le complexe de composé organique de bore et d'amine, R, R_1 et R_2 représentent des groupes alkyle ayant 1 à 4 atomes de carbone, R_3, R_4 et R_5 représentent l'hydrogène ou des groupes alkyle ayant 1 à 4 atomes de carbone, R_6 représente l'hydrogène, m a une valeur de 2 à 6 et n est égal à 1 ou 2, et dans laquelle le groupe R de l'acide organique de la partie B est un groupe alkyle ou alcényle ayant 1 à 4 atomes de carbone ou un groupe aryle ayant 6 à 8 atomes de carbone.

11. Composition suivant la revendication 9 ou 10, dans laquelle un rapport d'environ 0,1:1 à 200:1 parties en poids de l'acide au complexe d'amine est utilise.

12. Composition suivant la revendication 11, dans laquelle la seconde partie B contient également un composé à fonction hydroperoxy.

13. Composition suivant la revendication 12, dans laquelle le composé à fonction hydroperoxy répond à la formule R-OOH, dans laquelle R représente l'hydrogène, un groupe alkyle ayant 1 à 10 atomes de carbone ou un groupe aryle ou alkaryle ayant 6 à 14 atomes de carbone, et dans laquelle le complexe est une association de tributylbore et d'éthylènediamine ou de propylènediamine.

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14. Procédé pour lier des surfaces à mettre en contact, qui comprend les étapes consistant à interposer entre lesdites surfaces la composition d'adhésif durcissable suivant la revendication 1 ou 5, à placer les surfaces en contact l'une avec l'autre et à laisser l'adhésif durcir.

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