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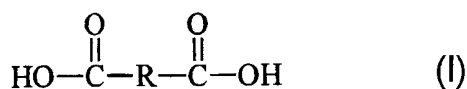
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(54) Title: ANAEROBIC ADHESIVE COMPOSITION



(57) Abstract: The present invention relates to an anaerobic adhesive composition and more particularly, to the anaerobic adhesive composition which blends a difunctional carboxylic acid, expressed by formula (I), to the anaerobic adhesive

composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents, showing some useful physical properties; a) the rapid velocity in a hardening reaction, b) the good stability in long-term storage, and c) the break-loose torque which is sufficiently applied in the assembly of bolt-nuts, precision apparatuses and electric/electronic parts, wherein R is (CH₂)_n or CH₂C(=CH₂) and n is an integer in the range of 2 to 10.

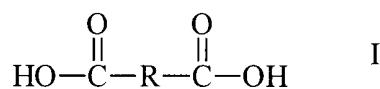
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ANAEROBIC ADHESIVE COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention

- 5 The present invention relates to an anaerobic adhesive composition and more particularly, to the anaerobic adhesive composition which blends a difunctional carboxylic acid, expressed by the following formula I, to the anaerobic adhesive composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents, showing some useful characteristics;
- 10 a)the rapid velocity in a hardening reaction, b)the good stability in long-term storage, and c)the break-loose torque which is sufficiently applied in the assembly of bolt-nuts, precision apparatuses or electric/electronic parts:



- 15 wherein R is $(\text{CH}_2)_n$ or $\text{CH}_2\text{C}(=\text{CH}_2)$ and n is an integer in the range of 2 to 10.

Description of the Related Art

- For the enhancement of hardening velocity within the scope of an anaerobic adhesive composition not to have a poor effect on the stability during
- 20 long-term storage, the anaerobic adhesive composition of common type was prepared by chemicals such as monomers, oligomers, inhibitors, peroxide-typed oxidizers(e.g., hydrogen peroxide and cumene hydroperoxide) and reducers(e.g., amines and imides) as disclosed in the following conventional methods[European Patent Appln. No. 446,144(1991), 443,916(1991);
- 25 499,483(1992); and Japanese Patent Kokai No. Pyeong2-187,401]. Also, an oxidizer and a reducer were used together in the preparation of anaerobic adhesive composition, as described in the following methods: Hung. Telies Hu 44, 280(1988) as a method using a complex alkaline solution, US Patent No.

4,731,146 as a method using a copper compound, and closed German Patent No. 3,611,307 as a method using a phosphate compound, etc.

In order to improve the stability in storage, the anaerobic adhesive composition in its initial development stage was prepared in such a method
5 that an inhibitor was added to a mixture of monomers and oligomers: the oligomers are derived from multi-functional (metha)acrylates (Japanese Patent Kokai No. Sho43-6545, Sho44-852). Then, the inhibitor was used as a scavenger for radicals which can spontaneously generate in the state of preparation or storage.

10 Japanese Patent Kokai No. Sho46-3160, Sho57-83572 and Pyeong6-66308 disclosed the anaerobic adhesive composition containing acrylic acid, methacrylic acid or thiosalicylic acid in order to increase its break-loose torque.

Japanese Patent Kokai No. Sho52-39694 and Sho57-83572 reported that organic phosphates were added to the anaerobic adhesive composition so as to
15 improve both its break-loose torque and the stability in storage.

Closed German Patent No. 3,611,307 also reported that methylenediphosphonic acid was added to the anaerobic adhesive composition in order to increase its break-loose torque.

To improve the stability in storage, glycerol dimethacrylate esterified
20 by succinic acid anhydride was used as a component of the anaerobic adhesive composition, as described by closed German Patent No. 3,527,717.

In addition, in order to increase its break-loose torque, Japanese Patent Kokai No. Sho62-184,076 disclosed that methylsulfamic acid was added to the anaerobic adhesive composition, but it brought about corrosion on the surface
25 of metallic materials.

Further, when an anaerobic adhesive composition is used to assemble parts into a complete whole, the enhancement of adhesive force as well as workability is powerfully required toward higher productivity. In the anaerobic

adhesive composition, a reducer containing the groups like imides, mercaptos or amines is concurrently used with a peroxide-typed initiator, where it is very important to select a useful reducer/oxidizer catalyst.

As above-mentioned, in the case that an oxidizer and a reducer existing
5 in the same vessel, the anaerobic adhesive composition is very unstable under its coexistence and can be easily initiated by radicals spontaneously produced between them. Although it is extremely difficult that a hardening reaction in progress is stopped or controlled the reaction in storage at room temperature was generally controlled by the addition of inhibitor above-mentioned.
10 Therefore, it is previously added to a mixture of monomers and oligomers in the preparation of anaerobic adhesive composition.

For more application, the anaerobic adhesive composition always requires access to the proper regulation of physical properties like strength and flexibility by way of the enhancement of both the rapid velocity in hardening
15 and the stability in storage.

SUMMARY OF THE INVENTION

To be free from the above-mentioned shortcomings, a difunctional carboxylic acid is essentially added to an anaerobic adhesive composition in
20 this invention.

An object of this invention is to provide the anaerobic adhesive composition with the stability in storage as well as the rapid hardening in fastening by mixing the difunctional carboxylic acid, where the anaerobic adhesive composition as a product shows useful break-loose torque.

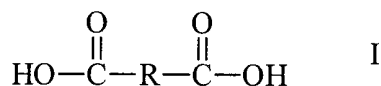
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Detailed Description of the Invention

This invention relates to an anaerobic adhesive composition which blends 0.0001 - 10 parts in weight of a difunctional carboxylic acid, expressed by

the following formula I, in proportion to 100 parts in weight of a mixture of monomers and oligomers, to the anaerobic adhesive composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents:

5



wherein R is $(\text{CH}_2)_n$ or $\text{CH}_2\text{C}(=\text{CH}_2)$, and n is an integer in the range of 2 to 10.

This invention explains in more detail as follows:

The anaerobic adhesive composition applicable to prevent a bolt which is jointed nuts from releasing requires the rapid hardening in fastening as well as the stability in storage, thereby enhancing its break-loose torque and workability.

In this invention, the difunctional carboxylic acid expressed by formula I is largely mixed to a mixture of monomers and oligomers.

15 In Table 1 in this invention, the values of pK_a (acid dissociation constant) of aliphatic difunctional carboxylic acids gradually increased with increasing the values of n above-mentioned, and then slightly decreased with increasing the values of n above 2. Then, the values of pK_1 in non-aliphatic difunctional carboxylic acids were less than those of aliphatic difunctional carboxylic acids.
20 Especially, when the value of n was at zero, pK_1 was the lowest value in various difunctional carboxylic acids.

In relation to this, the anaerobic adhesive composition containing a difunctional carboxylic acid brings about a rapid hardening reaction as well as the stability in storage: as the value of n gradually increases, the acidity of
25 difunctional carboxylic acid decreases. The break-loose torque of the anaerobic adhesive composition also increases with shortening the hardening time, and then its molecular weight grows bigger.

From the observation for above tendency, the value of n is limited as an

integer in the range of 2-10 according to this invention, and then the difunctional carboxylic acid is in the range of 1-5 of pKa. Under such condition, since the carboxylic acid scarcely give any effects on the acidity of an oxidizer like cumene hydroperoxide, the stability in storage of the anaerobic adhesive composition gets better. The anaerobic adhesive composition showed useful break-loose torque caused by a rapid hardening reaction in the presence of difunctional carboxylic acid. When a bolt and a nut are jointed, the small quantity of air solubilized in the anaerobic adhesive composition is excluded, and at the same time a hardening reaction is initiated. The reaction proceeds of itself under the condition.

In the preparation of anaerobic adhesive composition of this invention, first of all, monomers, oligomers and inhibitors are mixed and agitated under oxygen atmosphere. Subsequently, each of reducers and oxidizers is added to the mixture, followed by the addition of difunctional carboxylic acid. Thereafter, in order to increase the viscosity of the anaerobic adhesive composition, polyethylene resin (particle size: below $10\text{ }\mu\text{m}$) and fumed silica (particle size: below $5\text{ }\mu\text{m}$) as thickening agents are added.

Monomers used in this invention are one or more selected from ethyleneglycol di(metha)acrylate, diethyleneglycol di(metha)acrylate, triethyleneglycol di(metha)acrylate, tetraethyleneglycol di(metha)acrylate, trimethylolpropane tri(metha)acrylate, styrene, chlorostyrene, vinyltoluene, α -methylstyrene, vinylacetate, methylacrylate, ethylacrylate, butylacrylate and methylmethacrylate.

Besides above monomers, oligomers used in this invention are one or more selected from mono or poly(metha)acrylate oligomer of bisphenolic compound, α, ω -diacryloyl-(bisethyleneglycol)-phthalate and α, ω -tetraacryloyl-(bistrimethylolpropane)-tetrahydrophthalate, and the acrylic oligomers containing aliphatic and aromatic urethane groups or polyether groups.

In order to get the enhancement of adhesive force through a rapid hardening reaction, a difunctional carboxylic acid, represented by formula I is used in this invention. The difunctional carboxylic acid is one or more selected from malonic acid, succinic acid, adipic acid, itaconic acid, pimelic acid, terephthalic acid and decanoic acid.

The quantity of difunctional carboxylic acid can be blended within 0.0001-10 parts in weight in proportion to 100 parts in weight of a mixture of monomers and oligomers. If the amount is less than 0.0001 part in weight, the promotion of a hardening reaction may be negligible, but may be possible in the quantity more than 10 parts in weight: the storage stability of the anaerobic adhesive composition may be lowered, so that the composition of the carboxylic acid should be properly controlled within above range.

According to this invention, an inhibitor is one or more selected from hydroquinone, methylhydroquinone, hydroquinone monomethylether, naphthoquinone, penanthraquinone, anthraquinone, sebenzoquinone, catechol, *t*-butylcatechol, 2,6-*t*-butyl-4-methylphenol, phenothiazine, picric acid phenothiazine and hydroxydiphenylamine. In addition, a metal ion chelating agent is used one or more selected from ethylenediamine tetraacetic acid and its salt.

The quantity of inhibitor can be added 0.0001-3 parts in weight in proportion to 100 parts in weight of a mixture of monomers and oligomers. If the quantity is less than 0.0001 part in weight, the effect of inhibition may be insufficient, finally lowering the stability in storage, but in the quantity more than 3 parts in weight, the break-loose torque may be lowered, as the hardening time lengthened.

According to this invention, the combination of oxidizer/reducer as an initiator is used. An oxidizer is one or more selected from *t*-butylhydroperoxide, cumenhydroperoxide, di-*t*-butylhydroperoxide, methylethylketoneperoxide,

dicumylperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide, diisopropylbenzene hydroperoxide, *t*-butylbenzoate and *t*-butylperoxyacetate.

A reducer is one or more selected from phenyl- α -naphthylamine, *N,N'*-dimethyl-*p*-toluidine, *N,N'*-dimethylaniline, triethylenetetramine, 5 diethylenetriamine, tri-*N*-butylamine, *o*-benzoic sulfimide, acetylthiourea, ethylene thiourea and 2-mercaptobenzothiazole.

An initiator is used as the form combined one or more. The quantity of initiator can be added 0.001-10 parts in weight in proportion to 100 parts in weight of a mixture of monomers and oligomers. If the quantity is less than 10 0.001 part in weight, the effect of initiation is insufficient, but in the quantity more than 10 parts in weight, the storage stability of the anaerobic adhesive composition may be lowered, so that the composition of the initiator should be properly controlled within above range.

Further features and advantages will be apparent from the following 15 examples containing some Tables. The following examples illustrate the ways in which the principle of this invention has been applied, but are not to be construed as limiting its scope.

Table 1. Anaerobic adhesive compositions blended difunctional carboxylic acids.

Run	Difunctional carboxylic acid				Anaerobic adhesive composition		
	Name	Structural formula	Acid dissociation constant*		Hardening time (min)	Break-loose torque (kg-cm)	Stability in storage**
			pK ₁	pK ₂			
1	Oxalic Acid	HO ₂ CCO ₂ H	1.27	4.27	15	51	O
2	Malonic Acid	HO ₂ CCH ₂ CO ₂ H	2.83	5.70	13	73	O
3	Succinic Acid	HO ₂ C(CH ₂) ₂ CO ₂ H	4.21	5.64	10	57	O
4	Maleic Acid	HO ₂ C(CH=CH)CO ₂ H	1.91	6.33	10	85	O
5	Adipic Acid	HO ₂ C(CH ₂) ₄ CO ₂ H	4.42	5.41	8	93	O
6	Itaconic Acid	HO ₂ CCH ₂ C(=CH ₂)CO ₂ H	-	-	8	91	O
7	Pimelic Acid	HO ₂ C(CH ₂) ₅ CO ₂ H	4.50	5.40	10	49	O
8	Terephthalic Acid	HO ₂ C(C ₆ H ₄)CO ₂ H	2.95	5.40	14	69	O
9	Decanoic Acid	HO ₂ C(CH ₂) ₈ CO ₂ H	4.59	5.59	15	61	O
10	Cumene Hydroperoxide	C ₆ H ₅ C(CH ₃) ₂ OOH	12.60	-	-	-	O
11	None	-	-	-	30	30	O

* John A. Dean, Handbook of Organic Chemistry, Section 8, McGRAW-HILL, New York,

5 1987; Section 8, pp.8-2~8-55.

** The observation whether the viscosity increases or not; not noticed: O, noticed: X.

Examples ①~1-13:

By separate experiments as shown in Table 1 above-mentioned,
 10 anaerobic adhesive compositions containing difunctional carboxylic acids were prepared and briefly estimated: it was found that the anaerobic adhesive composition without a difunctional carboxylic acid exhibited longer hardening time and less break-loose torque, whereas the anaerobic adhesive composition

with it exhibited a hardening time less than 15 min. and the break-loose torque after 24 hr was also very useful.

In relation to this, the anaerobic adhesive composition (Table 2a, run ①~12) was prepared as follows. That is, 10g of ethyleneglycol dimethacrylate, 10g of 2-hydroxyethyl methacrylate and 10g of tetraethyleneglycol dimethacrylate as components of monomers and oligomers were added to a reactor with reflux condenser and agitated at 120rpm under 120cc/min of oxygen flow. Then, 0.05g of hydroquinone methylether as an inhibitor was added and agitated for 10mins, followed by the addition of 3g of cumene hydroperoxide as an oxidizer.

Thereafter, 0.15g of *o*-benzoic sufimide and 0.40g of *N,N'*-dimethyl-*p*-toluidine as reducers were added and then sufficiently agitated. Finally, 1.46g(0.010 mol) of adipic acid (cf. run 5 of Table 1) and 3.30g of polyethylene powder(5 μ m) were added and further agitated for 20min, consequently preparing an anaerobic adhesive composition of this invention.

In addition, some physical properties of the anaerobic adhesive composition were measured as follows:

- (1) Hardening time(min): after a part of bolt(1/4 inch of diameter, 3 inch of length) made by stainless steel is coated, a nut made by stainless steel as a counter part is loosely jointed on its coated surface at 25°C. A hardening time based on the earliest time until the nut is not moved by fingers is measured.
- (2) Break-loose torque(kg-cm): the bolt-nut was fastened at 25°C, and left to postcure at 25°C for 24 hrs. The test was performed by using a torque wrench.
- (3) Stability in storage: the anaerobic adhesive composition which a hardening reaction in a bath at 80°C didn't happen in 10 days was required.
- (4) Viscosity: the value is measured by RVDVI+ viscometer.

Comparative Examples ②~1-15:

An anaerobic adhesive composition was prepared in the same methods

as described in Examples ①~1-13.

Table 2a*. Anaerobic adhesive compositions.

Run		Anaerobic adhesive composition												
		Basic composition (g)					Hardening promotor						Thicken- ing agent	
M ₁	M ₂	M ₃	M ₄	HQ	QH	A ₁	A ₂	A ₃	CA ₁ (mol)	CA ₂ (mol)	T ₁	T ₂		
①	1	20	10	-	-	003	20	050	010	-	-	0003	-	-
	2	15	15	-	-	003	20	050	010	-	-	0003	-	-
	3	10	20	-	-	003	20	050	010	-	-	0003	-	-
	4	10	20	-	-	004	20	050	010	-	-	0005	-	-
	5	10	12	6	2	004	20	050	010	-	-	0003	-	-
	6	10	12	4	4	004	20	050	010	-	-	0003	-	-
	7	12	12	6	-	004	30	050	010	-	-	0008	-	-
	8	12	12	-	6	004	30	040	010	-	-	0008	-	-
	9	12	10	2	6	004	30	040	015	-	-	0008	-	-
	10	12	10	8	-	004	30	040	015	-	-	0010	-	-
	11	10	10	10	-	004	30	040	015	-	-	0010	-	-
	12	10	10	10	-	005	30	040	015	-	-	0010	330	-
	13	10	10	10	-	005	30	040	015	-	-	0010	450	-
②	1	20	20	-	-	003	20	050	-	-	-	-	-	-
	2	15	15	-	-	003	20	050	010	-	-	-	-	-
	3	15	15	-	-	003	20	050	010	-	-	-	-	-
	4	10	15	-	-	003	20	050	-	020	-	-	-	-
	5	10	10	-	-	003	20	030	-	040	-	-	-	-
	6	10	10	-	-	003	20	030	030	-	-	-	-	-
	7	10	10	-	-	003	20	050	010	-	0003	-	-	-
	8	10	10	-	-	004	30	100	010	-	-	0008	-	-
	9	12	12	-	6	004	30	200	040	-	-	0008	-	-
	10	12	12	6	-	004	90	050	010	-	-	0008	-	-
	11	12	12	8	-	001	30	050	010	-	-	0001	-	-
	12	12	12	8	-	004	30	050	010	-	-	0300	-	-
	13	12	12	10	-	005	30	045	015	-	-	0010	-	330
	14	10	10	10	-	005	30	040	015	-	-	0010	-	450
	15	10	10	10	-	005	30	040	015	-	-	0010	750	-

* ① : examples; ② : comparative examples; M₁ : ethyleneglycol dimethacrylate; M₂ : 2-hydroxyethyl methacrylate; M₃ : tetraethyleneglycol dimethacrylate; M₄ : urethaneacrylate (Aronics M-1100, Dong-A Synthetic Industrial Co., Japan); HQ : hydroquinone methylether; QH : cumene hydroperoxide; A₁ : *o*-benzoic sulfimide; A₂ : *N,N'*-dimethyl-*p*-toluidine; A₃ : titanium dioxide; CA₁ : oxalic acid; CA₂ : adipic acid; each of CA₁ and CA₂ :

calculated by mol concentration; T₁ : polyethylene powder(5 μ m of average diameter); T₂ : fumed silica(5 μ m of average diameter).

Table 2b*. Physical properties of anaerobic adhesive compositions.

Run		Hardening time (min)	Break-loose torque (kg-cm)	Stability in storage	Viscosity (cp)
①	1	15	61	O	-
	2	13	65	O	-
	3	8	66	O	-
	4	8	69	O	-
	5	9	80	O	105
	6	15	73	O	156
	7	8	86	O	183
	8	9	68	O	232
	9	9	72	O	240
	10	9	86	O	202
	11	8	93	O	214
	12	11	119	O	680
	13	12	129	O	1236
②	1	45	32	O	-
	2	23	34	O	-
	3	370	16	O	-
	4	10	10	X	-
	5	8	55	X	-
	6	22	47	O	-
	7	25	39	O	-
	8	23	45	X	-
	9	150	23	X	232
	10	10	55	X	186
	11	18	37	X	203
	12	10	84	X	211
	13	11	93	X	544
	14	11	101	X	832
	15	39	53	X	-

5 * ① and ② represent examples and comparative ones, respectively.

As shown in Table 2b, anaerobic adhesive compositions using an
hardening promoter without difunctional carboxylic acid groups(comparative
examples ②~1-7); the anaerobic adhesive compositions using titanium dioxide
10 as an auxiliary oxidizer(comparative examples ②~4,5); the anaerobic adhesive

composition using oxalic acid (comparative example ②~7); the anaerobic adhesive compositions containing an excessive quantity of reducer and oxidizer as an initiator (comparative examples ②~8,9); the anaerobic adhesive composition using an excessive quantity of urethaneacrylate (comparative example ②~9); the anaerobic adhesive composition containing an excessive quantity of cumene hydroperoxide (comparative example ②~10); the anaerobic adhesive composition using an insufficient quantity of difunctional carboxylic acid (comparative example ②~11) showed relatively longer hardening time and less break-loose torque. By separate samples, the anaerobic adhesive composition using an excessive quantity of difunctional carboxylic acid or fumed silica (comparative examples ②~12-14) showed the increase of acidity in solution, followed by the poor stability in storage. Also, the anaerobic adhesive composition containing an excessive quantity of thickening agent (comparative example ②~15) showed a great difficulty in mixing. On the other hand, comparative examples ②~4, 5, 8-15 showed the poor stability in storage.

Especially, referring to the examples ①~1-13 of this invention, it was found that the break-loose torque of anaerobic adhesive compositions using a thickening agent (examples ①~12,13) was better than that without a thickening agent (examples ①~1-11).

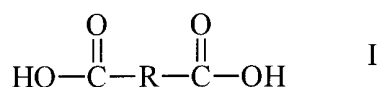
As above-mentioned, the anaerobic adhesive composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents in the presence of difunctional carboxylic acid exhibited the rapid velocity in a hardening reaction, the good stability in storage, and the good strength in break-loose torque.

In this context, the anaerobic adhesive composition according to this invention is applicable to the fastening between a bolt and a nut, and the assembly of precision apparatuses and electric/electronic parts.

CLAIMS

What is claimed is:

1. An anaerobic adhesive composition comprising monomers, oligomers, inhibitors, oxidizers, reducers and thickening agents which blends 0.0001 - 10
5 parts in weight of a difunctional carboxylic acid, expressed by the following formula I, in proportion to 100 parts in weight of a mixture of monomers and oligomers:



- 10 wherein R is $(\text{CH}_2)_n$ or $\text{CH}_2\text{C}(\text{=CH}_2)$ and n is an integer of 2 to 10.

2. The anaerobic adhesive composition according to claim 1, wherein the difunctional carboxylic acid is one or more selected from malonic acid, succinic acid, adipic acid, itaconic acid, pimelic acid, terephthalic acid and decanoic acid.

15

3. The anaerobic adhesive composition according to claim 1, wherein the monomers are one or more selected from ethyleneglycol di(metha)acrylate, diethyleneglycol di(metha)acrylate, triethyleneglycol di(metha)acrylate, tetraethyleneglycol di(metha)acrylate, trimethylolpropane tri(metha)acrylate,
20 styrene, chlorostyrene, vinyltoluene, α -methylstyrene, vinylacetate, methylacrylate, ethylacrylate, butylacrylate and methylmethacrylate.

4. The anaerobic adhesive composition according to claim 1, wherein the oligomers are one or more selected from mono or poly-(metha)acrylate
25 oligomer of bisphenolic compound containing α, ω -diacryloyl-(bisethyleneglycol)-phthalate and α, ω -tetraacryloyl-(bistrimethylolpropane)-tetrahydrophthalate, and acrylic oligomers having aliphatic/aromatic urethane groups and polyether groups.

5. The anaerobic adhesive composition according to claim 1, wherein the inhibitors are one or more selected from hydroquinone, methylhydroquinone, hydroquinonemonomethylether, naphthoquinone, penanthraquinone, anthraquinone, sebenzoquinone, catechol, *t*-butylcatechol, 2,6-*t*-butyl-4-methylphenol, phenothiazine, picric acid phenothiazine and hydroxydiphenylamine.

6. The anaerobic adhesive composition according to claim 1, wherein the oxidizers are one or more selected from *t*-butylhydroperoxide, cumenehydroperoxide, di-*t*-butylhydroperoxide, methylethylketoneperoxide, dicumylperoxide, 2,5-dimethylhexyl-2,5-dihydroperoxide, diisopropylbenzendhydroperoxide, *t*-butylbenzoate and *t*-butylperoxyacetate.

7. The anaerobic adhesive composition according to claim 1, wherein the reducers are one or more selected from phenyl- α -naphthylamine, *N,N'*-dimethyl-*p*-toluidine, *N,N'*-dimethylaniline, triethylenetetramine, diethylenetriamine, tri-*N*-butylamine, *o*-benzoic sulfimide, benzoic acid sulfimide, acetylthiourea, ethylene thiourea and 2-mercaptobenzothiazole.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00285

CLASSIFICATION OF SUBJECT MATTER IPC ⁷ : C 09 J 4/00 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) IPC ⁷ : C 09 J 4/00 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) Questel WPI		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 06219038 A (IAPC) 19 January 1987 (19.01.87) (abstract) WPI, London, U.K.: Derwent Publications Ltd., Questel/ Orbit, Paris/ France. DW 198708, Accession No. 1987-053881.	1
A	DD 290776 A7 (KOLLOIDCHEMIE GMBH) 13 June 1991 (13.06.91) claims. -----	
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
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Date of the actual completion of the international search 7 April 2000 (07.04.2000)		Date of mailing of the international search report 2 August 2000 (02.08.2000)
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 99/00285

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DD	A7	290776	13-06-1991	none	