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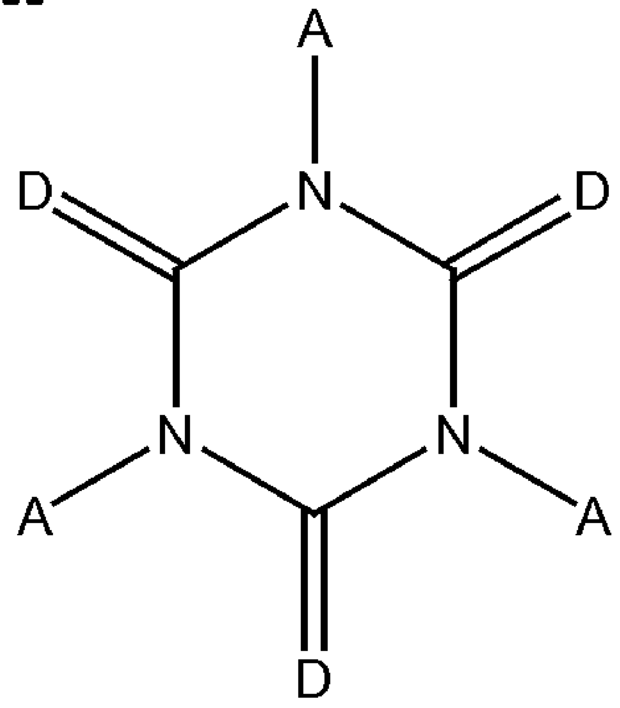
*[Continued on next page]*

(54) **Title**: CYANOACRYLATE COMPOSITIONS

**A**



(57) **Abstract**: This invention relates to cyanoacrylate compositions that include, in addition to the cyanoacrylate component, a compound embraced by structure A: where D is independently a member selected from O or S, and A is independently a member selected from hydrogen, linear, branched or cyclic alkyl groups having from 1 to about 20 carbon atoms, alkenyl groups having from 2 to about 20 carbon atoms, alkynyl groups having from 2 to about 20 carbon atoms, and aryl groups having from 6 to about 20 carbon atoms, with or without interruption or substitution by a member selected from halogen, silicon, hydroxy, ester, and sulfate, provided that at least one A is not H and that at least one A has at least one carboxyl group attached thereto.

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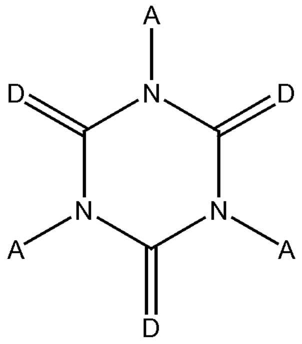
# CYANOACRYLATE COMPOSITIONS

## BACKGROUND OF THE INVENTION

### Field of the Invention

**[0001]** This invention relates to cyanoacrylate compositions that include, in addition to a cyanoacrylate component, a compound embraced by structure **A**:



**A**

where D is independently a member selected from O or S, and

A is independently a member selected from hydrogen, linear, branched or cyclic alkyl groups having from 1 to about 20 carbon atoms, alkenyl groups having from 2 to about 20 carbon atoms, alkynyl groups having from 2 to about 20 carbon atoms, and aryl groups having from 6 to about 20 carbon atoms, with or without interruption or substitution by a member selected from halogen, silicon, hydroxy, ester, and sulfate, provided that at least one A is not H and that at least one A has at least one carboxyl group attached thereto.

## Brief Description of Related Technology

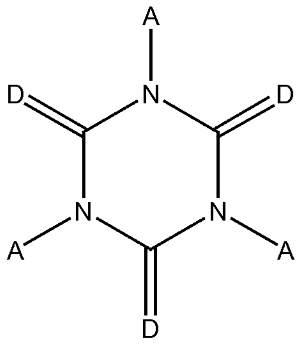
**[0002]** Cyanoacrylate adhesive compositions are well known, and widely used as quick setting, instant adhesives with a wide variety of uses. See H.V. Coover, D.W. Dreifus and J.T. O'Connor, "Cyanoacrylate Adhesives" in Handbook of Adhesives, 27, 463-77, I. Skeist, ed., Van Nostrand Reinhold, New York, 3rd ed. (1990). See also G.H. Millet, "Cyanoacrylate Adhesives" in Structural Adhesives: Chemistry and Technology, S.R. Hartshorn, ed., Plenun Press, New York, p. 249-307 (1986).

**[0003]** However, some substrates to be adhesively bonded are routinely acknowledged as having less than desirable performance with cyanoacrylate compositions as the adhesive material. One of those substrates is aluminum.

**[0004]** Thus, it would be desirable to provide cyanoacrylate compositions that demonstrate desirable performance on difficult-to-bond substrates, such as aluminum.

## SUMMARY OF THE INVENTION

**[0005]** The present invention is directed to a cyanoacrylate composition, which includes beyond a cyanoacrylate component, a compound embraced by structure **A**:



**A**

where D is independently a member selected from O or S, and

A is independently a member selected from hydrogen, linear, branched or cyclic alkyl groups having from 1 to about 20 carbon atoms, alkenyl groups having from 2 to about 20 carbon atoms, alkynyl groups having from 2 to about 20 carbon atoms, and aryl groups having from 6 to about 20 carbon atoms, with or without interruption or substitution by a member selected from halogen, silicon, hydroxy, ester, and sulfate, provided that at least one A is not H and that at least one A has at least one carboxyl group attached thereto.

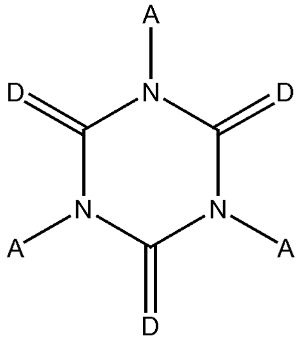
**[0006]** This invention is also directed to a method of preparing the inventive compositions. Also, the invention is directed to a method of bonding together two substrates, which method includes applying to at least one of the substrates a composition as described above, and thereafter mating together the substrates. In one aspect, at least one of the substrates should be constructed of a metal, such as steel or aluminum.

**[0007]** In addition, the present invention is directed to reaction products of the inventive compositions.

**[0008]** The invention will be more fully understood by a reading of the section entitled "Detailed Description of the Invention", which follows.

## DETAILED DESCRIPTION OF THE INVENTION

**[0009]** As noted above, this invention is directed to a cyanoacrylate composition, which includes beyond a cyanoacrylate component, a compound embraced by structure **A**:



**A**

where D is independently a member selected from O or S, and

A is independently a member selected from hydrogen, linear, branched or cyclic alkyl groups having from 1 to about 20 carbon atoms, alkenyl groups having from 2 to about 20 carbon atoms, alkynyl groups having from 2 to about 20 carbon atoms, and aryl groups having from 6 to about 20 carbon atoms, with or without interruption or substitution by a member selected from halogen, silicon, hydroxy, ester, and sulfate, provided that at least one A is not H and that at least one A has at least one carboxyl group attached thereto.

**[0010]** The cyanoacrylate component includes cyanoacrylate monomers which may be chosen with a raft of substituents, such as those represented by $H_2C=C(CN)-COOR$, where R is selected from $C_{1-15}$ alkyl, $C_{2-20}$ alkoxyalkyl, $C_{3-20}$ cycloalkyl, $C_{2-20}$ alkenyl, $C_{7-20}$ aralkyl, $C_{6-20}$ aryl, allyl and $C_{1-15}$ haloalkyl groups. Desirably, the cyanoacrylate monomer is selected from methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl cyanoacrylates, butyl cyanoacrylates (such as n-butyl-2-cyanoacrylate), octyl cyanoacrylates, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylate and combinations thereof. A particularly desirable one is ethyl-2-cyanoacrylate.

**[0011]** The cyanoacrylate component should be included in the compositions in an amount within the range of from about 50% to about 99% by weight, with the range of about 75% to about 98% by weight being desirable, and about 85 to about 95% by weight of the total composition being particularly desirable.

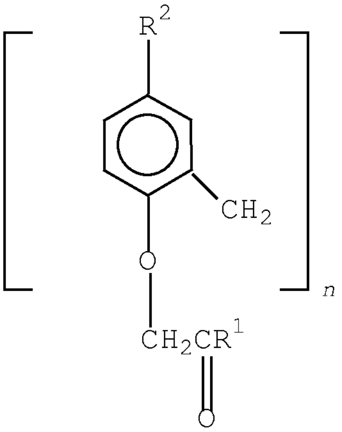
**[0012]** The compound embraced by structure **A** may include a variety of possible materials. Particularly desirable compounds include those where D is O. In addition, particularly desirable compounds include those where at least one A is a methyl, ethyl or propyl carboxylic acid, such as where each A is ethylene carboxylic acid.

**[0013]** The compound embraced by structure **A** should be present in a concentration of about 0.0001% to about 10% by weight, such as about 0.0003% to about 3% by weight, with about 0.05% to about 1% being particularly desirable.

**[0014]** Accelerators may also be included in the inventive rubber toughened cyanoacrylate compositions, such as any one or more selected from calixarenes and oxacalixarenes, silacrowns, crown ethers, cyclodextrins, poly(ethyleneglycol) di(meth)acrylates, ethoxylated hydric compounds and combinations thereof.

**[0015]** Of the calixarenes and oxacalixarenes, many are known, and are reported in the patent literature. See e.g. U.S. Patent Nos. 4,556,700, 4,622,414, 4,636,539, 4,695,615, 4,718,966, and 4,855,461, the disclosures of each of which are hereby expressly incorporated herein by reference.

**[0016]** For instance, as regards calixarenes, those within the following structure are useful herein:

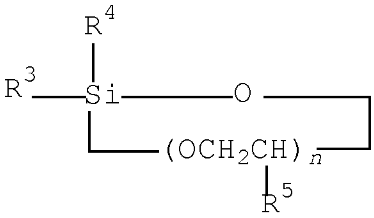


where here $R^1$ is $C_{1-20}$ alkyl, $C_{1-20}$ alkoxy, substituted alkyl or substituted alkoxy; $R^2$ is H or $C_{1-20}$ alkyl; and n is 4, 6 or 8.

**[0017]** One particularly desirable calixarene is tetrabutyl tetra[2-ethoxy-2-oxoethoxy]calix-4-arene.

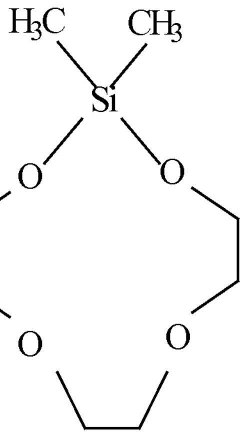
**[0018]** A host of crown ethers are known. For instance, examples which may be used herein either individually or in combination include 15-crown-5, 18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5-dibenzo-24-crown-8, dibenzo-30-crown-10, tribenzo-18-crown-6, asym-dibenzo-22-crown-6, dibenzo-14-crown-4, dicyclohexyl-18-crown-6, dicyclohexyl-24-crown-8, cyclohexyl-12-crown-4, 1,2-decalyl-15-crown-5, 1,2-naphtho-15-crown-5, 3,4,5-naphtyl-16-crown-5, 1,2-methyl-benzo-18-crown-6, 1,2-methylbenzo-5, 6-methylbenzo-18-crown-6, 1,2-t-butyl-18-crown-6, 1,2-vinylbenzo-15-crown-5, 1,2-vinylbenzo-18-crown-6, 1,2-t-butyl-cyclohexyl-18-crown-6, asym-dibenzo-22-crown-6 and 1,2-benzo-1,4-benzo-5-oxygen-20-crown-7. See U.S. Patent No. 4,837,260 (Sato), the disclosure of which is hereby expressly incorporated here by reference.

**[0019]** Of the silacrowns, again many are known, and are reported in the literature. For instance, a typical silacrown may be represented within the following structure:

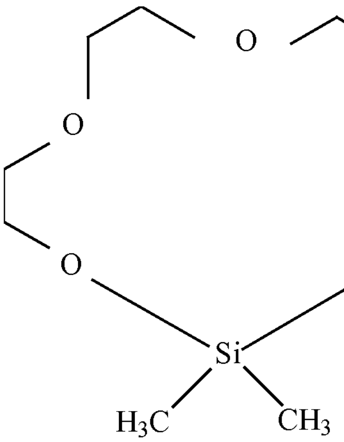


where here $R^3$ and $R^4$ are organo groups which do not themselves cause polymerization of the cyanoacrylate monomer, $R^5$ is H or $CH_3$ and n is an integer of between 1 and 4. Examples of suitable $R^3$ and $R^4$ groups are R groups, $C_{1-20}$ alkoxy groups, such as methoxy, and $C_{6-20}$ aryloxy groups, such as phenoxy. The $R^3$ and $R^4$ groups may contain halogen or other substituents, an example being trifluoropropyl. However, groups not suitable as $R^4$ and $R^5$ groups are basic groups, such as amino, substituted amino and alkylamino.

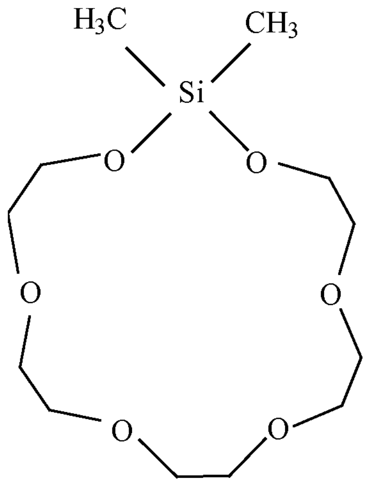
**[0020]** Specific examples of silacrown compounds useful in the inventive compositions include:



dimethylsila-11-crown-4;



dimethylsila-14-crown-5;

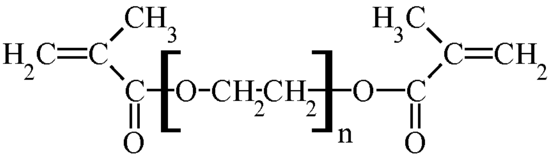


and dimethylsila-17-crown-6.

<u>See</u> <u>e.g.</u> U.S. Patent No. 4,906,317 (Liu), the disclosure of which is hereby expressly incorporated herein by reference.

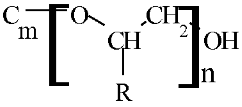
**[0021]** Many cyclodextrins may be used in connection with the present invention. For instance, those described and claimed in U.S. Patent No. 5,312,864 (Wenz), the disclosure of which is hereby expressly incorporated herein by reference, as hydroxyl group derivatives of an α, β or γ-cyclodextrin which is at least partly soluble in the cyanoacrylate would be appropriate choices for use herein as the first accelerator component.

**[0022]** For instance, poly(ethylene glycol) di(meth)acrylates suitable for use herein include those within the following structure:



where n is greater than 3, such as within the range of 3 to 12, with n being 9 as particularly desirable. More specific examples include PEG 200 DMA, (where n is about 4) PEG 400 DMA (where n is about 9), PEG 600 DMA (where n is about 14), and PEG 800 DMA (where n is about 19), where the number (e.g., 400) represents the average molecular weight of the glycol portion of the molecule, excluding the two methacrylate groups, expressed as grams/mole (i.e., 400 g/mol). A particularly desirable PEG DMA is PEG 400 DMA.

**[0023]** And of the ethoxylated hydric compounds (or ethoxylated fatty alcohols that may be employed), appropriate ones may be chosen from those within the following structure:



where $C_m$ can be a linear or branched $C_{1-20}$ alkyl or $C_{2-20}$ alkenyl chain, m is an integer between 1 to 30, such as from 5 to 20, n is an integer between 2 to 30, such as from 5 to 15, and R may be H or alkyl, such as $C_{1-6}$ alkyl.

**[0024]** When used, the accelerator embraced by the above structures should be included in the compositions in an amount within the range of from about 0.01% to about 10% by weight, with the range of about 0.1 to about 0.5% by weight being desirable, and about 0.4% by weight of the total composition being particularly desirable.

**[0025]** A stabilizer package is also ordinarily found in cyanoacrylate compositions. The stabilizer package may include one or more free radical stabilizers and anionic stabilizers, each of the identity and amount of which are well known to those of ordinary skill in the art. See e.g. U.S. Patent Nos. 5,530,037 and 6,607,632, the disclosures of each of which are hereby incorporated herein by reference.

**[0026]** Other additives may be included in the inventive cyanoacrylate compositions to confer additional physical properties, such as improved shock resistance, thickness (for instance, polymethyl methacrylate ("PMMA")), thixotropy (for instance fumed silica), silicia (for coefficient of thermal expansion ("CTE") matching), color, and enhanced resistance to thermal degradation [for instance, maleimide compounds such as N,N'-meta-phenylene bismaleimide (see U.S. Patent No. 3,988,299 (Malofsky)), certain mono, poly or hetero aromatic compounds characterized by at least three substitutions on an aromatic ring thereof, two or more of which being electron withdrawing groups (U.S. Patent No. 5,288,794 (Attarwala)), certain quinoid compounds (U.S. Patent No. 5,306,752 (Attarwala)), certain sulfur-containing compounds, such as an anhydrosulfite, a sulfoxide, a sulfite, a sulfonate, a methanesulfonate or a p-toluenesulfonate (U.S. Patent No. 5,328,944 (Attarwala)), or certain sulfur-containing compounds, such as a sulfinate, a cyclic sultinate naphthosultone compound substituted with at least one strong electron withdrawing group at least as strongly electron withdrawing as nitro (U.S. Patent No. 5,424,343 (Attarwala)), and alkylating agents such as polyvinyl benzyl chloride, 4-nitrobenzyl chloride, and combinations thereof, silylating agents, and combinations thereof (U.S. Patent No. 6,093,780 (Attarwala)), the disclosures of each of which are hereby incorporated herein by reference]. Such additives therefore may be selected from certain acidic materials (like citric acid), thixotropy or gelling agents, thickeners, dyes, thermal degradation resistance enhancers, and combinations thereof. See e.g. U.S. Patent Application Publication No. 2006/0094833 and U.S. Patent Nos. 5,306,752, 5,424,344 and 6,835,789, the disclosures of each of which are hereby incorporated herein by reference.

**[0027]** These other additives may be used in the inventive compositions individually in an amount from about 0.05% to about 20%, such as about 1% to 15%, desirably 5% to 10% by weight, depending of course on the identity of the additive.

**[0028]** The inventive compositions may also be prepared in a two part format, in which the cyanoacrylate component is present in one chamber of a dual chamber cartridge and the compound embraced by structure **A** is present in a second chamber. The contents of the first and second chambers may be expressed and mixed through a mixing nozzle. The so-mixed composition may then be applied to the desired substrate(s) prior to mating.

**[0029]** In addition, the inventive composition may be split and applied in a two step manner. That is, the compound embraced by structure **A** may be first applied onto a substrate surface followed by application of a cyanoacrylate composition. The compound embraced by structure **A** may be dissolved or dispersed in a liquid, which may evaporate or be otherwise removed from the substrate surface prior to application of the cyanoacrylate composition. To the extent the liquid used to dissolve or disperse the compound embraced by structure **A** has a higher boiling point and may be itself reactive, a residue of the liquid may desirably remain on the surface of the substrate.

**[0030]** In another aspect of the invention, there is provided a method of preparing the so-described compositions. The method includes providing a cyanoacrylate component, and combining therewith with mixing a compound embraced by structure **A**.

**[0031]** In another aspect of the invention, there is provided a method of bonding together two substrates, which method includes applying to at least one of the substrates a composition as described above, and thereafter mating together the substrates for a time sufficient to permit the adhesive to fixture. For many applications, the substrate should become fixed by the inventive compositions in less than about 150 seconds, and depending on the substrate as little as about 30 seconds. In addition, the inventive composition should develop shear strength on the substrates between which they have been applied, as well as side impact strength and fracture toughness.

**[0032]** These aspects of the invention will be further illustrated by the examples which follow.

## EXAMPLES

### Example 1

**[0033]** Four samples were evaluated for their tensile shear strength on a variety of substrates.

**[0034]** Sample Nos. 1-4 were prepared by mixing together the noted constituents for a sufficient period of time to ensure substantial homogeneity of the constituents. Ordinarily, about 30 minutes should suffice, depending of course on the quantity of the constituents used.

**Table 1**

| Constituents | | Sample No./Amt. (wt. %) | | | |
|---|---|---|---|---|---|
| **Type** | **Identity** | **1** | **2** | **3** | **4** |
| CA | Ethyl-2-CA | 91.75 | 91.75 | 98.67 | 98.64 |
| Compound A | CIC[1] | -- | 0.5 | -- | 0.03 |
| Accelerator | Crown Ether | 0.25 | 0.25 | 0.26 | 0.26 |
| Stabilizer | $BF_3$ | 2 | 2 | 1.07 | 1.07 |
| Thickener | PMMA | 6 | 6 | -- | -- |

[1] Tris-(2-carboxyethyl) isocyanurate

**[0035]** Each sample was applied to the substrates listed below in Table 2 and tensile shear strength was measured.

**[0036]** By way of the background, the tensile shear strength was measured using 1"x4"x1/8" [2.54 cm x 10.12cm x 0.3 cm] metal or plastic substrates, with a 0.5 square inch (1.27 $cm^2$) overlap of the substrates, and the sample between the substrate overlap. The sample was allowed to cure at room temperature for 24 hours, after which time the resulting bond strength was measured using an Instron instrument, and is recorded below in Table 2.

**Table 2**

| Tensile Shear Strength in psi (conversion to kPa)/Substrate | Sample No. | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| Mild Steel | 10.74 (74.05) | 18.03 (124.31) | 8.52 (58.74) | 14.41 (99.35) |
| Aluminum | 10.37 (71.50) | 15.99 (110.25) | 10.46 (72.12) | 14.16 (97.63) |
| PVC | 13.27 (91.49) | 8.84 (60.95) | -- | -- |
| PC | 2.81 (19.37) | 2.57 (17.72) | -- | -- |
| ABS | 9.57 (65.98) | 9.96 (68.67) | -- | -- |

**[0037]** In addition, the tensile shear strength of Sample Nos. 3 and 4 was evaluated on mild steel and aluminum substrates after curing for 24 hours at a temperature of 60°C, as above. The results are recorded below in Table 3.

**Table 3**

| Tensile Shear Strength in psi (conversion to kPa)/Substrate | Sample No. | |
|---|---|---|
| | 3 | 4 |
| Mild Steel | 9.7<br>(68.88) | 22.64<br>(156.10) |
| Aluminum | 14.93<br>(102.94) | 18.71<br>(129.00) |

**[0038]** From the results set forth in Tables 2 and 3, it may be seen that cyanoacrylate compositions of the present invention show improved tensile shear strength on metal substrates and comparable tensile strength on plastic substrates, apart from PVC. In addition, curing at a temperature of 60°C seems to dramatically improve the measured tensile shear strength of unthickened cyanoacrylate compositions, particularly where the substrates are constructed from mild steel.

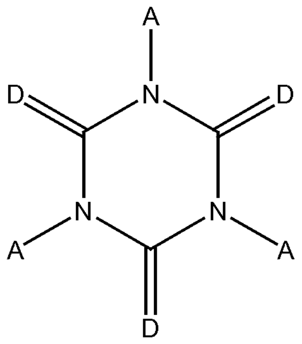
**[0039]** It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

**What is Claimed is**:

1. A cyanoacrylate composition comprising:

(a) a cyanoacrylate component; and

(b) a compound embraced within structure **A**:



**A**

wherein D is independently a member selected from the group consisting of O and S, and

A is independently a member selected from the group consisting of hydrogen, linear, branched or cyclic alkyl groups having from 1 to about 20 carbon atoms, alkenyl groups having from 2 to about 20 carbon atoms, alkynyl groups having from 2 to about 20 carbon atoms, and aryl groups having from 6 to about 20 carbon atoms, with or without interruption or substitution by a member selected from the group consisting of halogen, silicon, hydroxy, ester, and sulfate, provided that at least one A is not H and that at least one A has at least one carboxyl group attached thereto.

2. The composition of Claim 1, further comprising an accelerator.

3. The composition of Claim 2, wherein the accelerator is a member selected from the group consisting of calixarenes and oxacalixarenes, silacrowns, crown ethers, cyclodextrins,

poly(ethyleneglycol) di(meth)acrylates, ethoxylated hydric compounds and combinations thereof.

4. The composition as claimed in any preceding claim, further comprising a thickener.

5. The composition as claimed in any preceding claim further comprising a thixotrope.

6. The composition as claimed in any preceding claim wherein in the compound D is O and A is ethylene carboxylic acid.

7. The composition as claimed in any preceding claim wherein the compound is present in an amount between about 0.01 and about 10 percent by weight.

8. The composition as claimed in any preceding claim further comprising a filler.

9. The composition as claimed in any preceding claim further comprising a stabilizing amount of an acidic stabilizer and a free radical inhibitor.

10. The composition as claimed in any preceding claim wherein the cyanoacrylate component is selected from materials within the structure $H_2C=C(CN)-COOR$, wherein R is selected from $C_{1-15}$ alkyl, $C_{2-20}$ alkoxyalkyl, $C_{3-20}$ cycloalkyl, $C_{2-20}$ alkenyl, $C_{7-20}$ aralkyl, $C_{6-20}$aryl, allyl and $C_{1-15}$ haloalkyl groups.

11. The composition as claimed in any preceding claim wherein the cyanoacrylate component comprises ethyl-2-cyanoacrylate.

12. Reaction products of the composition as claimed in any preceding claim.

13. A method of bonding together two substrates, comprising the steps of:

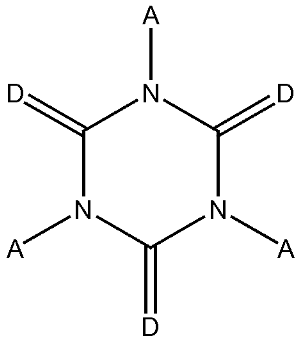
applying a cyanoacrylate composition as claimed in any of Claims 1 to 11, to at least one of the substrates and

mating together the substrates for a time sufficient to permit the composition to fixture.

14. A method of preparing a cyanoacrylate composition as claimed in any preceding claim, comprising the steps of:

providing a cyanoacrylate component, and

combining therewith with mixing a compound embraced by structure **A**:



**A**

wherein D is independently a member selected from the group consisting of O and S, and

A is independently a member selected from the group consisting of hydrogen, linear, branched or cyclic alkyl groups having from 1 to about 20 carbon atoms, alkenyl groups having from 2 to about 20 carbon atoms, alkynyl groups having from 2 to about 20 carbon atoms, and aryl groups having from 6 to about 20 carbon atoms, with or without interruption or substitution by a member selected from the group consisting of halogen, silicon, hydroxy, ester, and sulfate, provided that at least one A is not H and that at least one A has at least one carboxyl group attached thereto.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/055931

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. C08K5/3467 C08L35/00 C09J4/00 C09J133/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
C08K C08L C09J

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 practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 4 196 271 A (KIMURA KAORU [JP] ET AL)<br>1 April 1980 (1980-04-01)<br>the whole document<br>----- | 1-14 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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

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

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

| | |
|---|---|
| Date of the actual completion of the international search<br>28 July 2010 | Date of mailing of the international search report<br>04/08/2010 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040,<br>Fax: (+31–70) 340–3016 | Authorized officer<br>Trauner, H |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2010/055931

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US 4196271 A | 01-04-1980 | NONE | |

Form PCT/ISA/210 (patent family annex) (April 2005)