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(54) Title: TOUGHENED CYANOACRYLATE COMPOSITIONS

(57) Abstract: A cyanoacrylate adhesive composition having a toughening agent comprising poly(vinylidene-co-acrylonitrile) in combination with fumed silica. A useful amount of poly(vinylidene-co-acrylonitrile) is about 1.0 % by weight to about 20.0% by weight fumed silica is usefully present in amounts of 1-10% by weight.



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TOUGHENED CYANOACRYLATE COMPOSITIONS

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BACKGROUND OF THE INVENTION

Field Of The Invention

[0001] This invention relates to toughened cyanoacrylate compositions which exhibit improved peel strengths.

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Brief Description Of Related Technology

[0002] Cyanoacrylate compositions are well known as one component reactive adhesives, quick bonding and suitable for a variety of substrates. However, traditional cyanoacrylate-based adhesives tend to be brittle, and to have low peel strengths. A variety of additives and fillers have been proposed for addition to cyanoacrylate adhesive compositions to improve toughness and peel strengths.

[0003] U.S. Patent 4,102,945 describes a cyanoacrylate adhesive having enhanced peel strengths in which a cyanoacrylate is thickened by a copolymer or terpolymer including vinylidene chloride-acrylonitrile copolymers.

[0004] U.S. Patent No. 4,440,910 to O'Connor is directed to cyanoacrylate compositions having improved toughness, achieved through the addition of elastomers, i.e., acrylic rubbers. These rubbers are either (i) homopolymers of alkyl esters of

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acrylic acid; (ii) copolymers of another polymerizable monomer, such as lower alkenes, with an alkyl ester of acrylic acid or with an alkoxy ester of acrylic acid; (iii) copolymers of alkyl esters of acrylic acid; (iv) copolymers of alkoxy esters of acrylic acid; and (v) mixtures thereof.

[0005] U.S. Patent 4,444,933 to Columbus suggests the addition of a vinyl chloride/vinyl acetate copolymer to a cyanoacrylate adhesive to reduce adhesion to human skin.

[0006] U.S. Patent No. 4,560,723 to Millet et al. discloses a cyanoacrylate adhesive composition containing a toughening agent comprising a core-shell polymer and a sustainer comprising an organic compound containing one or more unsubstituted or substituted aryl groups. The sustainer is reported to improve retention of toughness after heat aging of cured bonds of the adhesive.

[0007] U.S. Patent No. 5,340,873 to Mitry discloses a cyanoacrylate adhesive composition having improved toughness by including an effective toughening amount of a polyester polymer derived from a dibasic aliphatic or aromatic carboxylic acid and a glycol.

[0008] U.S. Patent No. 5,994,464 to Ohsawa et al. discloses a cyanoacrylate adhesive composition containing a cyanoacrylate monomer, an elastomer miscible or compatible with the cyanoacrylate monomer, and a core-shell polymer being compatible, but not miscible, with the cyanoacrylate monomer.

[0009] There continues to be a need for cyanoacrylate adhesives with improved toughness and peel strengths.

SUMMARY OF THE INVENTION

[0010] As used herein, all compositions values are given in weight percent unless otherwise noted.

[0011] The present invention is directed to, in a first aspect, a cyanoacrylate composition which demonstrates enhanced peel strength including: a cyanoacrylate component; and a toughening agent comprising poly(vinylidene chloride-co-acrylonitrile) in combination with fumed silica.

[0012] In another aspect, the present invention is directed to a cyanoacrylate composition which demonstrates enhanced toughness including: a cyanoacrylate material; a toughening agent comprising poly(vinylidene chloride-co-acrylonitrile) in combination with fumed silica; and one or more additives selected from the group consisting of plasticizers, accelerators, fillers, opacifiers, thickeners, viscosity modifiers, inhibitors, thixotrophy conferring agents, stabilizers, dyes, thermal degradation reducers, and combinations thereof, where upon cure, the cyanoacrylate composition has an average peel strength of more than about 1 N/mm after curing at room temperature for about 72 hours and a post cure at about 121°C for about 2 hours.

[0013] In still yet another aspect, the present invention is directed to cyanoacrylate adhesive composition including about 1% to about 20% by weight of a toughening agent including poly(vinylidene chloride-co-acrylonitrile) in combination with about 1 to about 10% by weight fumed silica; one or more additives selected from the group consisting of accelerators, fillers, opacifiers, thickeners, viscosity modifiers, inhibitors, thixotrophy conferring agents, stabilizers, and combinations thereof; with the balance being cyanoacrylate.

[0014] In yet another aspect, the present invention is directed to a method of bonding two or more substrates including the steps of: providing at least two substrates; dispensing, on at least a portion of a surface of one or both

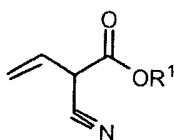
of the at least two substrates, a cyanoacrylate composition including about 1- about 20% by weight of poly(vinylidene chloride-co-acrylonitrile) in combination with from about 1 to about 10% by weight of fumed silica; contacting the surfaces of the at least two substrates having the cyanoacrylate composition there between; and curing the cyanoacrylate adhesive composition.

[0015] In still another aspect, the present invention is directed to a bonded assembly including: a first substrate having a first surface; another substrate having a second surface; and a cured cyanoacrylate composition disposed between the first and second surfaces, the composition having included prior to cure: a cyanoacrylate component; and a toughening agent comprising about 1 to about 20% by weight poly(vinylidene chloride-co-acrylonitrile) in combination with from about 1-10% by weight of fumed silica. Once cured, the toughening agent is copolymerized with the cyanoacrylate component forming an interpenetrating molecular network with the cyanoacrylate component. Preferably, the peel strength of the composition is greater than about 1N/mm after room temperature cure for about 72 hours.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The cyanoacrylate compositions of the present invention include toughening agents which provide enhanced peel strengths while providing thermal resistance and toughness in the cured compositions. The toughening agent useful in the present invention comprises poly(vinylidene chloride-co-acrylonitrile). A method of bonding substrates and the resultant bonded assembly are disclosed herein as well.

[0017] The cyanoacrylate compositions of the present invention include a cyanoacrylate component which include cyanoacrylate monomers, such as those represented by the structure:



where R¹ is selected from C₁₋₁₆ alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.

Preferably, 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, β-methoxyethyl cyanoacrylate and combinations thereof. A particularly desirable cyanoacrylate monomer is ethyl-2-cyanoacrylate. The cyanoacrylate component should be included in the compositions in an amount within the range of about 70% by weight to about 90% by weight, preferably about 75% by weight to about 85% by weight.

[0018] The compositions of the present invention may also contain additives such as stabilizers, accelerators, plasticizers, fillers, opacifiers, thickeners other than silica, viscosity modifiers, inhibitors, thixotrophy conferring agents other than silica, dyes, fluorescence markers, thermal degradation reducers, adhesion promoters, and combinations thereof, and the like. These additives are known to those of skill in the art.

[0019] The cyanoacrylate monomers are preferably stabilized using acid stabilizers of the Lewis or protonic types although combinations of nonvolatile sulfonic acids with gaseous

stabilizers such as NO, SO₂, SO₃, BF₃, and HF can provide a synergistic effect. A preferred stabilizer system for the present invention includes methane sulfonic acid ("MSA") and SO₂. Preferably, the amount of MSA is about 5 to about 25 ppm and a preferred amount of SO₂ is about 2 to about 30 ppm based on the amount of the cyanoacrylate monomer. More preferably, BF₃, another acidic gaseous stabilizer, may also be added in amounts of about 5 ppm to about 50 ppm based on the amount of the cyanoacrylate monomer. Advantageously, such small amounts of stabilizers used with the compositions of the present invention provide optimal performance without stability concerns.

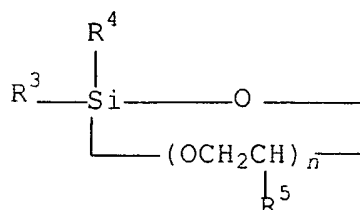
[0020] Inhibitors or free radical scavengers that may be useful in the cyanoacrylate compositions are of the phenolic type such as hydroquinone, *t*-butyl catechol, *p*-methoxy-phenol, and the like. A preferred inhibitor of the present invention is hydroquinone. The inhibitor is present in an amount of about 0.001% by weight to about 2.0% by weight, preferably about 0.02% to about 0.5% by weight. Other inhibitors suitable for use herein include butylated hydroxytoluene and butylated hydroxyanisole.

[0021] Accelerators that may be useful in the cyanoacrylate compositions include for example calixarenes, oxacalixarenes, and combinations thereof. 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.

[0022] Another potentially useful accelerator component is a crown ether. A host of crown ethers are known. For instance,

examples which may be used herein either individually or in combination, or in combination with the calixarenes and oxacalixarenes described above include 15-crown-5, 18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5, dibenzo-24-crown-8, 5 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-naphthyl-16-crown-5, 1,2-methyl-benzo-18-crown-6, 1,2-methylbenzo-5, 6-methylbenzo-10 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.

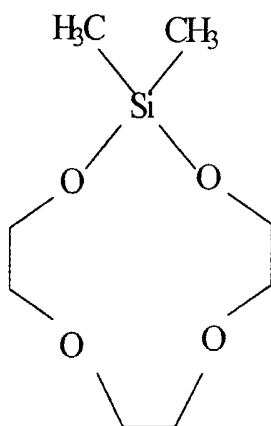
15 **[0023]** Other suitable accelerators include those described in U.S. Patent No. 5,312,864 (Wenz), which are hydroxyl group derivatives of an α -, β - or γ -cyclodextrin which is at least partly soluble in the cyanoacrylate; in U.S. Patent No. 4,906,317 (Liu), which are silacrown compounds to accelerate 20 fixturing and cure on de-activating substrates such as wood, examples of which are within the following structure:



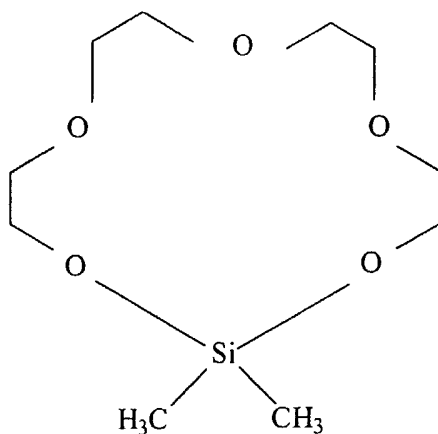
wherein R^3 and R^4 are organo groups which do not themselves cause polymerization of the cyanoacrylate monomer, R^5 is H or CH_3 and n is an integer of between 1 and 4. Examples of suitable R^3 and R^4 groups are R groups, alkoxy groups such as

methoxy, and 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.

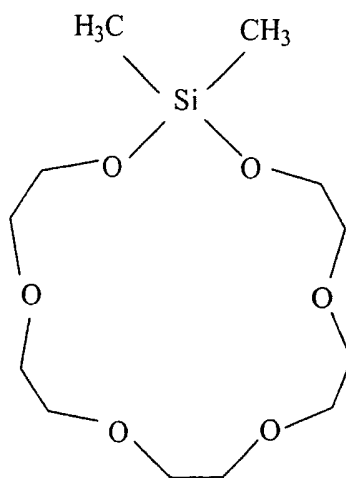
[0024] Specific examples of silacrown compounds useful in the inventive compositions include:



dimethylsila-11-crown-4;



dimethylsila-14-crown-5;



and dimethylsila-17-crown-6.

[0025] The accelerator component should be included in the compositions in an amount within the range of from about 0.1% to about 10% by weight, with the range of about 0.5% to about 5% by weight being desirable, and about 0.1% to about 1% by weight of the total composition being particularly desirable.

[0026] Phthalic anhydride and other plasticizers may also be added to the cyanoacrylate component to further aid in durability and impact, heat, and moisture resistance. The plasticizer is preferably present in an amount of about 0.005% by weight to about 5.0% by weight, more preferably about 0.01% by weight to about 2.0% by weight of the total composition.

[0027] The inventive compositions may also be thickened by the addition of thickeners, such as polymethyl methacrylate, in order to increase viscosity. Thickeners should be included in the inventive composition in an amount less than about 15%, such as within the range of about 0.5% to about 10%, by weight of the total composition.

[0028] The combination of the cyanoacrylate monomer and the additives will be referred to herein as the cyanoacrylate component.

[0029] The cyanoacrylate compositions of the present invention are typically cured using an anionic mechanism. The layer of moisture inherently adsorbed on the surfaces of virtually all materials is sufficient to initiate
5 polymerization of the cyanoacrylate component. Further, most substrates also contain alkaline or nucleophilic ingredients or as impurities which can initiate the anionic polymerization. The hydroxyl groups of the water molecules effectively act to initiate polymerization as carbanions are generated at a rapid
10 rate. The polymerization reaction will continue until all available monomer is consumed or until growth is inhibited by an acidic species.

[0030] The toughening agent of the present invention comprise poly(vinylidene-co-acrylonitrile) in combination with
15 fumed silica.

[0031] The invention cyanoacrylate adhesive compositions are readily prepared by adding predetermined amounts of the toughening agent and the fumed silica to the cyanoacrylate component and stirring or agitating for a sufficient time at an
20 appropriate temperature to achieve a homogenous solution or suspension. Typically, temperatures much above room temperature are not necessary as the polymer toughening agents, except for silica, tend to readily dissolve in the cyanoacrylate component. However, in formulations containing
25 high levels of fillers, thickeners, and the like, moderate heating may be desirable to speed up dissolution.

[0032] The cyanoacrylate adhesive compositions of the present invention are useful in bonding two or more substrates. A sufficient portion of the adhesive composition may be placed
30 on a surface of one of the two or more substrates. The other substrate is then positioned adjacent to the cyanoacrylate

composition and the two substrates are placed contact to form an assembly, upon curing of the cyanoacrylate. Unexpectedly, typical fixturing speeds of the cyanoacrylate compositions of the present invention for bonding EPDM rubber were less than
5 about 70 seconds, and typically between 12 and 40 seconds.

[0033] The improved toughness of the cured compositions of this invention is manifested through various physical properties, such as 180° peel strength. High peel strengths are indicative of tough bonds. Peel strength was determined in
10 accordance with American Standard Test Method (ASTM) No. D-903-49, the substance of which is hereby expressly incorporated herein by reference.

[0034] The present invention may be better understood through consideration of the following examples which are
15 intended to be illustrative rather than limiting.

EXAMPLES

[0035] The following examples describe the preparation and use of the cyanoacrylate compositions of the present invention.
20 These examples are presented for the purpose of further illustrating and explaining the invention, and are not to be taken as limiting the scope of the invention.

[0036] A series of cyanocrylate adhesive compositions were prepared and tested. The samples were prepared by
25 agitation/mixing or tumbling a closed vessel to obtain a homogenous dispersion or solution of the additions in the cyanoacrylate. Peel strengths were evaluated by bonding flexible steel strips together and curing for 24 hours at a temperature of 25°C. The force required to cause the bond to
30 fail was measured, the results are presented in units of force per unit length of bond. The peel test procedure was performed

according to ASTM D-903-49. Also measured was the fixturing time, the time required to develop a bond on EPDM rubber samples, shorter fixturing times are generally preferred.

5 [0037] The adhesive compositions and the test results are presented in Table I.

[0038] The substrates used in determining peel strength are sand blasted steel bonded to sand blasted, flexible steel shims. Unexpectedly, typical fixturing speeds of the
10 cyanoacrylate compositions of the present invention for these substrates were less than about 70 seconds, and in most cases, from 12-40 seconds.

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Table 1. Test results of adhesive compositions

	Composition	Peel Strength [N/mm]	EPDM [s]	Remark
01	EtCA	0.4		control
02	LOCTITE 424	0.4		control
03	LOCTITE 380	2.9	120	control
04	LOCTITE 480	4.1	75	control
05	EtCA+ 7.5% PVeneCAN	2.3		
06	EtCA+ 9% PVeneCAN	3.3	20	
07	EtCA+ 10% PVeneCAN	2.9	30	
08	EtCA+ 15% PVeneCAN	2.5		
09	EtCA+ 20% PVeneCAN	2.1		
10	EtCA+ 30% PVeneCAN	0.5		
11	EtCA+ 10% PVeneCAN+ 0.4% Calix.	3.1	22	
12	EtCA+ 9 % PVeneCAN+ 4% PMMA	2.8		
13	EtCA+ 9% PVeneCAN + 3% Silica	3.2		
14	EtCA+ 9% PVeneCAN+ 4% Silica	3.4		
15	EtCA+ 11% PVeneCAN+ 3% Silica	3.1		
16	EtCA+ 11% PVeneCAN+ 6% Silica	3.6		
17	EtCA+ 9% PVeneCAN+ 4% BzBuPht	2.9		
18	EtCA+ 9% PVeneCAN+ 4% GTA	3.6		
19	EtCA+ 9% PVeneCAN+ 4% nBuCA	2.6		
20	Loctite424+ 10% PVeneCAN	4.2		
21	Loctite431+ 5% PVeneCAN	1.3	17	After 1/2 yr: 30s; 1.68 N/mm
22	Loctite431+ 5% PVeneCAN+ 4% Silica	1.6	18	After 1/2 yr: 24s; 3.61 N/mm
23	Loctite431+ 9% PVeneCAN+ 4% Silica	3.7	28	
24	EtCA+ 10% PVCVA(I)	1.3		
25	EtCA+ 10% PVCVA(II)	1.4		
26	EtCA+ 10% PVCVA(III)	1.1		
27	EtCA+ 15% PVCVA(III)	1.1		
28	EtCA+ 20% PVCVA(III)	0.7		
29	Loctite431+ 5% PVeneCAN+ 5% PVCVA(III)	2.2		
30	{Loctite431 + EtCA [1:1]} + 4.5% PVeneCAN	2.1	26	After 1/2 yr: 32s; 1.67 N/mm
31	{Loctite431 + EtCA [1:1]} + 4.5% PVeneCAN + 4%Silica	4.5	28	After 1/2 yr: 30s; 3.99 N/mm
32	EtCA + 7% PVeneCAN + 5% PMMA + 2.75% Silica	5.4	35	
33	EtCA + 7% PVeneCAN + 5% PMMA + 2.75% Silica +4 % GTA	5.6	40	
34	EtCA + 7% PVeneCAN + 5% PMMA + 2.75% Silica +4 % TEAC	5.0	40	
35	iPrCA+ 10 % PVeneCAN	2.1	50	
36	iPrCA+ 10 % PVeneCAN+ 4% Silica	2.8	60	After 1/2 yr: 65s; 3.48 N/mm
37	Loctite431+ 10 % PVCVA (II)	1.99	12	
38	Loctite431+ 10 % PVCVA (II) + 3 % Silica	0.96	18	
39	{Loctite431 / EtCA [19:3]} + 6% PVCVA(II) + 3% Silica	2.36	17	

BzBuPht	=	Benzyl butyl phthalate
Calix.	=	Calixarene derivative (fixture speed accelerator)
EPDM	=	Fixture time on EPDM foam rubber cord
EtCA	=	Ethylcyanoacrylate monomer
GTA	=	Glycerol triacetate
IPrCA	=	Iso-Propyl cyanoacrylate monomer
NBuCA	=	nButyl cyanoacrylate monomer
Peel Strength	=	Peel Strength on degreased mild steel
PMMA	=	Polymethylmethacrylate (thickening agent)
PVCVA(I)	=	Poly(vinylchloride-co-vinyl acetate), 86 % vinylchloride
PVCVA(II)	=	Poly(vinylchloride-co-vinyl acetate), 90 % vinylchloride
PVCVA(III)	=	Poly(vinylchloride-co-vinyl acetate), 81 % vinylchloride
PVenCAN	=	Poly(vinylidene chloride-co-acrylonitrile), 20 % acrylonitrile
TEAC	=	Triethyl-O-acetyl citrate

[0039] Non toughened cyanoacrylate adhesive compositions have
 5 low peel strengths, typically from about 0.2 - 0.4 N/mm.
 Example 01 and 02 illustrate the low peel strengths of non
 toughened cyanoacrylate adhesives.

[0040] Examples 05-10 demonstrate the effect of adding
 various amount of poly(vinylidene-chloride-co-acrylonitrile) to
 10 an ethyl cyanoacrylate monomer. It can be seen that
 poly(vinylidene-chloride-co-acrylonitrile) additions of up to
 30% provide enhanced peel strengths relative to Example 01.
 Maximum benefits are seen at about 9-10% poly(vinylidene-
 chloride-co-acrylonitrile), and toughness drops when more than
 15 about 20% poly(vinylidene-chloride-co-acrylonitrile) is added.

[0041] Examples 06, 13 and 14 suggest that adding fumed
 silica to poly(vinylidene chloride-co-acrylonitrile) toughened
 cyanoacrylate further and improves peel strength. Examples 07,
 15 and 16 further support the observation that fumed silica, in
 20 combination with poly(vinylidene-chloride-co-acrylonitrile),
 provides improved peel strengths. The benefit of fumed silica
 additions to poly(vinylidene-chloride-co-acrylonitrile) in

cyanoacrylate adhesive compositions can also be seen by comparing Examples 21 and 22, Examples 35 and 36, and Examples 30 and 31.

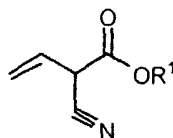
[0042] These Examples confirm the benefit provided by adding
5 fumed silica to poly(vinylidene chloride-co-acrylonitrile)
toughened cyanoacrylate compositions.

[0043] The cyanoacrylate adhesive compositions of the
present invention exhibit improved peel strengths in comparison
with cyanoacrylate compositions toughened with prior art
10 tougheners such as BLACK MAX[®] (Loctite 380 cyanoacrylate
adhesive, an adhesive known for its high peel strength).

WHAT IS CLAIMED IS:

1. A cyanoacrylate composition comprising:
- 5 a. a cyanoacrylate component; and
- b. a toughening agent comprising
- poly(vinylidene-chloride-co-acrylonitrile) in combination with
- fumed silica.

- 10 2. A cyanoacrylate composition as claimed in claim
- 1 wherein the cyanoacrylate component comprises a monomeric
- structure represented by:



- wherein R¹ is C₁₋₁₅ alkyl, alkoxyalkyl, cycloalkyl, alkenyl,
- 15 aryl, aralkyl, allyl, alkyhalide, or haloalkyl and mixtures
- thereof.

3. A cyanoacrylate composition as claimed in claim
- 1 or claim 2 wherein the cyanoacrylate component comprises a
- 20 member selected from the group consisting of methyl
- cyanoacrylate, ethyl-2-cyanoacrylate, propyl cyanoacrylates,
- butyl cyanoacrylates, octyl cyanoacrylates, allyl
- cyanoacrylates, β-methoxyethyl cyanoacrylate, and mixtures
- thereof.

- 25 4. A cyanoacrylate composition as claimed in any
- one of claims 1 to 3 wherein said cyanoacrylate component
- comprises ethyl-2-cyanoacrylate.

5. A cyanoacrylate composition as claimed in any one of claims 1 to 4 wherein the poly(vinylidene-chloride-co-acrylonitrile) is present in an amount of about 1% to about 20% by weight.

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6. A cyanoacrylate composition as claimed in any one of claims 1 to 5 wherein the fumed silica is present in an amount (by weight) of from about 0.5 to about 10%.

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7. A cyanoacrylate composition as claimed in any one of claims 1 to 6 further comprising at least one additive selected from the group consisting of stabilizers, accelerators, plasticisers, fillers other than fumed silica, opacifiers, thickeners, viscosity modifiers, inhibitors, thixotrophy conferring agents other than fumed silica, dyes, thermal degradation reducers, and combinations thereof.

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8. A cyanoacrylate composition as claimed in any one of claims 1 to 7 wherein upon cure, the cyanoacrylate composition has an average peel strength in excess of about 1.0 N/mm after 72 hours at room temperature cure.

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9. A cyanoacrylate composition as claimed in any one of claims 1 to 8 wherein the fumed silica is present in an amount, by weight of 1-10%.

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10. A method of bonding two or more substrates comprising the steps of:

a. providing at least two substrates;

b. dispensing, on a surface of one or both of the at least two substrates, a cyanoacrylate adhesive composition as claimed in any one of claims 1 to 9;

5 c. contacting the surfaces of the at least two substrates having the cyanoacrylate adhesive composition thereon; and

d. exposing the cyanoacrylate adhesive composition to cure conditions.

10 11. A method of bonding two or more substrates as claimed in claim 10 wherein after the step of contacting the surfaces of the at least two substrates having the cyanoacrylate adhesive composition thereon, the fixturing time of the cyanoacrylate composition is less than about 70 seconds.

15 12. A method of bonding two or more substrates as claimed in claim 11 or claim 12 wherein the at least two substrates comprise EPDM rubber and the bond has a fixturing time of less than 70 seconds, and after curing the bond has a
20 peel strength in excess of 1 N/mm.

13. A method of bonding two or more substrates as claimed in any one of claims 10 to 12 wherein a bonded assembly comprises:

25 a. a first substrate having a first surface;
b. another substrate having a second surface;
and

c. a cured cyanoacrylate adhesive composition disposed between said first and second surfaces, said
30 composition, prior to cure, comprising:

i. a cyanoacrylate component; and

ii. a toughening agent comprising poly(vinylidene-chloride-co-acrylonitrile) in combination with fumed silica; the toughening agent forming an interpenetrating molecular network with the cyanoacrylate component upon curing.

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14. A bonded assembly as claimed in claim 13 wherein the bonded assembly demonstrates a peel strength greater than about 1.0 N/MM after room temperature cure of about 72 hours.

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15. A bonded assembly as claimed in claim 13 or claim 14 wherein the cured cyanoacrylate adhesive has a multi-phase structure comprising a matrix phase which comprises a solid solution of the cyanoacrylate material, said matrix containing a second phase which comprises the toughening agent, and a dispersion of silica particles.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/IE 03/00113

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09J4/06 C08F22/32 C08F259/06

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 C09J C08F

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 102 945 A (GLEAVE EDWARD ROGER) 25 July 1978 (1978-07-25) cited in the application column 5, lines 17-19 -----	1-4
Y	US 4 636 539 A (ROONEY JOHN M ET AL) 13 January 1987 (1987-01-13) claim 1 -----	1-4
A	US 4 713 405 A (HIRAI KENICHIRO ET AL) 15 December 1987 (1987-12-15) the whole document -----	1
A	US 5 994 464 A (FUJII TATSUO ET AL) 30 November 1999 (1999-11-30) the whole document -----	1

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

☒ Patent family members are listed in 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

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

22 October 2003

Date of mailing of the international search report

04/11/2003

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IE 03/00113

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