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(54) Title: TOUGHENED CYANOACRYLATE COMPOSITIONS

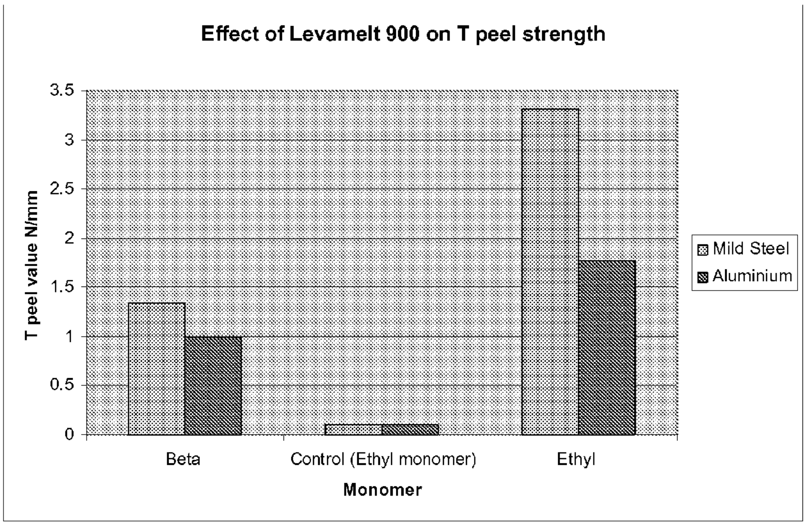

Fig. 1

(57) Abstract: This invention relates to toughened cyanoacrylate compositions which exhibit improved peel strengths and fixture speeds. The toughened cyanoacrylate compositions described include a toughening agent comprising a co-polymer of polyethylene and polyvinyl acetate.

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TOUGHENED CYANOACRYLATE COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates to toughened cyanoacrylate compositions which exhibit improved peel strengths and fixture speeds. The compositions according to the invention are suitable for use as adhesives for quick bonding of a variety of substrates.

Brief Description Of Related Technology

[0002] Cyanoacrylate compositions are well known in the art as excellent adhesives. In particular they are well known as one-component reactive adhesives, quick bonding and suitable for a wide variety of substrates. However, one of the main drawbacks of these compositions is that they tend to be brittle following cure and 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 No. 4,102,945 (Gleave) 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 (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 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 (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 (Millet) 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. 4,713,405 (Koga) discloses an α-cyanoacrylate adhesive composition of matter consisting essentially of α-cyanoacrylate, fumed silica having a surface treated with a dimethyldichlorosilane, and trialkyl borate.

[0008] U.S. Patent No. 5,340,873 (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.

[0009] U.S. Patent No. 5,739,205 (Nishino) discloses an α-cyanoacrylate adhesive composition which comprises (a) 100 parts by weight of an α-cyanoacrylate compound, (b) 10 through 20 parts by weight of (I) polyalkyl methacrylates having a weight average molecular weight of 100,000 through 300,000, or (II) copolymers of alkyl methacrylates and other methacrylates or acrylates, said copolymers having the same weight average molecular weight as that of the polyalkyl methacrylates (I), (c) 2 through 20 parts by weight of ultrafine anhydrous silicas, and (d) 0.001 through 20 parts by weight of certain quick curing additives, (b)-(d) being on the basis of (a) 100 parts by weight of α-cyanoacrylate compounds.

[0010] U.S. Patent No. 5,994,464 (Ohsawa) 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.

[0011] U.S. Patent No. 6,475,331 (O'Connor) discloses a cyanoacrylate adhesive composition comprising: (a) a cyanoacrylate component; and (b) an accelerator component consisting essentially of (i) calixarenes, oxacalixarenes, or a combination thereof, and (ii) at least one crown ether, wherein said composition exhibits a fixturing speed of less than 20 seconds for bonding two substrates, at least one of which is constructed of a material selected from steel, epoxy glass, and balsawood.

[0012] The use of elastomeric polymers as toughening agents in cyanoacrylate adhesive compositions is known. One group of particularly suitable elastomeric polymers is the group comprising copolymers of methyl acrylate and ethylene, manufactured by DuPont, under the name of VAMAC, such as VAMAC N123 AND VAMAC B-124. VAMAC N123 and VAMAC B-124 are reported by DuPont to be a master batch of ethylene/acrylic elastomer.

[0013] Henkel Corporation (as successor to Loctite Corporation) has sold for a number of years rubber toughened cyanoacrylate adhesive products under the trade name BLACK MAX, which employ as the rubber toughening component the DuPont materials called VAMAC B-124 and N123. In addition Henkel has sold in the past clear and substantially colorless rubber toughened cyanoacrylate adhesive products, namely LOCTITE 4203, 4204, and 4205, which employ as the rubber toughening component the DuPont material, VAMAC G. While VAMAC G contains no fillers to provide color or stabilizers, it does contain processing aids. These processing aids, or release systems are reported to be ARMEEN 18D and stearic acid in combination with GAFAC RL-210 (or with VANFRE UN, or SERVOXYL VPAZ-100). In addition it is believed that polyethylene glycol ether wax is also used as a processing aid. Waxes such as this interfere with the physical properties of cyanoacrylate compositions. In particular, it is believed that the processing aids used in the manufacture of the VAMAC type elastomers are detrimental to adhesion and therefore give poor performance.

[0014] VAMAC VCS rubber appears to be the base rubber, from which the remaining members of the VAMAC product line are compounded. VAMAC VCS is a reaction product of the combination of ethylene, methyl acrylate and monomers having carboxylic acid cure sites, which once formed is then substantially free of processing aids such as the release agents octadecyl amine, complex organic phosphate esters and/or stearic acid, and anti-oxidants, such as substituted diphenyl amine.

[0015] Recently DuPont has provided to the market under the trade designation VAMAC VMX 1012 and VCD 6200, rubbers which are made from ethylene and methyl acrylate. It is believed that the VAMAC VMX 1012 rubber possesses little or no carboxylic acid in the polymer backbone. Like the VAMAC VCS rubber, the VAMAC VMX 1012 and VCD 6200 rubbers are substantially free of processing aids such as the release agents octadecyl amine, complex organic phosphate esters and/or stearic acid, and anti-oxidants, such as substituted diphenyl amine, noted above.

[0016] Notwithstanding the state of the art and the commercial success experienced by Henkel Corporation with its line of rubber toughened cyanoacrylate adhesive products, it would be desirable to provide an alternative, more cost-effective cyanoacrylate adhesive composition with improved toughness and peel strengths, while maintaining a high fixture speed.

SUMMARY OF THE INVENTION

[0017] The present invention is thus directed to an alternative cyanoacrylate adhesive composition which provides improved performance and toughness compared to known toughened cyanoacrylate compositions.

[0018] The invention provides a cyanoacrylate composition comprising:

(i) a cyanoacrylate component; and

(ii) a toughening agent comprising a co-polymer of polyethylene and polyvinyl acetate.

[0019] The composition according to the invention has been found to demonstrate increased performance over known cyanoacrylate compositions. In particular, the present invention is directed to a cyanoacrylate composition which demonstrates substantially enhanced toughness and has an improved peel strength and fixturing speed compared to known toughened cyanoacrylate compositions.

[0020] The toughening agent comprises a co-polymer of polyethylene and polyvinyl acetate. Agents which are particularly suitable for use in accordance with the present invention are those agents comprising co-polymers of polyethylene and polyvinyl acetate which are sold under the trade name LEVAMELT by Lanxess Limited.

[0021] A range of LEVAMELT agents is available and includes for example, LEVAMELT 400, LEVAMELT 600 and LEVAMELT 900. These agents differ in the amount of vinyl acetate present. For example, LEVAMELT 400 represents an ethylene-vinyl acetate copolymer comprising 40 wt% vinyl acetate. The LEVAMELT products are supplied in granular form. The granules are almost colourless and dusted with silica and talc. The product may also be supplied in bales of 25 kg under the trade name LEVAPREN.

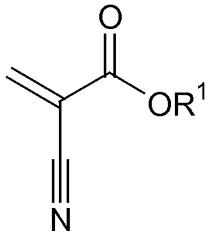
[0022] The use of a toughening agent comprising a co-polymer of polyethylene and polyvinyl acetate allows different cyanoacrylate esters to be formed as tough adhesives.

[0023] The use of toughening agents comprising a copolymer of polyethylene and polyvinyl acetate permits the use of other monomers such as methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl cyanoacrylates, butyl cyanoacrylates (such as n-butyl-2-cyanoacrylate), octyl cyanoacrylates, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylate, propargyl cyanoacrylates and combinations thereof.

[0024] The monomers can be toughened by varying the ratios of polyethylene and polyvinyl acetate in the elastomer. Suitable elastomers can be selected for use in toughening a particular monomer. Elastomers comprising copolymers comprising different ratios of polyethylene and polyvinyl acetate may be used to toughen different monomers. A particularly preferred toughening agent for use in accordance with the present invention comprises a copolymer of polyethylene and polyvinyl acetate wherein the vinyl acetate is present in an amount of 90 wt%.

[0025] The compositions according to the invention provide increased performance compared to known toughened cyanoacrylate compositions. In particular, cyanoacrylate compositions according to the present invention show increased toughness, measured for instance as an increased peel strength.

[0026] The cyanoacrylate component suitably comprises a monomeric structure represented by:



where R^1 is C_{1-15} alkyl, C_{2-15} alkoxyalkyl, C_{3-15} cycloalkyl, C_{2-15} alkenyl, C_{6-15} aryl, C_{7-15} aralkyl, C_{3-15} allyl, C_{1-15} alkylhalide, or C_{1-15} haloalkyl and mixtures thereof.

[0027] The cyanoacrylate component may be selected from the group consisting of methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl cyanoacrylates, butyl cyanoacrylates, octyl cyanoacrylates, allyl cyanoacrylates, alkoxyalkyl cyanoacryalates (such as β-methoxyethyl cyanoacrylate), propargyl cyanoacrylate and mixtures thereof.

[0028] In one aspect of the invention, the cyanoacrylate component comprises ethyl-2-cyanoacrylate.

[0029] As used herein all composition values are given in weight percent unless otherwise noted.

[0030] Desirably, the co-polymer of polyethylene and polyvinyl acetate is present in an amount of 1 to about 20% by weight.

[0031] Desirably, the co-polymer of polyethylene and polyvinyl acetate is present in an amount of 5 to about 10% by weight.

[0032] In another aspect the present invention is directed to a cyanoacrylate composition which demonstrates enhanced toughness including a cyanoacrylate material; a toughening agent comprising a co-polymer of polyethylene and polyvinyl acetate and one or more additives selected from plasticizers, accelerators, fillers, opacifiers, inhibitors, thixotrophy conferring agents, stabilizers, dyes, thermal degradation reducers, adhesion promoters, shock resistance conferring agents and combinations thereof, where upon cure, the cyanoacrylate composition has an average T peel strength on mild steel of more than about 3 N/mm after curing at room temperature for about 72 hours and a fixture speed on mild steel of less than 360 seconds.

[0033] 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 to about 20% by weight of the toughening agent comprising a co-polymer of polyethylene and polyvinyl acetate; contacting the surfaces of the at least two substrates having the cyanoacrylate composition therebetween; and curing the cyanoacrylate composition.

[0034] 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 of the toughening agent comprising a co-polymer of polyethylene and polyvinyl acetate. Preferably, the T peel strength on mild steel is greater than about 3 N/mm after room temperature cure for about 72 hours, and a fixture speed on mild steel of less than 360 seconds.

[0035] In addition the invention is directed to reaction products of the inventive compositions.

[0036] Also, the invention is directed to a method of preparing the inventive compositions.

[0037] And the invention is directed to a method of conferring one or more of the following properties to rubber toughened cyanoacrylate compositions, improved shelf life, fixture speed, improved shear strength development over time and improved side impact strength and fracture toughness, which includes the method of providing a cyanoacrylate component and a toughening agent component comprising a co-polymer of polyethylene and polyvinyl acetate and mixing together said components.

[0038] The invention will be more fully understood by a reading of the section entitled “Detailed Description of the Invention” which follows.

BRIEF DESCRIPTION OF THE FIGURES

[0039] The invention will be described in more detail with reference to the accompanying drawing in which:

Fig. 1 depicts a plot of the effect of LEVAMELT 900 (copolymer of polyethylene and polyvinyl acetate comprising 90 wt% vinyl acetate) on T peel strength for each of the monomers β-methoxyethyl cyanoacrylate and ethyl cyanoacrylate.

Fig. 2 depicts a plot of the effect of LEVAMELT 900 (copolymer of polyethylene and polyvinyl acetate comprising 90 wt% vinyl acetate) on T peel strength for the monomer β-methoxyethyl cyanoacrylate over a period of 3 days at room temperature and a period of 3 days at room temperature and 1 day at 80 °C.

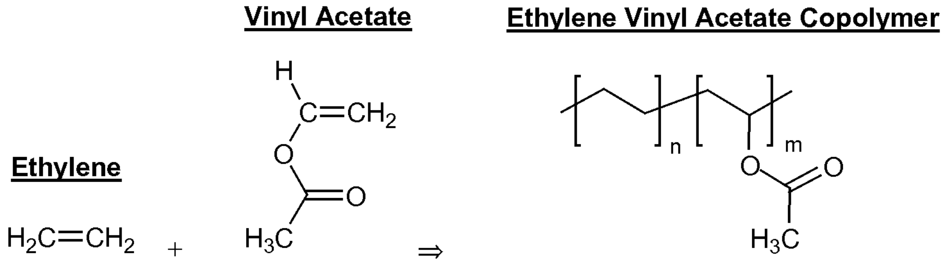
Fig. 3 depicts a plot of the effect of LEVAMELT 900 (copolymer of polyethylene and polyvinyl acetate comprising 90 wt% vinyl acetate) on T peel strength for the monomer ethyl cyanoacrylate over a period of 3 days at room temperature and a period of 3 days at room temperature and 1 day at 80 °C.

DETAILED DESCRIPTION OF THE INVENTION

[0040] The cyanoacrylate compositions of the present invention comprise toughening agents which provide enhanced toughness, such as improved peel strengths in the cured compositions.

Toughening Agent

[0041] The preferred toughening agent comprises an elastomeric co-polymer of polyethylene and polyvinyl acetate. The toughening agents which are preferably used in the compositions according to the invention comprise LEVAMELT elastomers which are available from Lanxess. It will be appreciated that other suitable copolymers of polyethylene and polyvinyl acetate could also be used.



[0042] The LEVAMELT elastomers are high performance elastomers. Various grades of LEVAMELT elastomers are available from Lanxess. They dissolve more readily than other tougheners currently used in the art, for example, VAMAC. They are readily available in both monomers and perform better than VAMAC in ethyl cyanoacrylate. LEVAMELT consists of methylene units forming a saturated main chain with pendant acetate groups. The presence of a fully saturated main chain is an indication that LEVAMELT is a particularly stable polymer. It does not contain any reactive double bonds which make conventional rubbers prone to aging reactions, ozone and UV light. The saturated backbone makes it robust.

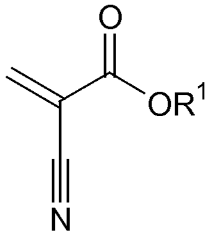
[0043] Further, the LEVAMELT elastomers are available without any of the processing aids that are used for the most of the VAMAC elastomers. As a result, these elastomers facilitate the use of other monomers such as methyl cyanoacrylate, ethyl-2-

cyanoacrylate, propyl cyanoacrylates, butyl cyanoacrylates, octyl cyanoacrylates, allyl cyanoacrylates, β-methoxyethyl cyanoacrylate, propargyl cyanoacrylate and mixtures thereof. This allows different cyanoacrylate esters to be formulated as tough adhesives. Interestingly, depending on the ratio of polyethylene/polyvinylacetate, the solubilities of these materials change in different monomers and also the ability to toughen changes as a result of the solubility.

[0044] The LEVAMELT elastomers are available in pellet form and are easier to formulate than other known elastomeric toughening agents. Furthermore, these elastomers are less expensive than other known elastomers. Thus these elastomers allow for the formulation of a more cost-effective toughened cyanoacrylate composition which provides better performance compared to known toughened cyanoacrylate compositions.

Cyanoacrylate Component

[0045] The cyanoacrylate compositions of the present invention include a cyanoacrylate component which includes cyanoacrylate monomers, such as those represented by the structure:



where R^1 is selected from R^1 is $C_{1\text{-}15}$ alkyl, $C_{2\text{-}15}$ alkoxyalkyl, $C_{3\text{-}15}$ cycloalkyl, $C_{2\text{-}15}$ alkenyl, $C_{6\text{-}15}$ aryl, $C_{7\text{-}15}$ aralkyl, $C_{3\text{-}15}$ allyl, $C_{1\text{-}15}$ alkylhalide, or $C_{1\text{-}15}$ haloalkyl and mixtures thereof. 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, ß-methoxyethyl cyanoacrylate, propargyl 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 95% by weight, preferably about 75% by weight to about 90% by weight.

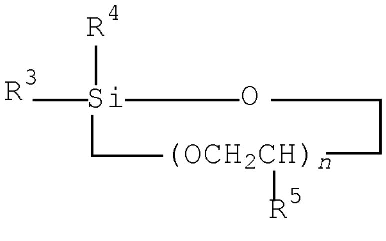
[0046] The compositions of the present invention may also contain additives such as stabilizers, accelerators, plasticizers, fillers, opacifiers, inhibitors, thixotrophy conferring agents, dyes, fluorescence markers, thermal degradation reducers, adhesion promoters, thermal resistance conferring agents and combinations thereof, and the like. Cured cyanoacrylate compositions are typically rigid, brittle materials, having low crack resistance and therefore low T peel strength. Additives may be included in order to modify these properties. These additives are known to those of skill in the art.

[0047] The compositions according to the invention may further comprise free radical inhibitors, such as hydroquinones or MMBP (2,2'-methylenebis(6-tert-butyl-4-methylphenol). The inhibitor, when present, is preferably present in an amount of about 0.001% by weight to about 2.0% by weight, preferably 0.02% to about 0.5% by weight.

[0048] 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.

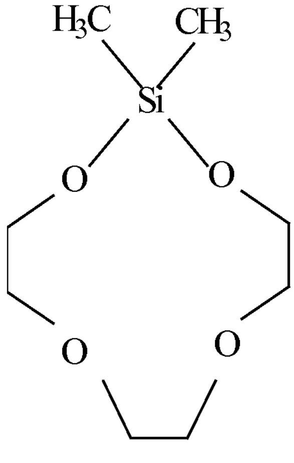
[0049] Another potentially useful accelerator component is a crown ether. A host of crown ethers are known. For instance, examples which may be used herein either individually or in combination, or in combination with the calixarenes and oxacalixarenes described above include 15-crown-5, 18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5, dibenzo-24-crown-8, 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-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.

[0050] 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 fixturing and cure on de-activating substrates such as wood, examples of which are within the following structure:

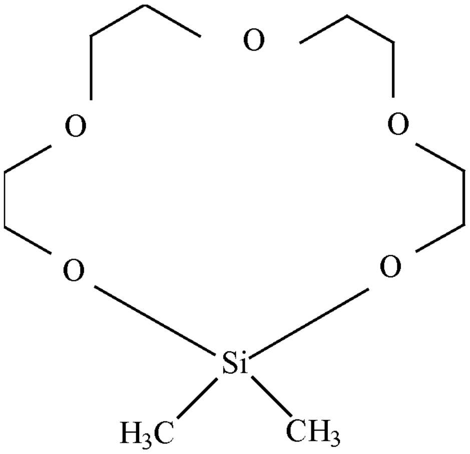


where R^3 and R^4 are organo groups which do not themselves cause polymerization of the cyanoacrylate monomer, R^5 is H or CH_3 and n is an integer of between 1 and 4. Examples of suitable R^3 and R^4 groups are C_{1-15} alkyl groups, C_{1-15} alkoxy groups such as methoxy, and C_{1-15} aryloxy groups 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^3 groups are basic groups such as amino, substituted amino and alkylamino.

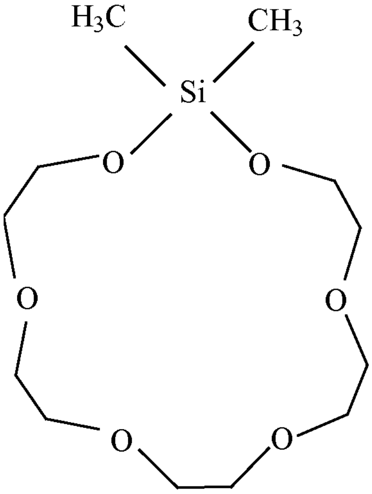
[0051] Specific examples of silacrown compounds useful in the inventive compositions include:



dimethylsila-11-crown-4;

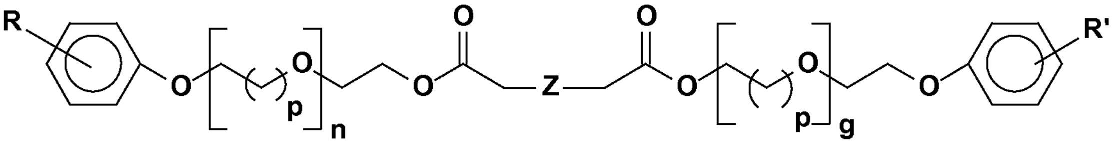


dimethylsila-14-crown-5;

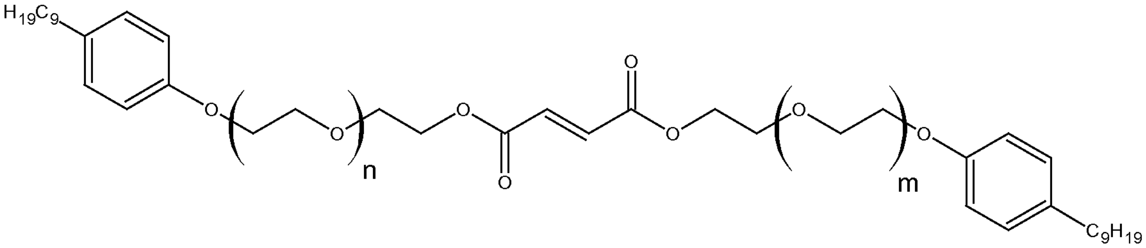


and dimethylsila-17-crown-6.

[0052] Other accelerators, and accelerator packages (i.e., the combination of two or more accelerators) may be found in U.S. Patent Nos. 6,294,629 -- an accelerator component including (i) calixarenes, oxacalixarenes, silacrowns, cyclodextrins or a combination thereof, and (ii) poly(ethyleneglycol) di(meth)acrylates, ethoxylated hydric compounds, and combinations thereof --, 6,475,331-- an accelerator component including (i) calixarenes, oxacalixarenes, or a combination thereof, and (ii) at least one crown ether --, and 6,835,789 -- chemical class embraced by



where R is a member selected from the group consisting of hydrogen, C_{1-15} alkyl, C_{1-15} alkyloxy, C_{2-15} alkyl thioethers, C_{1-15} haloalkyl, C_{1-15} carboxylic acid and esters thereof, C_{0-15} sulfinic, C_{0-15} sulfonic and C_{0-15} sulfurous acids and esters thereof, C_{0-15} phosphinic, C_{0-15} phosphonic and C_{0-15} phosphorous acids and esters thereof, Z is a single or double bond, n is 1-12, p is 1-3, R' is the same as R, and g is the same as n; such as



where n and m combined is greater than or equal to 12, the disclosures of each of which are hereby expressly incorporated herein by reference. Desirably, however, the accelerator component used in accordance with the present invention comprises 18-crown-6.

[0053] The accelerator component 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 0.05% to about 2% by weight being desirable, and about 0.1% to about 1% by weight of the total composition being particularly desirable.

[0054] Itaconic anhydride may also be added to the cyanoacrylate component to further aid in durability and impact, heat, and moisture resistance. Itaconic anhydride when present in the composition increases adhesion to mild steel.

[0055] Plasticizers may also be added to the cyanoacrylate component, and when so added are preferably present in an amount of about 10% by weight to about 50% by weight, more preferably about 10% by weight to about 25% by weight of the total composition.

[0056] The inventive compositions may also be rendered thixotropic by the addition of thixotrophy conferring agents, such as fumed silica. See U.S. Patent Nos. 4,533,422 (Litke) and 4,477,607 (Litke). These agents, when used, should be used in an amount less than about 15% by weight, such as within the range of about 0.5% by weight to about 10% by weight of the total composition.

[0057] The combination of the cyanoacrylate monomer and the additives will be referred to herein as the cyanoacrylate component.

[0058] Thermal resistance conferring agents, such as citric acid, are also desirable for use herein.

[0059] The compositions according to the invention may be readily prepared by adding predetermined amounts of the toughening agent components to the cyanoacrylate component and stirring or agitating for a sufficient time at an appropriate temperature to achieve a homogenous solution or suspension. Typically, temperatures much above room temperature are not necessary, though in formulations containing high levels of fillers, thickeners, and the like, moderate heating may be desirable to speed dissolution of the various additives.

[0060] The improved toughness of the cured compositions of the invention is manifested through various physical properties, e.g. 180° peel strength, impact strength and tensile shear strength. These strengths are useful properties of an adhesive bond, being parameters of what is loosely referred to as the bond strength. Referring for simplicity to the procedures of American Standard Test Methods, peel strength is determined in accordance with ASTM No. D 903-49; impact strength is determined in accordance with ASTM No. D-950; and tensile shear strength is determined in accordance with ASTM No. D-1002. The reader is referred to these standards for a full description of the tests.

EXAMPLES

[0061] The following examples are illustrative of the invention and not intended to limit the scope of the invention in any way. The examples describe the preparation and use of the cyanoacrylate compositions of the present invention.

Example 1

[0062] The following formulations were prepared from the constituents listed in Table 1 in the respective amounts. The effect of LEVAMELT 900 on T peel strength for each of the monomers, β-methoxyethyl cyanoacrylate and ethyl cyanoacrylate, is demonstrated contrasted to a control without LEVAMELT 900. The results are shown in Table 2 and Figure 1.

Table 1

Constituent	Sample No./Amt (grams)		
	1	2	3
β-Methoxy CA	90	-	-
Ethyl CA	-	100	-
Ethyl CA	-	-	90
stabiliser	1	1	1
LEVAMELT 900	10	-	10

Table 2

Substrate	Sample No./T Peel Strength (N/mm)		
	1	2	3
Mild Steel	1.35 N/mm	0.1 N/mm	3.31 N/mm
Aluminium	1.0 N/mm	0.1 N/mm	1.71 N/mm

Example 2

[0063] Formulations A and B were prepared with methane sulfonic acid and SO_2 as stabilisers according to the following process. Itaconic anhydride and phosphoric acid were added to the stabilised cyanoacrylate. Crown ether (18-crown-6) was then added and dissolved microparticles (55µm polyethylene microparticles available from Inhance, which are constructed of polyethylene in the form of a particle having an average particle size of less than 500 µm and whose surface has been modified such that the outermost surface thereof has been activated through exposure to an oxidation process) were subsequently added and dispersed. LEVAMELT 900 was added portion wise to this solution and mixed thoroughly over 15 minutes.

[0064] Details of the compositions are set out in Table 3 below:

Table 3

Formulation	**A**	**B**
β-methoxyethylcyanoacrylate	86.35%	--
Ethylcyanoacrylate	--	86.35%
Itaconic anhydride	1.25%	1.25%
Phosphoric acid	0.25%	0.25%
Crown Ether	0.25%	0.25%
LEVAMELT 900	10.0%	10.0%
UH-1250 (55μm polyethylene microparticles available from Inhance)	0.5%	0.5%
Silica	1.0%	1.0%

[0065] The test results for each of Formulations A and B are presented in Table 4 and Figures 2 and 3. The substrates used in determining T peel strength in Table 4 are mild steel bonded to mild steel and aluminium bonded to aluminum.

Table 4

Performance

Formulation	**Results**	
	Mild Steel	**Aluminum**
A 3 days @ rt	3.19+/-0.10 N/mm	2.16+/-0.36 N/mm
B 3 days@ rt	6.01+/-0.10 N/mm	2.61+/-0.15 N/mm
A 3 days @rt; 1 day @ 80°C	0.65+/-0.04 N/mm	1.13+/-0.20 N/mm
B 3 days @rt; 1 day @ 80°C	7.28+/-1.57 N/mm	1.73+/-0.22 N/mm

[0066] Non-toughened cyanoacrylate compositions that are evaluated in adhesive applications have low T peel strengths, typically from about 0.2 –0.4 N/mm. It has been found that the addition of a copolymer of polyethylene and polyvinyl acetate to a cyanoacrylate monomer increases the T peel strength of the cured cyanoacrylate composition.

[0067] It is evident from the information provided in the table above that the elastomer LEVAMELT 900 works well with ethyl cyanoacrylate monomer.

[0068] The toughened cyanoacrylate compositions according to the invention appear to provide excellent adhesion on both mild steel and aluminium. The performance of the inventive compositions can be improved by the addition of fibres if necessary.

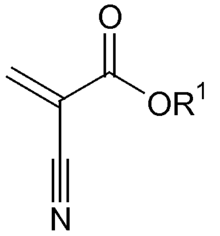
WHAT IS CLAIMED IS:

1. A cyanoacrylate composition comprising:

(i) a cyanoacrylate component; and

(ii) a toughening agent comprising a co-polymer of polyethylene and polyvinyl acetate.

2. The composition of claim 1 wherein said cyanoacrylate component comprises a monomeric structure represented by:



wherein R^1 is C_{1-15} alkyl, C_{2-15} alkoxyalkyl, C_{3-15} cycloalkyl, C_{2-15} alkenyl, C_{6-15} aryl, C_{7-15} aralkyl, C_{3-15} allyl, C_{1-15} alkylhalide, or C_{1-15} haloalkyl and mixtures thereof.

3. The composition of claim 2 wherein said cyanoacrylate component comprises a member selected from the group consisting of methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl cyanoacrylates, butyl cyanoacrylates, octyl cyanoacrylates, allyl cyanoacrylates, β-methoxyethyl cyanoacrylate, propargyl cyanoacrylates and combinations thereof.

4. The composition of claim 1 wherein said cyanoacrylate component comprises ethyl-2-cyanoacrylate.

5. The composition of claim 1 wherein said co-polymer of polyethylene and polyvinyl acetate is present in an amount of 1 to about 20% by weight.

6. The composition of claim 5 wherein said co-polymer of polyethylene and polyvinyl acetate is present in an amount of 5 to about 10% by weight.

7. The composition of claim 1 further comprising fumed silica.

8. The composition of claim 6, wherein said fumed silica is present in an amount (by weight) of from about 0.5 to about 10%.

9. The composition of claim 1 further comprising at least one additive selected from the group consisting of stabilizers, accelerators, plasticizers, fillers, opacifiers, thickeners, viscosity modifiers, inhibitors, thixotrophy conferring agents, dyes, thermal degradation inhibitors, adhesion promoters, shock resistance-conferring agents and combinations thereof.

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

providing at least two substrates;

dispensing, on a surface of one or both of the at least two substrates, a cyanoacrylate composition of claim 1;

contacting the surfaces of the at least two substrates having the cyanoacrylate composition thereon; and

exposing the cyanoacrylate composition to cure conditions.

11. A bonded assembly comprising:

a first substrate having a first surface;

another substrate having a second surface; and

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

a cyanoacrylate component;

a toughening agent comprising a co-polymer of polyethylene and polyvinyl acetate.

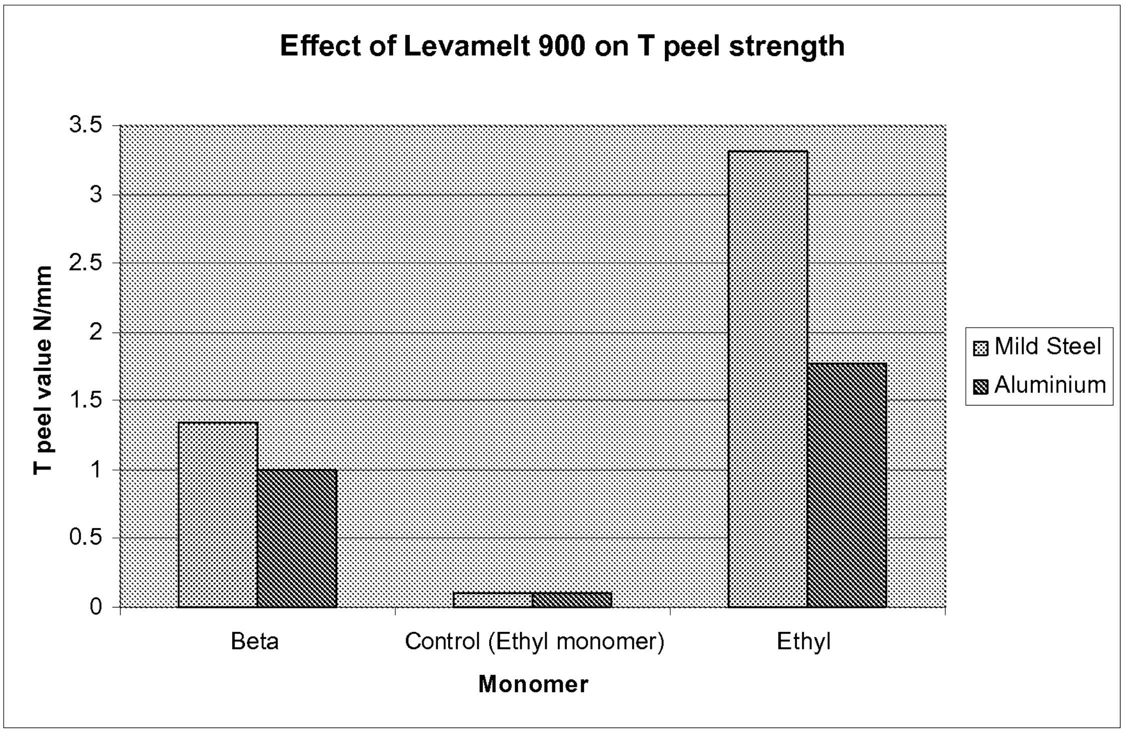

Effect of Levamelt 900 on T peel strength
T peel value N/mm
3.5
3
2.5
2
1.5
1
0.5
0
Beta
Control (Ethyl monomer)
Ethyl
Monomer
Mild Steel
Aluminium

Fig. 1

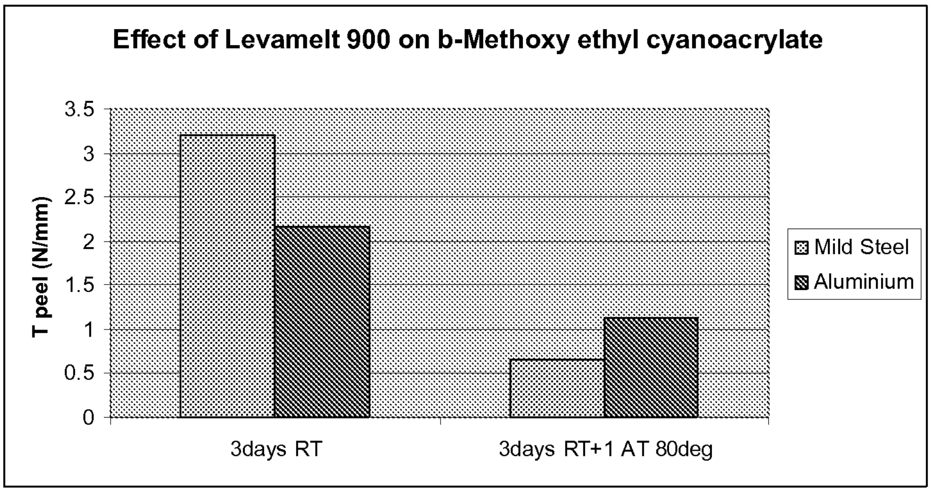

Effect of Levamelt 900 on b-Methoxy ethyl cyanoacrylate
T peel (N/mm)
3.5
3
2.5
2
1.5
1
0.5
0
3days RT
3days RT+1 AT 80deg
Mild Steel
Aluminium

Fig. 2

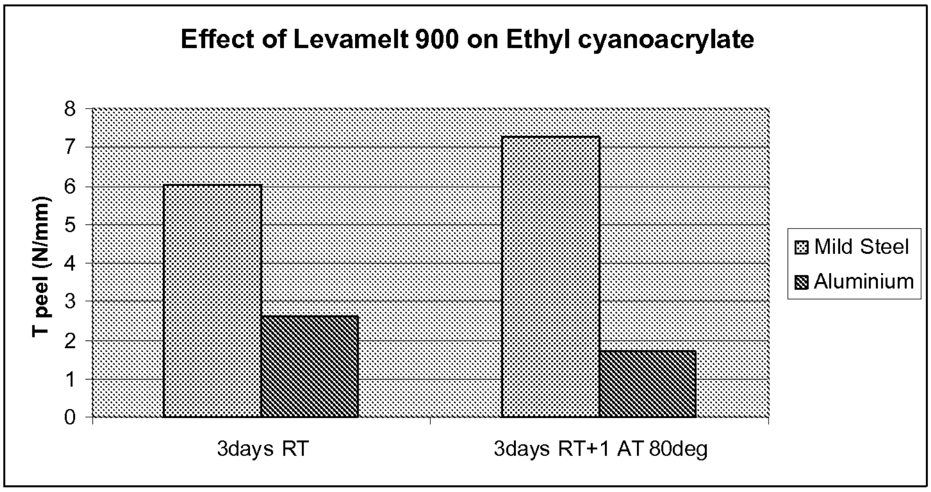

Effect of Levamelt 900 on Ethyl cyanoacrylate
T peel (N/mm)
8
7
6
5
4
3
2
1
0
3days RT
3days RT+1 AT 80deg
Mild Steel
Aluminium

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/061770

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J4/00 C08F210/00 C08F216/00 C09J4/06

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)
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.
X	JP 59 145271 A (TAOKA CHEMICAL CO LTD) 20 August 1984 (1984-08-20)	1-6,9-11
Y	abstract	1-11
Y	US 6 475 331 B1 (O'CONNOR JOHN T [US] ET AL) 5 November 2002 (2002-11-05) cited in the application the whole document	1-11
Y	US 7 390 851 B1 (MISIAK HANNS ROLAND [IE]) 24 June 2008 (2008-06-24) the whole document	1-11
Y	JP 62 025185 A (ALPHA TECHNO CO) 3 February 1987 (1987-02-03) abstract	1-11
	-/--	

☒ 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

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"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.

"&" document member of the same patent family

Date of the actual completion of the international search 18 December 2009	Date of mailing of the international search report 29/12/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Droghetti, Anna

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/061770

C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2004/131827 A1 (MISIAK HANNS ROLAND [IE]) 8 July 2004 (2004-07-08) the whole document -----	1-11
Y	US 4 533 422 A (LITKE ALAN E [US]) 6 August 1985 (1985-08-06) the whole document -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/061770

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 59145271 A	20-08-1984	NONE	
US 6475331 B1	05-11-2002	WO 03000815 A1	03-01-2003
US 7390851 B1	24-06-2008	NONE	
JP 62025185 A	03-02-1987	JP 1800183 C	12-11-1993
		JP 5008951 B	03-02-1993
US 2004131827 A1	08-07-2004	AU 2003263563 A1	29-07-2004
		WO 2004061030 A1	22-07-2004
		US 2006014882 A1	19-01-2006
US 4533422 A	06-08-1985	NONE	