

(21) Application No: **1717707.2**

(22) Date of Filing: **27.10.2017**

(71) Applicant(s):  
**Henkel IP & Holding GmbH**  
**(Incorporated in the Federal Republic of Germany)**  
**Henkelstr.67, Dusseldorf 40589, Germany**

(72) Inventor(s):  
**Isidro Cobo**  
**Marisa Phelan**  
**Viktorija Sadauskaite**  
**Emer Ward**  
**Raymond P Tully**  
**Barry M Burns**  
**Rory Barnes**  
**Rachel Hersee**

(74) Agent and/or Address for Service:  
**Tomkins & Co**  
**5 Dartmouth Road, Dublin 6, Ireland**

(51) INT CL:  
**C08F 222/32** (2006.01) **C08F 22/32** (2006.01)  
**C09J 133/14** (2006.01)

(56) Documents Cited:  
**WO 2017/077091 A1** **WO 2017/077089 A1**  
**WO 2010/029134 A1**  
**JPH06145606**

(58) Field of Search:  
INT CL **C08F, C08K, C09J**  
Other: **EPODOC, WPI, TXTE.**

(54) Title of the Invention: **Toughened, low odor/low bloom cyanoacrylate compositions**  
Abstract Title: **Toughened low odour cyanoacrylate compositions**

(57) A cyanoacrylate composition comprising [a] a  $\beta$ -alkoxyalkyl cyanoacrylate selected from  $\beta$ -methoxy ethyl cyanoacrylate,  $\beta$ -ethoxy ethyl cyanoacrylate and combinations thereof; [b] a cyanoacrylate selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate and combinations thereof; and [c] a rubber toughening component, such as acrylic rubber. Also disclosed is a composition comprising [a] a cyanoacrylate selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate and combinations thereof; and [b] a rubber toughening component. Further disclosed is a composition comprising a rubber toughening component dissolved in up to 20 weight percent cyanoacrylate component selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate and combinations thereof. Also disclosed is a method of preparing the cyanoacrylate composition and use of the cyanoacrylate composition in bonding together two substrates. The cured cyanoacrylate compositions demonstrate improved toughness without an odour typically found with cyanoacrylate-containing compositions.

### T- Peel on Aluminium

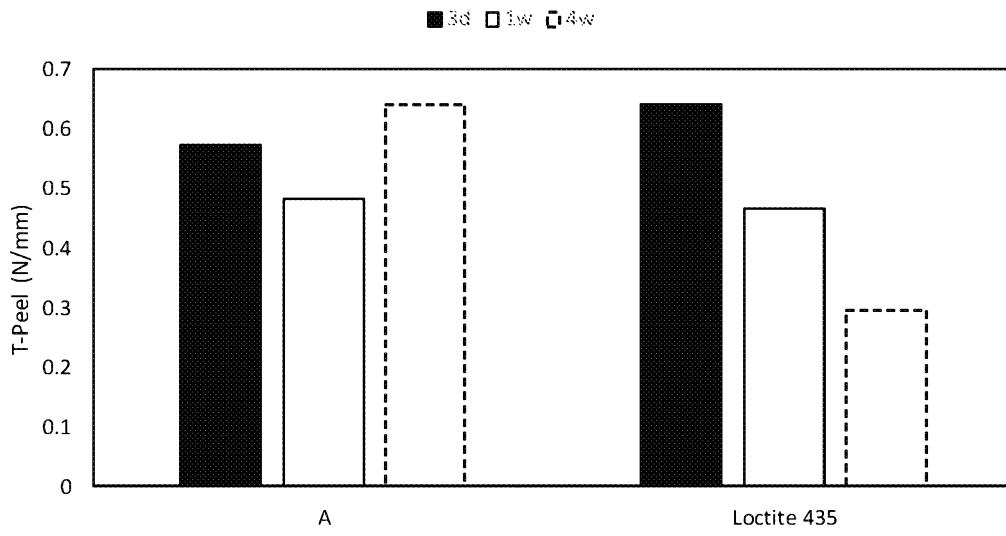


FIG. 1

### T- Peel on Mild Steel

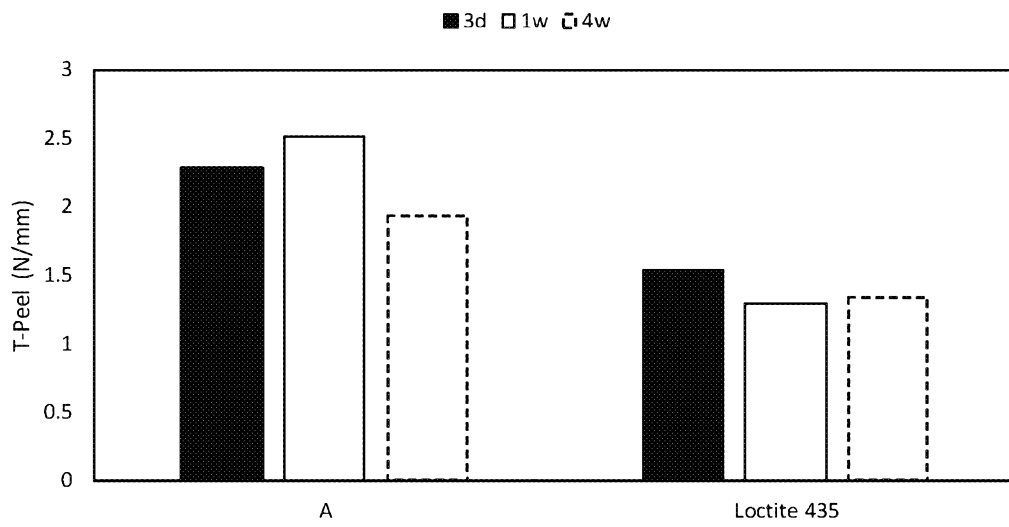


FIG. 2

### Side impact on Aluminium

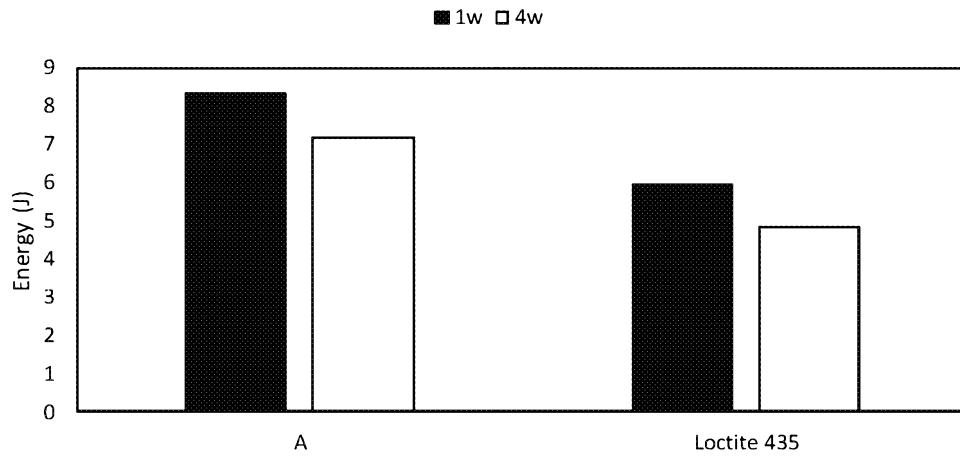


FIG. 3

### Side Impact on Mild Steel

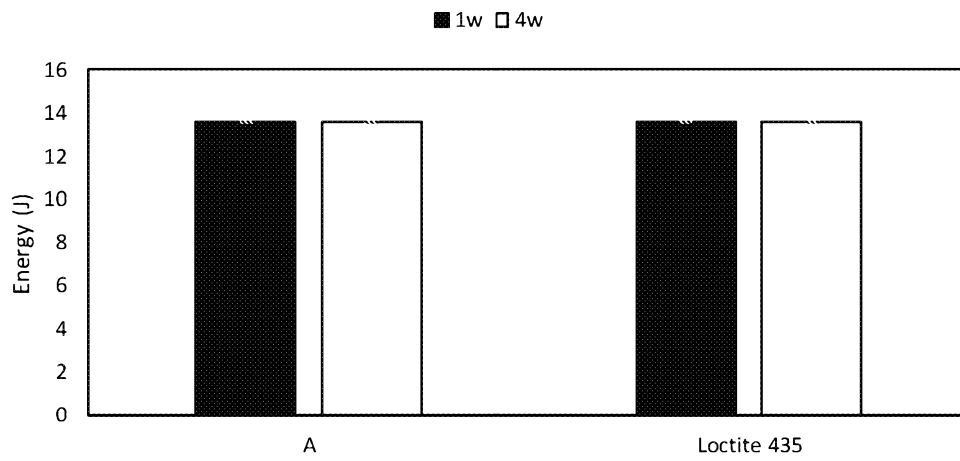


FIG. 4

### T- Peel on Aluminium

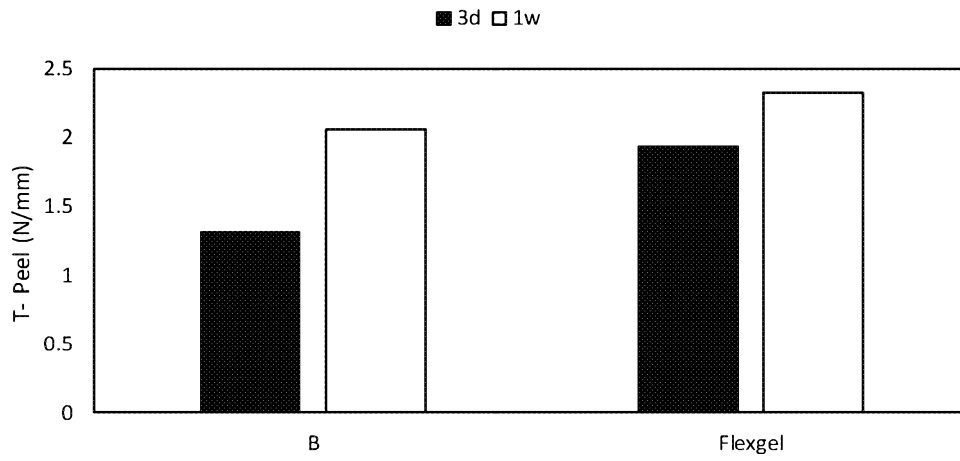


FIG. 5

### T-Peel on Mild Steel

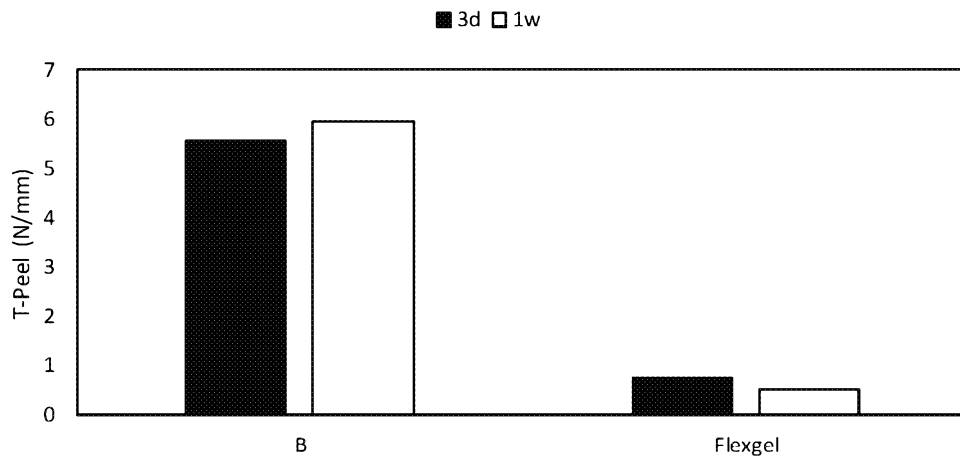


FIG. 6

### T-Peel on Aluminium

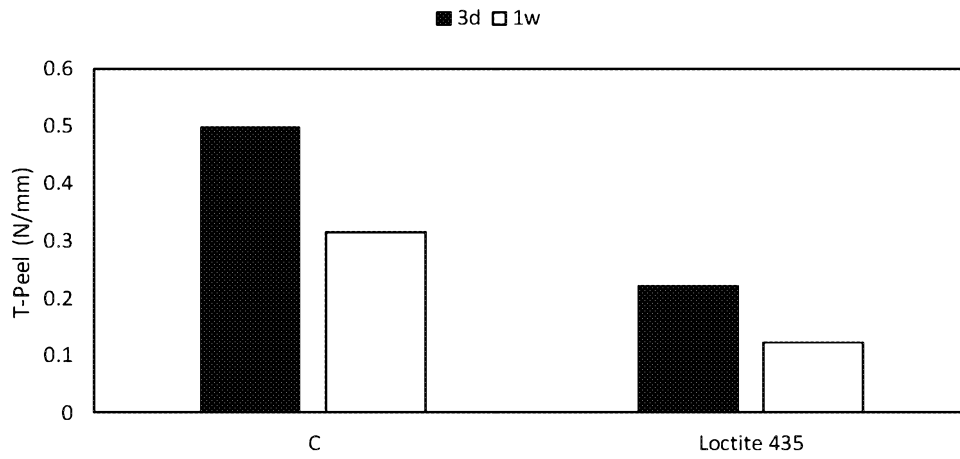


FIG. 7

### T-Peel on Mild Steel

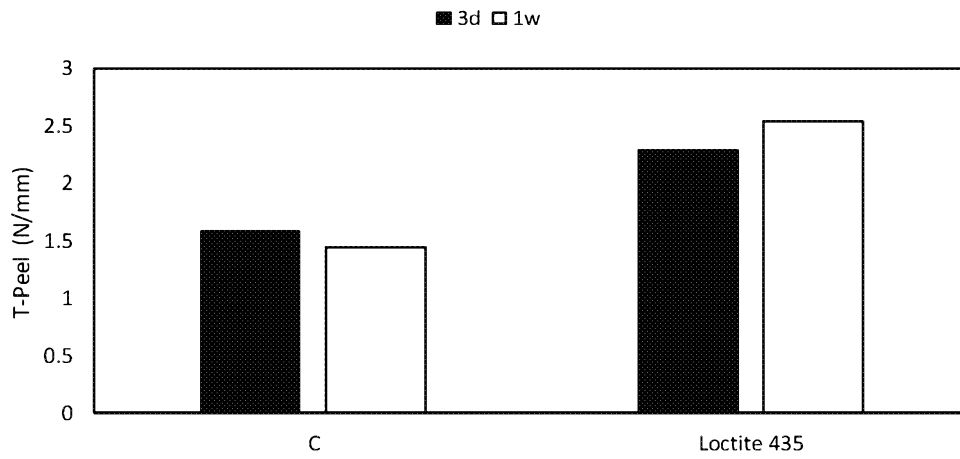


FIG. 8

### T-Peel on Aluminium

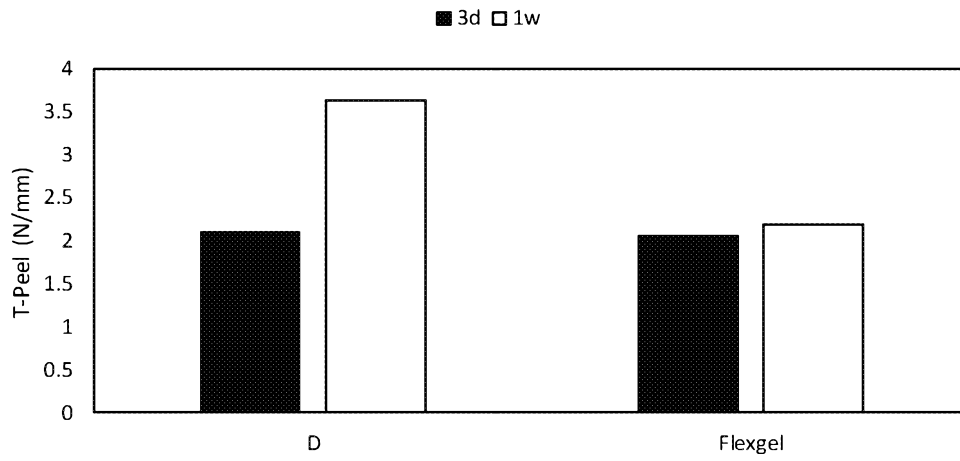


FIG. 9

### T-Peel on Mild Steel

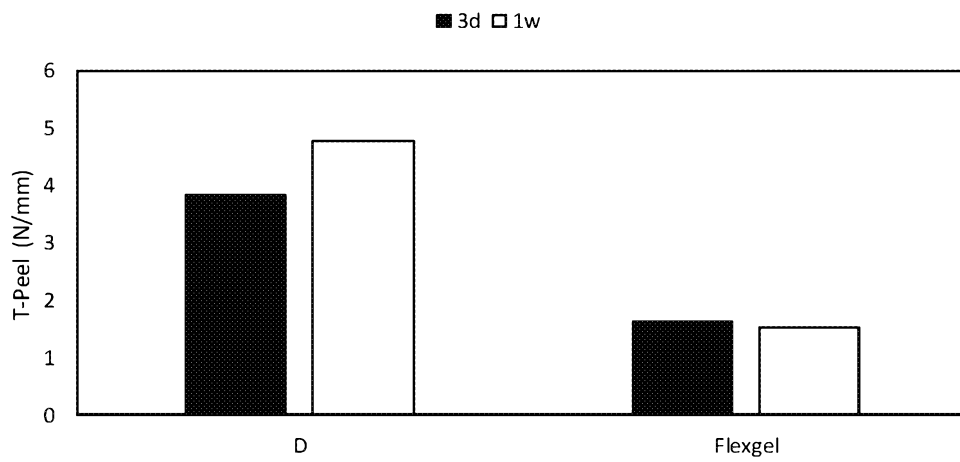
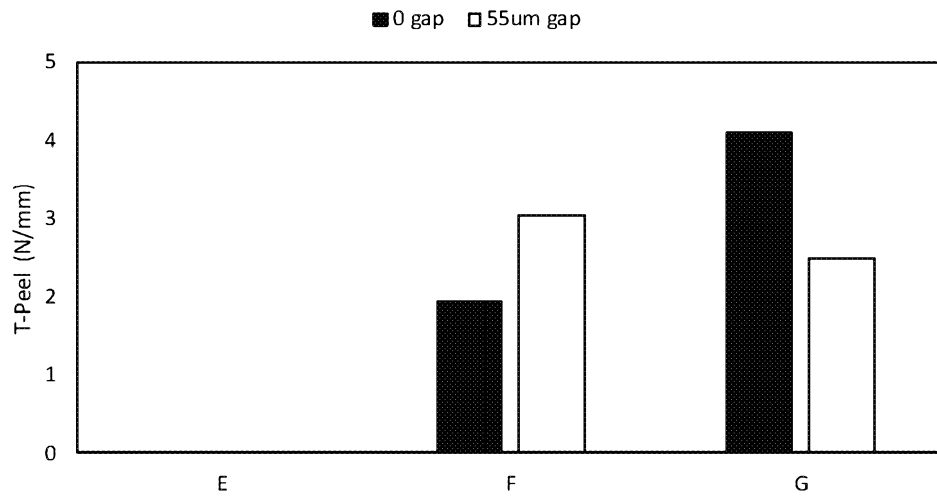


FIG. 10

### T-Peel on Mild Steel



**FIG. 11**

TOUGHENED, LOW ODOR/LOW BLOOM  
CYANOACRYLATE COMPOSITIONS

BACKGROUND

Field

[0001] This invention relates to cyanoacrylate-containing compositions that include (a) a  $\beta$ -alkoxyalkyl cyanoacrylate component, (b) a cyanoacrylate component selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof; and (c) a rubber toughening component. Cured products of the inventive cyanoacrylate compositions demonstrate improved toughness without an odor typically found with cyanoacrylate-containing compositions or blooming sometimes seen in cured products thereof.

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., Plenum Press, New York, p. 249-307 (1986).

[0003] U.S. Patent No. 4,440,910 (O'Connor) pioneered rubber toughened cyanoacrylate compositions through the use of certain



organic polymers as toughening additives that are elastomeric, i.e., rubbery, in nature. The '910 patent is thus directed to and claims a curable adhesive comprising a substantially solvent-free mixture of: (a) a cyanoacrylate ester, and (b) about 0.5% to about 20% by weight of an elastomeric polymer. The elastomeric polymer is selected from elastomeric copolymers of a lower alkene monomer and (i) acrylic acid esters, (ii) methacrylic acid esters or (iii) vinyl acetate. More specifically, the '910 patent notes that as toughening additives for cyanoacrylates, acrylic rubbers; polyester urethanes; ethylene-vinyl acetates; fluorinated rubbers; isoprene-acrylonitrile polymers; chlorosulfinated polyethylenes; and homopolymers of polyvinyl acetate were found to be particularly useful.

[0004] The elastomeric polymers are described in the '910 patent as either homopolymers of alkyl esters of acrylic acid; copolymers of another polymerizable monomer, such as lower alkenes, with an alkyl or alkoxy ester of acrylic acid; and copolymers of alkyl or alkoxy esters of acrylic acid. Other unsaturated monomers which may be copolymerized with the alkyl and alkoxy esters of acrylic include dienes, reactive halogen-containing unsaturated compounds and other acrylic monomers such as acrylamides.

[0005] Conventional commercial ethyl cyanoacrylate compositions have an odor, which some end users find offensive.  $\beta$ -methoxy ethyl cyanoacrylate is known to not have the same odor. Ethyl cyanoacrylate compositions are also known to show blooming when cured, which tends to be absent with  $\beta$ -methoxy ethyl cyanoacrylate.

[0006] Today there are no toughened, low odor/low bloom cyanoacrylate products commercially available in the market.

Commercially available toughened cyanoacrylate products are predominately based on ethyl cyanoacrylate monomer and exhibit (1) an odor that some end users find offensive and/or (2) sometimes blooming when cured.

[0007] Commercially available cyanoacrylate products are often toughened with an ethylene:methyl methacrylate terpolymer. This polymer contributes little toughness to cyanoacrylate compositions containing  $\beta$ -methoxy ethyl cyanoacrylate, one reason for which may be that the polymer shows sparing solubility in  $\beta$ -methoxy ethyl cyanoacrylate.

[0008] Notwithstanding the state of the art and the efforts to date to improve the toughness of  $\beta$ -alkoxyalkyl cyanoacrylate compositions, there remained a long felt, yet unmet, need to provide toughness to cured reaction products of such cyanoacrylate compositions, and while doing so minimize the odor and/or blooming oftentimes associated with cyanoacrylate compositions. Until now.

#### SUMMARY

[0009] Cyanoacrylate compositions comprising (a) a  $\beta$ -alkoxyalkyl cyanoacrylate component, (b) a cyanoacrylate component selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof; and (c) a rubber toughening component, are thus provided.

[0010] The inclusion of the  $\beta$ -alkoxyalkyl cyanoacrylate component provides a cyanoacrylate base for the composition that does not emit an odor commonly found in cyanoacrylate compositions. The cyanoacrylate component recited above

provides a vehicle by which to introduce a rubber toughening component to the  $\beta$ -alkoxyalkyl cyanoacrylate component. The rubber toughening component provides for improved toughness, as is shown in the Examples. Rubber toughening components are sometimes known to show sparing solubility in cyanoacrylate compositions, particularly cyanoacrylate compositions containing beta-alkoxyalkyl cyanoacrylates. As a result, the toughness observed in prior attempts has been limited at best. The cyanoacrylate component recited above aids in that regard.

[0011] This invention is also 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.

[0012] In addition, the present invention is directed to reaction products of the inventive compositions.

[0013] Also, the invention is directed to a method of preparing the inventive compositions, and a method of conferring improved toughness to a cured reaction product of a cyanoacrylate composition, while minimizing the odor oftentimes associated with cyanoacrylate compositions as well as bloom sometimes observed with cured product thereof.

[0014] And the invention is directed to a composition comprising a cyanoacrylate component selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof; and a rubber toughening component.

[0015] The invention will be more fully understood by a reading of the section entitled "Detailed Description", which follows.

**BRIEF DESCRIPTION OF THE FIGURES**

[0016] FIG. 1 depicts a bar chart of T-Peel strength on aluminum substrates bonded with Sample A and LOCTITE 435 after curing for a period of time of 3 days, 1 week and 4 weeks at room temperature.

[0017] FIG. 2 depicts a bar chart of T-Peel strength on mild steel substrates bonded with Sample A and LOCTITE 435 after curing for a period of time of 3 days, 1 week and 4 weeks at room temperature.

[0018] FIG. 3 depicts a bar chart of side impact strength on aluminum substrates bonded with Sample A and LOCTITE 435 after curing for a period of time of 1 week and 4 weeks at room temperature.

[0019] FIG. 4 depicts a bar chart of side impact strength on mild steel substrates bonded with Sample A and LOCTITE 435 after curing for a period of time of 1 week and 4 weeks at room temperature.

[0020] FIG. 5 depicts a bar chart of T-Peel strength on aluminum substrates bonded with Sample B and LOCTITE FlexGel after curing for a period of time of 3 days and 1 week at room temperature.

[0021] FIG. 6 depicts a bar chart of T-Peel strength on mild steel substrates bonded with Sample B and LOCTITE FlexGel after curing for a period of time of 3 days and 1 week at room temperature.

[0022] FIG. 7 depicts a bar chart of T-Peel strength on aluminum substrates bonded with Sample C and LOCTITE 435 after curing for a period of time of 3 days and 1 week at room temperature.

[0023] FIG. 8 depicts a bar chart of T-Peel strength on mild steel substrates bonded with Sample C and LOCTITE 435 after curing for a period of time of 3 days and 1 week at room temperature.

[0024] FIG. 9 depicts a bar chart of T-Peel strength on aluminum substrates bonded with Sample D and LOCTITE FlexGel after curing for a period of time of 3 days and 1 week at room temperature.

[0025] FIG. 10 depicts a bar chart of T-Peel strength on mild steel substrates bonded with Sample D and LOCTITE FlexGel after curing for a period of time of 3 days and 7 days at room temperature.

[0026] FIG. 11 depicts a bar chart of T-Peel strength on mild steel substrates bonded with Samples E, F and G, with and without a gap of 55  $\mu\text{m}$ .

#### DETAILED DESCRIPTION

[0027] As noted above, this invention is directed to a cyanoacrylate composition comprising (a) a  $\beta$ -alkoxyalkyl cyanoacrylate component, (b) a cyanoacrylate component selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof; and (c) a rubber toughening component.

[0028] The  $\beta$ -alkoxyalkyl cyanoacrylate component (a) may be chosen from  $\beta$ -methoxymethyl cyanoacrylate,  $\beta$ -methoxyethyl cyanoacrylate,  $\beta$ -ethoxymethyl cyanoacrylate,  $\beta$ -ethoxyethyl cyanoacrylate and combinations thereof. Particularly desirable among those  $\beta$ -alkoxyalkyl cyanoacrylates is  $\beta$ -methoxyethyl cyanoacrylate.

[0029] The  $\beta$ -alkoxyalkyl cyanoacrylate component (a) should be included in the compositions in an amount within the range of from about 40% to about 90% by weight, with the range of about 55% to about 75% by weight being desirable, and about 60% by weight of the total composition being particularly desirable.

[0030] The cyanoacrylate component (b) may be selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof. Particularly desirable among those cyanoacrylate components is isoamyl cyanoacrylate.

[0031] The cyanoacrylate component (b) should be included in the compositions in an amount within the range of from about 10% to about 50% by weight, with the range of about 20% to about 35% by weight being desirable, and about 30% by weight of the total composition being particularly desirable.

[0032] The rubber toughening component (c) may be selected from (i) reaction products of the combination of ethylene, methyl acrylate and monomers having carboxylic acid cure sites, (ii) dipolymers of ethylene and methyl acrylate, (iii) vinylidene chloride-acrylonitrile copolymers, (iv) vinyl chloride/vinyl acetate copolymer, (v) copolymers of polyethylene and polyvinyl acetate, and combinations thereof.

[0033] Desirably, the reaction products (c)(i) of the combination of ethylene, methyl acrylate and monomers having carboxylic acid cure sites, where the reaction products are substantially free of release agents, anti-oxidants, stearic acid and polyethylene glycol ether wax,  $\beta$ -alkoxyalkyl cyanoacrylate are chosen for use. DuPont supplies such a reaction product under the trade name VAMAC VCS 5500.

[0034] The rubber toughening component (c) should be included in the compositions in an amount within the range of from about 3% to about 20% by weight, with the range of about 5% to about 15% by weight being desirable, and about 8% by weight of the total composition being particularly desirable.

[0035] Thus, desirably the inventive composition in a preferred embodiment includes the following components in the by weight percent ranges noted in Table 1 below.

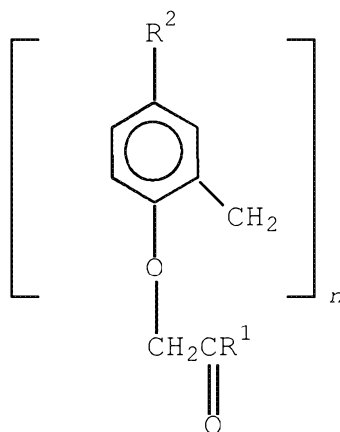
Table 1

Constituent	Broad range	Desirable range
$\beta$ - Methoxy Ethyl Cyanoacrylate	40-90 %	55-75 %
Isoamyl Cyanoacrylate	10-50 %	20-35 %
VAMAC VCS 5500	3-20 %	5-15 %

[0036] Accelerators may also be included in the inventive 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.

[0037] 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.

[0038] For instance, as regards calixarenes, those within the following structure are useful herein:



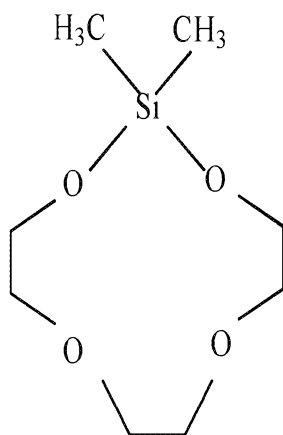
where R<sup>1</sup> is alkyl, alkoxy, substituted alkyl or substituted alkoxy; R<sup>2</sup> is H or alkyl; and n is 4, 6 or 8.

[0039] One particularly desirable calixarene is tetrabutyl tetra[2-ethoxy-2-oxoethoxy]calix-4-arene.

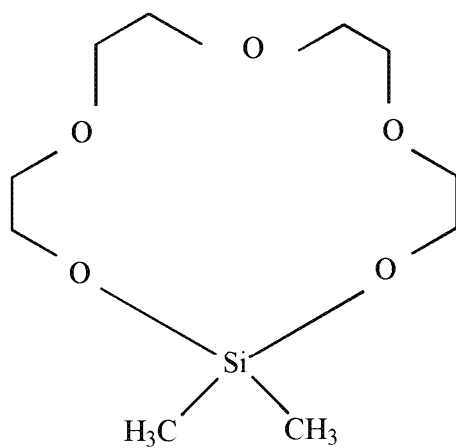
[0040] A host of crown ethers are known. For instance, any one or more of 15-crown-5, 18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5-dibenzo-24-crown-8, dibenzo-30-crown-10, tribenzo-18-crown-6, asym-dibenzo-22-crown-6, dibenzo-14-crown-4, dicyclohexyl-18-crown-6, dicyclohexyl-24-crown-8, cyclohexyl-12-crown-4, 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 may be used. See U.S. Patent No. 4,837,260 (Sato), the disclosure of which is hereby expressly incorporated herein by reference. Of the silacrowns, again many are known, and are reported in the literature.

[0041] Specific examples of silacrown compounds useful in the inventive compositions include:

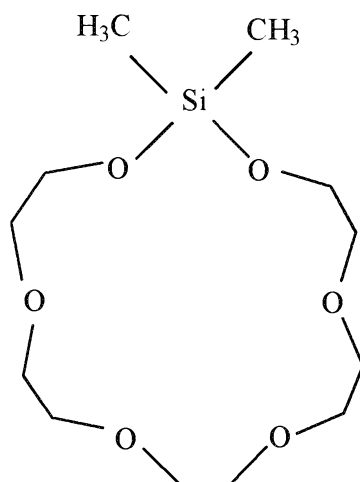




dimethylsila-11-crown-4;



dimethylsila-14-crown-5;

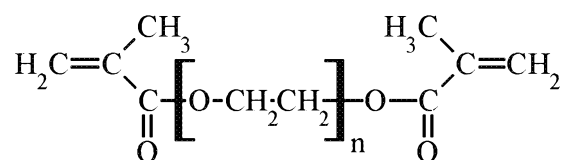


and dimethylsila-17-crown-6.

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

[0042] 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  $\alpha$ ,  $\beta$  or  $\gamma$ -cyclodextrin which is at least partly soluble in the cyanoacrylate would be appropriate choices for use herein as the first accelerator component.

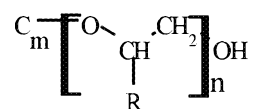
[0043] For instance, poly(ethylene glycol) di(meth)acrylates suitable for use herein include those within the following structure:



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.

[0044] 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 alkyl or 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.

[0045] When used, the accelerator 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.

[0046] 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.

[0047] Other additives may be included in the inventive cyanoacrylate compositions, such as certain acidic materials (like citric acid), thixotropy or gelling agents, thickeners, dyes, and combinations thereof.

[0048] Of the accelerators and these additives, those listed in the table below are desirable examples, particularly in the amounts noted.

Table 2

Constituent	Broad range	Desirable range
Crown Ether	0.1-0.5 %	0.1-0.2 %
Citric Acid	50-100 ppm	100 ppm
Silica	0-10 %	5-6 %

[0049] In addition, the cyanoacrylate component may include further 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<sub>1-15</sub> alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and 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, and combinations thereof.

[0050] 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.

[0051] In yet another aspect of the invention, there is provided reaction products of the so-described compositions.

[0052] In still another aspect of the invention, there is provided a method of preparing the so-described compositions. The method includes providing (a) a  $\beta$ -alkoxyalkyl cyanoacrylate component, and combining therewith with mixing (b) a

cyanoacrylate component selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof; and (c) a rubber toughening component, where desirably the rubber toughening component is dissolved in the cyanoacrylate component in an amount of up to about 20% by weight.

[0053] In still yet another aspect of the invention, there is provided a composition comprising a cyanoacrylate component selected from 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof; and a rubber toughening component, where desirably the rubber toughening component is dissolved in the cyanoacrylate component in an amount of up to about 20% by weight.

[0054] The invention will be further illustrated by the examples which follow.

#### EXAMPLES

[0055] Isoamyl cyanoacrylate and 2-methyl butyl cyanoacrylate unexpectedly solubilized traditional cyanoacrylate tougheners, namely VAMAC. The VAMAC rubber toughener was determined to be soluble in each of the monomers at an amount of up to about 20% by weight.

[0056] Due to this observation, VAMAC rubber toughener was added to approximately 30:70 blends of isoamyl cyanoacrylate containing  $\beta$ -methoxy ethyl cyanoacrylate and 2-methylbutyl cyanoacrylate containing  $\beta$ -methoxy ethyl cyanoacrylate in an

amount of 8% by weight to form a solution of the inventive cyanoacrylate compositions.

[0057] When isoamyl cyanoacrylate or 2-methyl butyl cyanoacrylate is used to solubilize the rubber toughener (here, VAMAC) and then it is introduced as a solution to  $\beta$ -methoxyethyl cyanoacrylate, toughness is observed. And when comparable compositions are prepared in a gel format, an increase in toughness is maintained. To illustrate the results comparisons were carried out with a rubber toughened ethyl cyanoacrylate product and a rubber toughened gel ethyl cyanoacrylate product.

[0058] All samples 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 identity and quantity of the constituents used.

[0059] Initially, a rubber toughening component (VAMAC VCS 5500, available from DuPont) was evaluated in  $\beta$ -methoxy ethyl cyanoacrylate and a cyanoacrylate component selected from isoamyl cyanoacrylate or 2-methylbutyl cyanoacrylate.

[0060] More specifically, 27.3% by weight isoamyl cyanoacrylate was blended with 63.7% by weight  $\beta$ -methoxy ethyl cyanoacrylates.  $\text{BF}_3$  [ $\text{BF}_3\text{OEt}_2$ ] 0.9% by weight was added followed by 8% by weight VAMAC VCS 5500. The mixture was heated to a temperature of  $65^\circ\text{C}$  and mixed for approximately 3-4 hours, until all of the VAMAC VCS 5500 was observed to have dissolved. Upon cooling, about 0.1% by weight dibenzo-18-crown-6 ether and about 0.001% by weight of citric acid were added to form Sample A. Sample B was formed by the further addition of 6% by weight of silica.

Table 3

Components	Sample / Amt (wt%)	
	A	B
Isoamyl cyanoacrylate	27.3	24.3
$\beta$ -Methoxy ethyl cyanoacrylate	63.7	60.7
VCS 5500	8	8
BF <sub>3</sub> as [BF <sub>3</sub> OEt <sub>2</sub> ]	0.9	0.9
Crown Ether	0.1	0.1
Citric Acid	0.001	0.001
Silica	--	6

[0061] Thus, Sample A in Table 3 has no silica, while Sample B has silica, thereby rendering it in gel form.

[0062] Separately, 27.3% by weight 2-methylbutyl cyanoacrylate was blended with 63.7% by weight  $\beta$ -methoxy ethyl cyanoacrylates. BF<sub>3</sub> [BF<sub>3</sub>OEt<sub>2</sub>] in an amount of 0.9% by weight was added followed by 8% by weight VAMAC VCS 5500. The mixture was heated to a temperature of 65°C and mixed for about 3-4 hours, until all of the VAMAC VCS 5500 was observed to have dissolved. Upon cooling, about 0.1% by weight of dibenzo-18-crown-6 ether and about 0.001% by weight of citric acid were added to form Sample C. Sample D was formed by the further addition of 6% by weight of silica.

Table 4

Components	Sample / Amt (wt%)	
	C	D
2-Methyl Butyl cyanoacrylate	27.3	24.3
$\beta$ -Methoxy cyanoacrylate	63.7	60.7
VCS 5500	8	8
BF <sub>3</sub> as [BF <sub>3</sub> OEt <sub>2</sub> ]	0.9	0.9
Crown Ether	0.1	0.1
Citric Acid	0.001	0.001
Silica	--	6

[0063] Thus, Sample C in Table 4 has no silica, while Sample D has silica, thereby rendering it in gel form.

[0064] By way of the background, toughness was measured by 180° T Peel testing on mild steel and aluminum substrates (each of which being about 1 inch wide and being aligned with a 90° tab at the end of the assembly to facilitate the peeling, in accordance with ASTM 710/ISO 11339).

[0065] For the performance evaluation, the control for Samples A and C was LOCTITE 435, which is a clear rubber toughened ethyl cyanoacrylate product containing 8% by weight VAMAC and for Samples B and D, the control was LOCTITE FlexGel, which is ethyl cyanoacrylate containing VAMAC, PMMA and silica.

[0066] Table 5 shows the data captured for the T-Peel strength performance for Samples A and B, as reflected in FIGs. 1, 2, 5 and 6, respectively.



Table 5

Time (weeks)/ Substrate	Sample/T-Peel (N/mm)			
	A	B	LOCTITE 435	LOCTITE FlexGel
3days/Al	0.57	1.31	0.64	1.93
1/Al	0.48	2.12	0.47	2.13
4/Al	0.64	-	0.29	-
3 days/MS	2.28	5.55	1.53	0.75
1/MS	2.51	5.94	1.28	0.50
4/MS	1.92	-	1.33	1.33

[0067] The results depicted in FIGs. 1 and 2 show comparable T-Peel strength performance for Sample A and LOCTITE 435 on aluminum substrates. However, on mild steel substrates Sample A shows improved toughness in terms of T Peel strength performance over LOCTITE 435.

Table 6

Time (weeks)/ Substrate	Sample/Side Impact (J)	
	A	LOCTITE 454
1/Al	8.33	5.93
4/Al	7.16	4.83
1/MS	>13.56	>13.56
4/MS	>13.56	>13.56

[0068] With reference to FIGs. 3 and 4 and the data captured in Table 6, the side impact evaluation shows significant improvement on the aluminum substrates for Sample A over LOCTITE 435. On the mild steel substrates, comparable toughness was observed with Sample A and LOCTITE 435, though in each case improved over that shown on aluminum substrates.

[0069] FIGs. 5 and 6 show the T-Peel strength performance of Sample B compared with LOCTITE FlexGel as evaluated on aluminum

and mild steel substrates after 3 days and 1 week of aging. On aluminum, the T-Peel strength performance was comparable with that shown by LOCTITE FlexGel.

[0070] But on mild steel substrates the surprising result was the T-Peel strength performance -- 5 N/mm. This performance is impressive for any cyanoacrylate adhesive, and exceptional for a low odor/low bloom cyanoacrylate adhesive that contains  $\beta$ -methoxy ethyl cyanoacrylate.

[0071] Table 7 shows the T-Peel strength performance for the 2-methyl butyl cyanoacrylate-containing compositions (shown in Table 4). FIGs. 7 and 8 highlights graphically the comparable T Peel strength performance for Sample C and LOCTITE 435 on aluminum substrates.

Table 7

Time (weeks) / Substrate	Sample/T-Peel (N/mm)			
	C	D	LOCTITE 435	LOCTITE FlexGel
3days/Al	0.49	2.10	0.22	2.05
1/Al	0.32	3.62	0.12	2.20
3 days/MS	1.57	3.84	2.30	1.62
1/MS	1.44	4.78	2.55	1.54

[0072] In FIGs. 9 and 10, Sample D was compared with LOCTITE FlexGel as the control and shows T-Peel strength performance on aluminum and mild steel LOCTITE FlexGel. Surprisingly by moving to a gel formulation, an improvement over LOCTITE FlexGel is observed in T-Peel strength performance on both the mild steel and the aluminum substrates.

[0073] In Table 8 below, three samples were prepared to evaluate the effect of silica and silica with citric acid. Each

sample was stabilized with methane sulfonic acid and sulfur dioxide.

Table 8

Components	Sample / Amt (wt%)		
	E	F	G
Isoamyl cyanoacrylate	28.05	26.25	25.80
$\beta$ -Methoxy cyanoacrylate	63.95	59.75	60.19
VCS 5500	8	8	8
MSA	0.0015	0.0015	0.0015
SO <sub>2</sub>	0.002	0.002	0.002
Silica	--	6	6
Citric Acid	--	--	0.005

[0074] Reference to FIG. 11 shows that T-Peel strength performance on mild steel substrates improved with the addition of silica (Sample F) and then again with the addition of silica and citric acid (Sample G), both with and without a gap of 55  $\mu$ m between the substrates although the performance with the added silica and citric acid (Sample G) reverses the relative performance of the gapped and ungapped substrates compared with only silica added (Sample F).

What is Claimed is:

1. A cyanoacrylate composition, comprising:
  - (a) a  $\beta$ -alkoxyalkyl cyanoacrylate component,
  - (b) a cyanoacrylate component selected from the group consisting of 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof; and
  - (c) a rubber toughening component.
  
2. The composition according to Claim 1, wherein the  $\beta$ -alkoxyalkyl cyanoacrylate component is selected from  $\beta$ -methoxy ethyl cyanoacrylate,  $\beta$ -ethoxy ethyl cyanoacrylate, and combinations thereof.
  
3. The composition according to Claim 1, wherein the rubber toughening component is selected from the group consisting of (a) reaction products of the combination of ethylene, methyl acrylate and monomers having carboxylic acid cure sites, (b) dipolymers of ethylene and methyl acrylate, (c) vinylidene chloride-acrylonitrile copolymers, (d) vinyl chloride/vinyl acetate copolymer, (e) copolymers of polyethylene and polyvinyl acetate, and combinations thereof.
  
4. The composition according to Claim 1, wherein the rubber toughening component is a reaction product of the combination of ethylene, methyl acrylate and monomers having carboxylic acid cure sites, wherein the reaction product is free of release agents, anti-oxidants, stearic acid and polyethylene glycol ether wax.

5. The composition according to Claim 1, further comprising one or more of a thixotrope, a gelling agent, a thickener, an accelerator and a shock resistance conferring agent.

6. The composition according to Claim 5, wherein the accelerator is selected from the group consisting of calixarene, oxacalixarene, silacrown, cyclodextrin, crown ether, poly(ethyleneglycol) di(meth)acrylate, ethoxylated hydric compound, and combinations thereof.

7. The composition according to Claim 6, wherein the calixarene is tetrabutyl tetra[2-ethoxy-2-oxoethoxy]calix-4-arene.

8. The composition according to Claim 6, wherein the crown ether is selected from members within the group consisting of 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 and combinations thereof.



alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.

15. Reaction products of the composition according to Claim 1.

16. A composition comprising:

(a) a cyanoacrylate component selected from the group consisting of 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof, and

(b) a rubber toughening component.

17. A composition comprising a rubber toughening component dissolved in an amount of up to about 20 weight percent in a cyanoacrylate component selected from the group consisting of 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof.

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

applying a cyanoacrylate composition according to Claim 1, to at least one of the substrates, and

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

19. A method of preparing a cyanoacrylate composition according to Claim 1, comprising the steps of:

providing a rubber toughening component dissolved in a cyanoacrylate component selected from the group consisting of 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof, and

combining therewith with mixing a  $\beta$ -alkoxyalkyl cyanoacrylate component.

20. A method of conferring at least one of improved peel strength and side impact strength to a cured product of a cyanoacrylate composition, comprising the steps of:

providing a  $\beta$ -alkoxyalkyl cyanoacrylate component; and

providing a rubber toughening component dissolved in a cyanoacrylate component selected from the group consisting of 2-methylbutyl cyanoacrylate, isoamyl cyanoacrylate, 2-ethylhexyl cyanoacrylate, 2-pentyl cyanoacrylate, 3-methylpentyl cyanoacrylate, 2-ethylbutyl cyanoacrylate, 3,7-dimethyloctyl cyanoacrylate, and combinations thereof.





**Application No:** GB1717707.2

**Examiner:** Dr Albert Mthupha

**Claims searched:** 1-15, 18-20

**Date of search:** 14 March 2018

**Patents Act 1977: Search Report under Section 17**

**Documents considered to be relevant:**

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-4, 6-10, 14-15, 18-20.	WO2017/077091 A1 (HENKEL), see abstract, para. [0029], [0030]-[0033], [0036], [0066], [0079], a cyanoacrylate composition comprising [a] a beta-methoxyethyl cyanoacrylate, [b] isoamyl cyanoacrylate, 2-pentyl cyanoacrylate, and [c] a rubber toughening component.
X	1-4, 6-10, 14-15, 18-20.	WO2017/077089 A1 (HENKEL), see abstract, para. [0010], [0030]-[0033], [0045], [0056]-[0059], [0064], a cyanoacrylate composition comprising [a] a beta-methoxyethyl cyanoacrylate, [b] isoamyl cyanoacrylate, 2-pentyl cyanoacrylate, and [c] a rubber toughening component.
X	1-9, 14-15, 18-20.	WO2010/029134 A1 (LOCTITE), see para. [0018], [0023], [0027], [0045], [0046], [0048]-[0050], [0052], disclosing a cyanoacrylate component (comprising beta-methoxyethyl cyanoacrylate, 2-pentyl cyanoacrylate mixture) and a toughening agent comprising a co-polymer of polyethylene and polyvinyl acetate.
X	1-2, 6-8, 15, 18-20.	JPH06145606 A (TOA GOSEI CHEM IND), see Machine Translation by EPO, note para. [0019]-[0021], [0025], disclosing a cyanoacrylate composition comprising [a] a beta-methoxyethyl cyanoacrylate or beta-ethoxyethyl cyanoacrylate, [b] pentyl cyanoacrylate, and [c] an acrylic rubber (a rubber toughening component).

**Categories:**

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

**Field of Search:**

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC<sup>X</sup> :

--

Worldwide search of patent documents classified in the following areas of the IPC

C08F; C08K; C09J
------------------

The following online and other databases have been used in the preparation of this search report



EPODOC, WPI, TXTE.

**International Classification:**

<b>Subclass</b>	<b>Subgroup</b>	<b>Valid From</b>
C08F	0222/32	01/01/2006
C08F	0022/32	01/01/2006
C09J	0133/14	01/01/2006