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(54) **Title:** CYANOACRYLATE COMPOSITIONS

(57) **Abstract:** This invention relates to cyanoacrylate-containing compositions, which when cured provide improved bonding performance on aluminum substrates.

CYANOACRYLATE COMPOSITIONS

BACKGROUND

Field

[0001] This invention relates to cyanoacrylate-containing compositions, which when cured provide improved bonding performance on aluminum substrates.

Brief Description of Related Technology

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

[0003] There are few reported instances of efforts to improve the bonding of cyanoacrylate adhesive composition to aluminum substrates.

[0004] Yet numerous examples of the addition of certain anhydrides to cyanoacrylate compositions have been reported.

[0005] For instance, U.S. Patent No. 3,832,334 is directed to the addition of maleic anhydride, which is reported to produce cyanoacrylate adhesives having increased thermal resistance (when cured) while preserving fast cure speed.

[0006] U.S. Patent No. 4,196,271 is directed to tri-, tetra- and higher carboxylic acids or their anhydrides, which are reported to be useful for improving heat resistance of cured cyanoacrylate adhesives.

[0007] U.S. Patent No. 4,450,265 is directed to the use of phthalic anhydride to improve heat resistance of cyanoacrylate adhesives. More specifically, the '265 patent is directed to and claims an adhesive composition comprising a polymerizable constituent the major part of which comprises at least one ester of 2-cyanoacrylic acid, characterized in that the composition additionally comprises a proportion of phthalic anhydride effective for favorably influencing the strength and/or durability of adhesive bonds formed from the composition, under exposure to moisture or elevated temperature. The effective amount is reported as 0.1% to 5.0%, such as 0.3% to 0.7%, by weight of the composition. The '265 patent reports the superiority of phthalic anhydride over compositions where no additive was used, and where maleic anhydride was used (though less pronounced in the case of stainless steel lap shears than in those of aluminium).

[0008] U.S. Patent No. 4,532,293 is directed to the use of benzophenonetetracarboxylic acid or its anhydride to provide a superior heat resistance for cyanoacrylate adhesives.

[0009] More recently, U.S. Patent Application Publication No. 2014/0326407 (Li) is directed to a cyanoacrylate adhesive composition, comprising: (a) a cyanoacrylate component, (b) an anhydride, and (c) a maleimide-, itaconimide-, or nadimide-containing compound, where the anhydride may be phthalic anhydride or dimethyl maleic anhydride.

[0010] And U.S. Patent Application Publication No. 2014/0124137 (Hedderman) is directed to a cyanoacrylate adhesive composition, comprising: (a) a cyanoacrylate component, and (b) a hydrogenated anhydride, such as a hydrogenated phthalic anhydride, like a tetrahydrophthalic anhydride. The composition may also comprise a benzonitrile.

[0011] Despite these efforts, there has been a long standing, but unmet, desire to achieve more robust bonding performance from cyanoacrylate compositions on aluminum substrates. It would accordingly be quite advantageous to provide a solution to that desire.

SUMMARY

[0012] The present invention remedies the shortcomings on aluminum bonding performance of cyanoacrylate compositions by providing a cyanoacrylate composition, which when cured provides at least improved tensile strength, through broadly speaking the combination of (a) a cyanoacrylate component and (b) an aromatic multifunctional anhydride component, such as an aromatic dianhydride component.

[0013] This invention is also directed to a method of bonding together two substrates, at least one of which is constructed from aluminum, which method includes applying to at least one of the substrates a composition as described above, and thereafter mating together the substrates.

[0014] In addition, the present invention is directed to reaction products of the inventive compositions.

[0015] Also, the invention is directed to a method of preparing the inventive compositions.

[0016] The invention will be more fully understood by a reading of the section entitled "DETAILED DESCRIPTION", which follows.

DETAILED DESCRIPTION

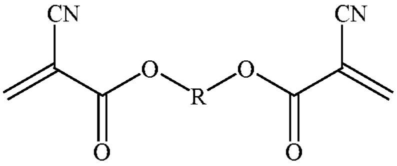
[0017] As noted above, this invention is directed to a cyanoacrylate composition, which when cured provides improved aluminum bonding performance.

[0018] The cyanoacrylate component includes at least one cyanoacrylate monomer which may be chosen with a raft of substituents, such as those represented by $H_2C=C(CN)-COOR$, where R is selected from C_{1-15} alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups. Desirably, the cyanoacrylate monomer is selected from at least one of methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl cyanoacrylates, butyl cyanoacrylates (such as n-butyl-2-cyanoacrylate), octyl cyanoacrylates, allyl cyanoacrylate, ß-methoxyethyl cyanoacrylate and combinations thereof.

[0019] The cyanoacrylate component should be included in the compositions in an amount within the range of from about 50% to about 99.98% by weight, with the range of about 70% to about 95% by weight, of the total composition being desirable.

[0020] In addition to the cyanoacrylate component a multi-functional cyanoacrylate component may be included as well. Multi-functional cyanoacrylate components are ordinarily bis-cyanoacrylates, but may be tri-functional, tetra-functional or penta-functional as well.

[0021] Bis-cyanoacrylates are embraced by structure I

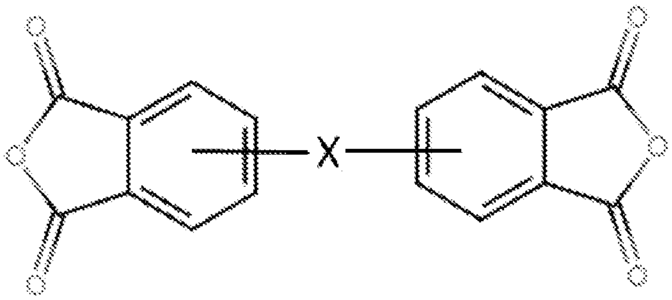


I

where R in structure I is a linkage selected from $(CH_2)_n$, with n being 2, 3, 4, 5, 6, 8, 9, 10, or 12, such as a linear or branched chain alkylene. Bis-cyanoacrylates of this sort may be prepared through a transesterification reaction using an appropriate diol to yield the alkylene center segment for "R". Desirable examples of these bis-cyanoacrylates include 1,10-decanediol bis-cyanoacrylate, 1,8-octanediol bis-cyanoacrylate, and 1,6-hexane bis-cyanoacrylate. An appropriate synthetic method to yield such bis-cyanoacrylates may be found generally in U.S. Patent Nos. 3,975,422 (Buck), 4,012,402 (Buck), and 6,096,848 (Gololobov), and International Patent Publication No. WO 2010/091975.

[0022] When used, the multi-functional cyanoacrylate component should be included in the compositions in an amount within the range of from about 5% to about 30% by weight, with the range of about 10% to about 20% by weight, of the total composition being desirable.

[0023] The aromatic multifunctional anhydride component may be chosen from a host of materials, such as an aromatic dianhydride component. For instance, the aromatic dianhydride component may be embraced by compounds within structure **II** below:

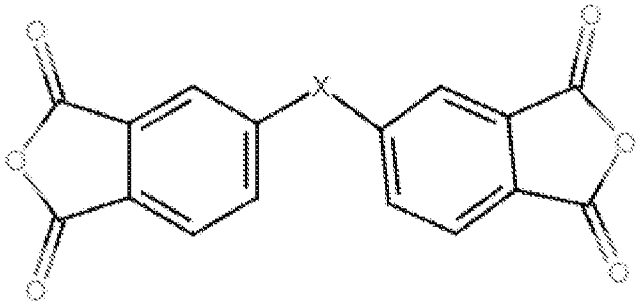


II

wherein X is selected from O; S; C=O; S=O; O=S=O; --; CRR^1 (wherein R and R^1 are independent of one another and are selected from the group consisting of H, C_1-C_3 alkyl and halogen); Y-Ar-Y^1 [wherein Y and Y^1 are independently selected from O, S, --, and CRR^1 (wherein R and R^1 are as described above), and Ar is an aromatic ring or a fused ring system comprising at least one aromatic ring]; Y-Ar-Y^1-Ar^1-Y^2 (wherein Y, Ar, and Y^1 are as described above, Ar^1 is selected from Ar, and Y^2 is selected from

Y or Y^1, and Ar is as described above); and $(O{=}CO)_n$-Z (wherein Z is C_1-C_6 alkylene.

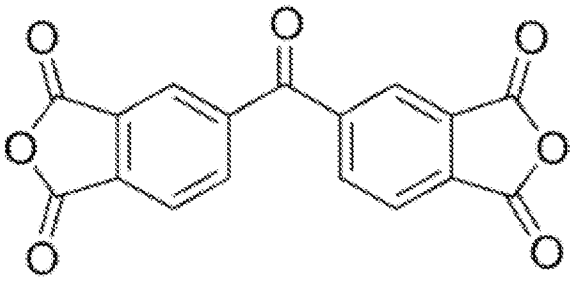
[0024] More specifically, the aromatic dianhydride component within the following structure:

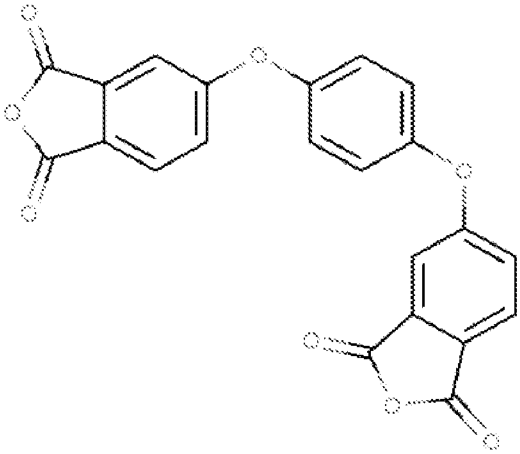


IIA

wherein X is as defined above.

[0025] Illustrative species of the aromatic dianhydride component include (some having acronyms beneath the respective structure):





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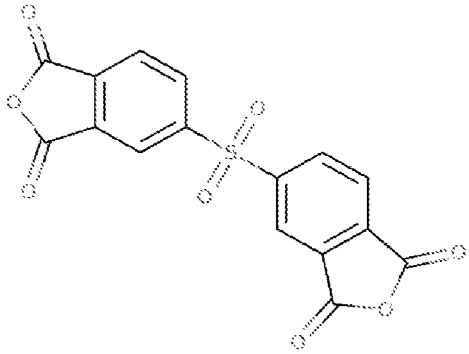
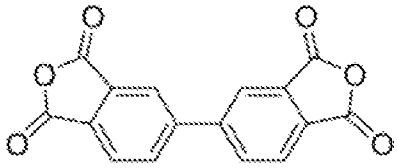
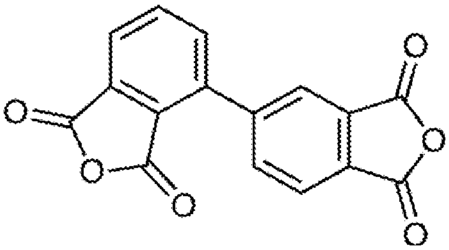
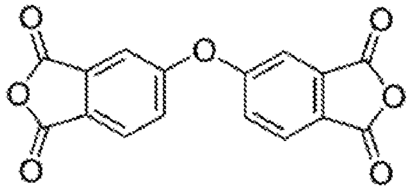


O
S

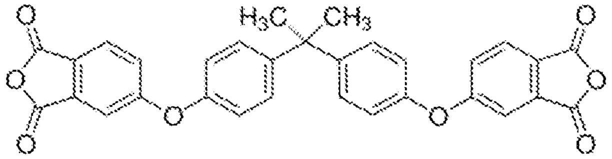


s-BPDPA

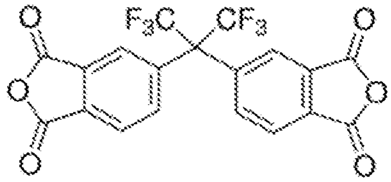




ODPA

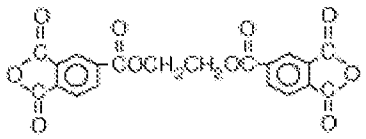


Bis-A DPA



6FDPA

and



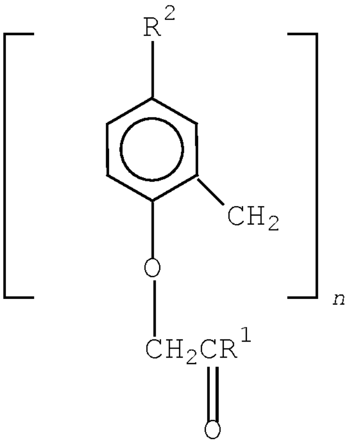
.

[0026] The aromatic multi-functional anhydride component should be present in the composition in an amount of from about 0.05 percent by weight to about 5 percent by weight, such as about 0.1 percent by weight to about 1 percent by weight.

[0027] 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.

[0028] 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.

[0029] For instance, as regards calixarenes, those within the following structure are useful herein:



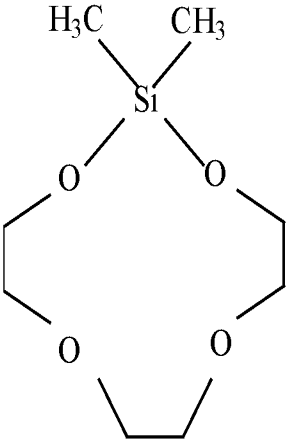
where R^1 is alkyl, alkoxy, substituted alkyl or substituted alkoxy; R^2 is H or alkyl; and n is 4, 6 or 8.

[0030] One particularly desirable calixarene is tetrabutyl tetra[2-ethoxy-2-oxoethoxy]calix-4-arene.

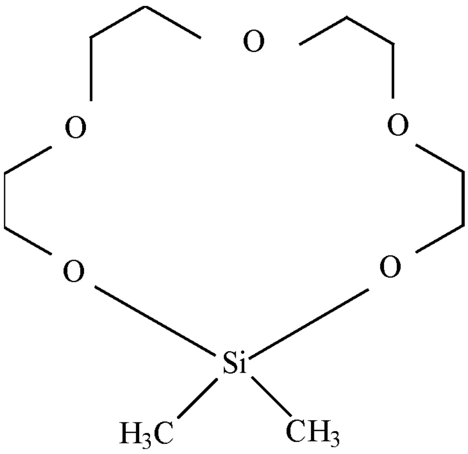
[0031] A host of crown ethers are known. For instance, examples which may be used herein either individually or in combination, include 15-crown-5, 18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5-dibenzo-24-crown-8, dibenzo-30-crown-10, tribenzo-18-crown-6, asym-dibenzo-22-crown-6, dibenzo-14-crown-4, dicyclohexyl-18-crown-6, dicyclohexyl-24-crown-8, cyclohexyl-12-crown-4, 1,2-decalyl-15-crown-5, 1,2-naphtho-15-crown-5, 3,4,5-naphtyl-16-crown-5, 1,2-methyl-benzo-18-crown-6, 1,2-methylbenzo-5, 6-methylbenzo-18-crown-6, 1,2-t-butyl-18-crown-6, 1,2-vinylbenzo-15-crown-5, 1,2-vinylbenzo-18-crown-6, 1,2-t-butyl-cyclohexyl-18-crown-6, asym-dibenzo-22-crown-6 and 1,2-benzo-1,4-benzo-5-oxygen-20-crown-7. See U.S. Patent No. 4,837,260 (Sato), the disclosure of which is hereby expressly incorporated herein by reference.

[0032] Of the silacrowns, again many are known, and are reported in the literature.

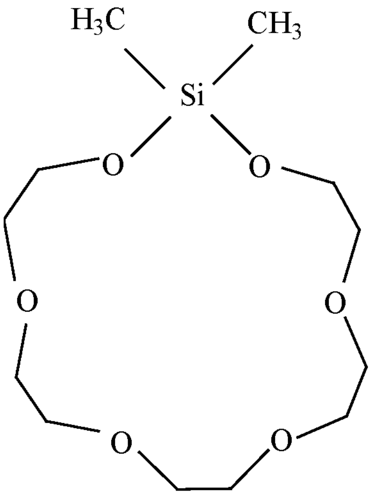
[0033] Specific examples of silacrown compounds useful in the inventive compositions include:



dimethylsila-11-crown-4;



dimethylsila-14-crown-5;

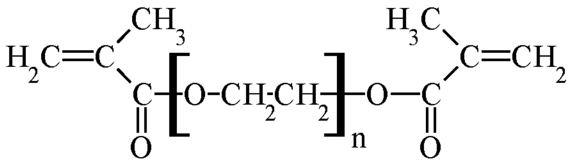


and dimethylsila-17-crown-6.

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

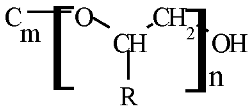
[0034] Many cyclodextrins may be used in connection with the present invention. For instance, those described and claimed in U.S. Patent No. 5,312,864 (Wenz), the disclosure of which is hereby expressly incorporated herein by reference, as hydroxyl group derivatives of an α, β or □□-cyclodextrin would be appropriate choices as an accelerator component.

[0035] 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.

[0036] 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.

[0037] When used, the accelerator embraced by the above structures should be included in the compositions in an amount within the range of from about 0.01% to about 10% by weight, with the range of about 0.1 to about 0.5% by weight being desirable, and about 0.4% by weight of the total composition being particularly desirable.

[0038] 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 incorporated herein by reference.

[0039] 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.

[0040] In another aspect of the invention, there is provided a method of bonding together two substrates, at least one of which is constructed of aluminum, 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.

[0041] In yet another aspect of the invention, there are provided cured products of the so-described compositions.

[0042] In still another aspect of the invention, there is provided a method of preparing the so-described compositions. The method includes providing a cyanoacrylate component and combining therewith an aromatic multifunctional anhydride component.

[0043] The invention will be further illustrated by the examples which follow.

EXAMPLES

[0044] Cyanoacrylate compositions were prepared from ethyl-2-cyanoacrylate and a series of aromatic dianhydrides. In one sample, ethyl-2-cyanoacrylate and phthalic anhydride are chosen as a control, Sample A.

[0045] In Table 1 below, four additional samples (B-E) were prepared with the identified constituents in the noted amounts.

Table 1

Constituents		**Sample/Amt. (wt%)**				
Type	**Identity**	**A**	**B**	**C**	**D**	**E**
CA	Ethyl-2-CA	Balance	Balance	Balance	Balance	Balance
Anhydride	Phthalic	0.1	--	--	--	--
	ODPA	--	0.1	--	--	--
	s-BPDPA	--	--	0.1	--	--
	6FDPA	--	--	--	0.1	--
	Bis-A DPA	--	--	--	--	0.1
Thickener	PMMA	9.6	9.6	9.6	9.6	9.6

[0046] Each of Samples A-E was applied to aluminum lap shears, and bonded assemblies were prepared for performance evaluation.

[0047] As shown in Table 2 below, when applied to aluminum substrates, the samples exhibit the following performance in terms of tensile strength [N/mm^2] after a room temperature cure of 24 hours:

Table 2

Sample				
A	**B**	**C**	**D**	**E**
4.1	10.1	7.7	7.4	6.0

[0048] Each of Samples B-E show an improvement in tensile strength performance on aluminum substrates as contrasted to Sample A. Samples B-E contain at a 0.1 percent by weight level a species of the genus of the aromatic multifunctional anhydride, whereas Sample A contains at that level phthalic anhydride as a control. Samples B-E show at least a fifty percent improvement over the control and upwards of a two hundred fifty percent improvement with refence to Sample B.

[0049] In Table 3 below, three samples (Samples F-H) were prepared.

Table 3

Constituents		**Samples**		
Type	**Identity**	**F**	**G**	**H**
CA	Ethyl-2-CA	Balance	Balance	Balance
Anhydride	Phthalic	0.1	--	--
	ODPA	--	0.1	0.5
Thickener	PMMA	6.5	6.5	6.5

[0050] Each of Samples F-H was applied to aluminum lap shears, and bonded assemblies were prepared for performance evaluation.

[0051] As shown in Table 4 below, when applied to aluminum substrates, the samples show the following performance in terms of tensile strength [N/mm^2] after a room temperature cure of 24 hours:

Table 4

Samples		
F	**G**	**H**
3.3	8.6	11

[0052] Each of Samples G-H show an improvement in tensile strength performance on aluminum substrates as contrasted to Sample F. Samples G-H contain 0.1 percent by weight and 0.5 percent by weight level of ODPA as a species of the genus of the aromatic multifunctional anhydride, whereas Sample F contains phthalic anhydride as a control at a 0.1 percent by weight level. Sample G shows more than a one hundred percent improvement over the control and Sample H shows a two hundred fifty percent improvement over the control, albeit at a higher loading level.

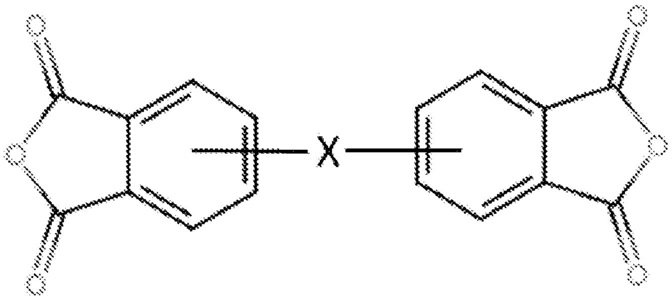
What is Claimed is:

1. A cyanoacrylate adhesive composition, comprising:

(a) a cyanoacrylate component, and

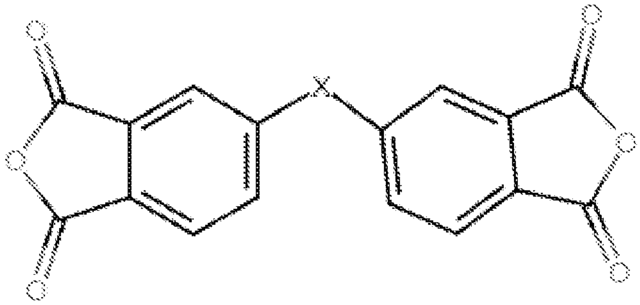
(b) an aromatic multifunctional anhydride component.

2. The composition according to Claim 1, wherein the aromatic multifunctional anhydride component is an aromatic dianhydride component within the following structure:



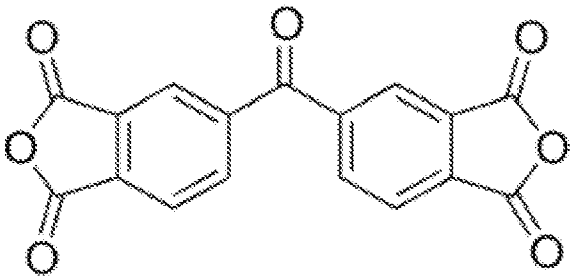
wherein X is selected from O; S; C=O; S=O; O=S=O; --; CRR^1 (wherein R and R^1 are independent of one another and are selected from the group consisting of H, C_1-C_3 alkyl and halogen); Y-Ar-Y^1 [wherein Y and Y^1 are independently selected from O, S, --, and CRR^1 (wherein R and R^1 are as described above), and Ar is an aromatic ring or a fused ring system comprising at least one aromatic ring]; Y-Ar-Y^1-Ar^1-Y^2 (wherein Y, Ar, and Y^1 are as described above, Ar^1 is selected from Ar, and Y^2 is selected from Y or Y^1, and Ar is as described above); and (O=CO)$_n$-Z (wherein Z is C_1-C_6 alkylene.

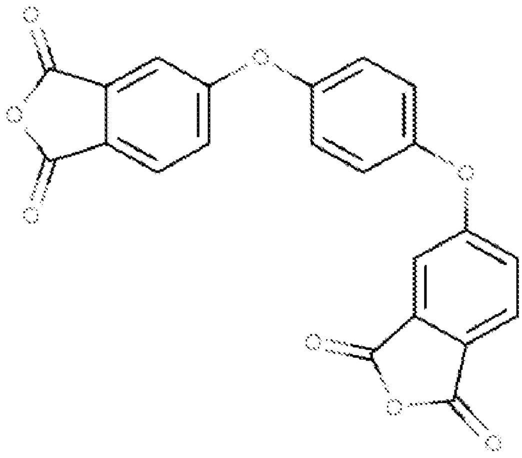
3. The composition according to Claim 2, wherein the wherein the aromatic multifunctional anhydride component is an aromatic dianhydride component within the following structure:

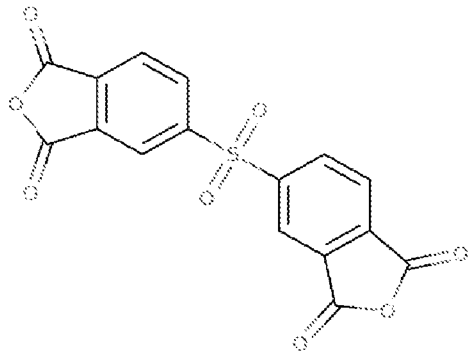


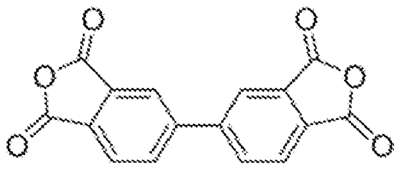
wherein X is as defined above.

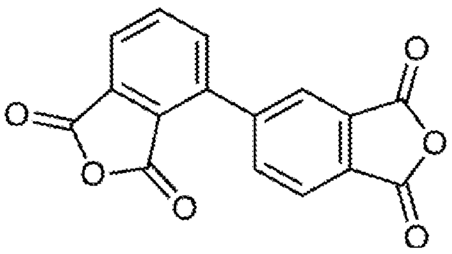
4. The composition according to Claim 1, wherein the wherein the aromatic multifunctional anhydride component is an aromatic dianhydride component selected from the group consisting of:

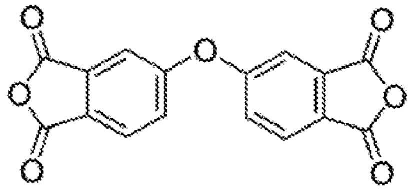


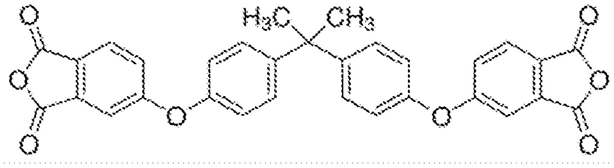


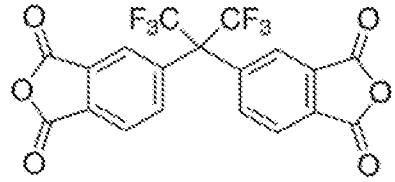












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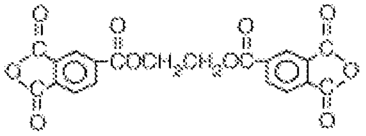

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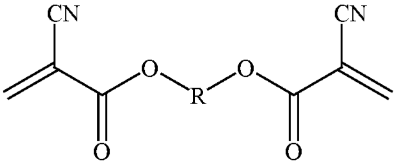
5. The composition according to Claim 1, wherein the cyanoacrylate component is selected from the group consisting of methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl cyanoacrylates, butyl cyanoacrylates, octyl cyanoacrylates, allyl cyanoacrylate and ß-methoxyethyl cyanoacrylate.

6. The composition according to Claim 1, further comprising a multi-functional cyanoacrylate component.

7. The composition according to Claim 6, wherein the multi-functional cyanoacrylate component is embraced by structure <u>I</u>



I

wherein R in structure I is a linkage selected from $(CH_2)_n$, with n being 2, 3, 4, 5, 6, 8, 9, 10, or 12.

8. The composition according to Claim 6, wherein the multi-functional cyanoacrylate component is selected from the group consisting of 1,10-decanediol bis-cyanoacrylate, 1,8-octanediol bis-cyanoacrylate, and 1,6-hexanediol bis-cyanoacrylate.

9. The composition of Claim 1, further comprising a stabilizing amount of an acidic stabilizer and a free radical inhibitor.

10. The composition according to Claim 1, further comprising an accelerator component.

11. The composition according to Claim 10, wherein the accelerator component is selected from the group consisting of calixarene, oxacalixarene, silacrown, cyclodextrin, crown ether, poly(ethyleneglycol) di(meth)acrylate, ethoxylated hydric compound, and combinations thereof.

12. The composition according to Claim 11, 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-naphtyl-16-crown-5, 1,2-methyl-benzo-18-crown-6, 1,2-methylbenzo-5, 6-methylbenzo-18-crown-6, 1,2-t-butyl-18-crown-6, 1,2-vinylbenzo-15-crown-5, 1,2-vinylbenzo-18-crown-6, 1,2-t-butyl-cyclohexyl-18-crown-6, asym-dibenzo-22-crown-6, and 1,2-benzo-1,4-benzo-5-oxygen-20-crown-7 and combinations thereof.

13. The composition according to Claim 1, further comprising additives selected from the group consisting of tougheners, shock resistant additives, thixotropy conferring agents, thickeners, dyes, and combinations thereof.

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

15. A method of bonding together two substrates, at least one of which is constructed from aluminum, comprising the steps of:

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

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

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

providing a cyanoacrylate component, and

combining therewith with mixing an aromatic multi-functional anhydride component.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2022/040499

A. CLASSIFICATION OF SUBJECT MATTER

C09J 133/20(2006.01)i; **C09J 5/00**(2006.01)i; **C08F 22/32**(2006.01)i; **C08F 2/44**(2006.01)i; **C08K 5/1539**(2006.01)i

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 133/20(2006.01); C08F 210/00(2006.01); C09J 11/06(2006.01); C09J 11/08(2006.01); C09J 133/14(2006.01); C09J 4/00(2006.01); C09J 4/06(2006.01); C09J 5/00(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal), STN(Registry, Caplus) & Keywords: cyanoacrylate adhesive, dianhydride, multi-functional cyanoacrylate, product, substrate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2017-0335151 A1 (HENKEL IP & HOLDINGS GMBH) 23 November 2017 (2017-11-23) claims 1, 11, 31, 32; paragraphs [0017], [0019]-[0021], [0027], [0072], [0073], [0093], [0097], [0105], [0107], [0121]; figure 3	1-5,9-16
Y		6-8
Y	US 2003-0158579 A1 (AZEVEDO, M.) 21 August 2003 (2003-08-21) claims 11-13; paragraph [0047]	6-8
Y	US 2020-0102480 A1 (HENKEL IP & HOLDING GMBH) 02 April 2020 (2020-04-02) claims 1, 12, 15, 16; paragraphs [0046]-[0049]	6-8
A	WO 2010-029134 A1 (LOCTITE (R&D) LIMITED) 18 March 2010 (2010-03-18) the whole document	1-16
A	US 5288794 A (ATTARWALA, S.) 22 February 1994 (1994-02-22) the whole document	1-16

☐ 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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"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
"&"	document member of the same patent family

Date of the actual completion of the international search **30 November 2022**	Date of mailing of the international search report **30 November 2022**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **189 Cheongsa-ro, Seo-gu, Daejeon** **35208, Republic of Korea** Facsimile No. **+82-42-481-8578**	Authorized officer **HEO, Joo Hyung** Telephone No. **+82-42-481-5373**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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