

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



WIPO | PCT



(10) International Publication Number

WO 2013/174430 A1

(43) International Publication Date
28 November 2013 (28.11.2013)

(51) International Patent Classification:
C09J 4/00 (2006.01) *C09J 7/02* (2006.01)
C09J 7/00 (2006.01)

[DE/DE]; Gassenweg 54, 56170 Bendorf (DE). **PETRICK, Patricia** [DE/DE]; Hinterm Graben 8, 56355 Oberbachheim (DE). **DOMANSKI, Reinhold** [DE/DE]; Auf dem Hahn 23, 56566 Neuwied (DE).

(21) International Application Number:

PCT/EP2012/059630

(74)

(22) International Filing Date:

23 May 2012 (23.05.2012)

(81)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicants (for all designated States except US): **HENKEL AG & CO. KGAA** [DE/DE]; Henkelstr. 67, 40589 Dusseldorf (DE). **HENKEL IRELAND LTD.** [IE/DE]; Alfred-Nobel-Strasse 10, 40789 Monheim (DE). **LOHmann GMBH & CO. KG** [DE/DE]; Irlicher Strasse 55, 56567 Neuwied (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **McARDLE, Ciaran** [IE/IE]; 17 Foxrock Manor, Leopardstown Road, Dublin, 18 (IE). **XIAO, Edward Schude** [CA/DE]; Hugelstrasse 32, Apt. 310, 40589 Dusseldorf (DE). **VAN WIJK, Kerstin** [DE/DE]; Dusselthalerstr. 48b, 40211 Dusseldorf (DE). **ZHAO, Ligang** [CN/DE]; Angerstr. 20, 40593 Dusseldorf (DE). **SCHNEIDER, Anja** [DE/DE]; Lerchenstr. 16, 40547 Dusseldorf (DE). **HANSJOERG, Ander**

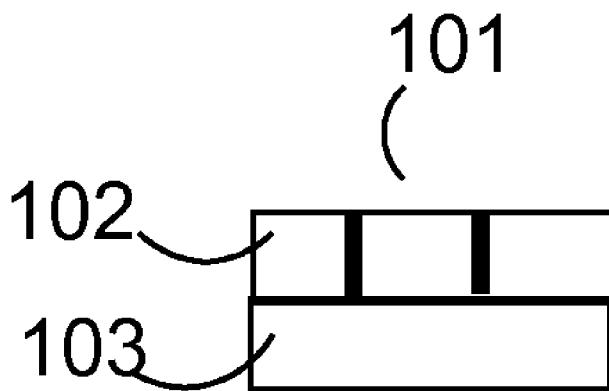
Agents: **MC COOEY, Séamus** et al.; Tomkins & Co., 5 Dartmouth Road, Dublin, 6 (IE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: AN ARTICLE COMPRISING A FILM ON A CARRIER OR RELEASE SUBSTRATE



(57) Abstract: The present invention relates generally to an article comprising a curable film on a release substrate and/or carrier substrate. More particularly, the curable film comprises at least one specific cyanoacrylate monomer and at least one film forming (co)polymer. The article may take the form of a label, a single-sided tape, a transfer tape or a double-sided tape.

Figure 1



Published:

— *with international search report (Art. 21(3))*

Title

An article comprising a film on a carrier or release substrate

Field of the Invention

[0001] The present invention relates to an article comprising a curable film on a carrier substrate and/or release substrate wherein the film comprises at least one specific cyanoacrylate monomer and at least one film forming (co)polymer.

Background to the Invention

[0002] Adhesive tapes and labels are attractive products from a consumer compliance perspective in that they are easily manipulated and stored, and they find utility in a wide range of bonding and masking applications, including bonding electrical, electronic, aerospace, and audio/video components.

[0003] Pressure sensitive adhesives are common components of adhesive tapes. Pressure sensitive adhesives are viscoelastic materials and can be provided carrierless in the form of transfer tapes or carrier-based as single- or double-sided tapes. They remain permanently tacky for a long period of time, and need only minimum pressure to stick to a surface, even to difficult to bond surfaces like polyethylene or polypropylene. Normally, they can be removed without leaving any adhesive residues, and without destroying the joined parts.

[0004] Applications of prior art pressure sensitive adhesives are generally limited to operations in which the requirements in relation to bond strength and/or heat resistance are not exacting. Thus, there is a need for a heat resistant adhesive tape combining high initial tack and high structural bonding strength and exhibiting good adhesion to a broad variety of different substrates.

[0005] For example, U.S. Patent Publication No. 2012/0082818 to Nitto Denko Corporation discloses pressure sensitive adhesive tapes. In particular, the pressure sensitive adhesive tapes disclosed in U.S. 2012/0082818 comprise a silicone based release layer on to which is coated a water-dispersed pressure sensitive adhesive layer. The water-dispersed pressure sensitive adhesive layer contains an acrylic polymer and a tackifier resin dispersed in the water. The Pressure sensitive adhesive tapes disclosed in U.S. 2012/0082818 are free from any aromatic hydrocarbon based solvents, such as toluene. Consequently, volatile organic carbon (VOC) emissions from the tapes are minimised.

[0006] Prior art pressure sensitive adhesive tapes can be single- or double-sided. Double-sided pressure sensitive adhesive tapes, for example, are reported in U.S. Patent Publication No. US2012/0115405 to Nitto Denko Corporation. In this patent application the double sided tape consists of a substrate coated on a first side with a rubber based pressure sensitive adhesive and on a second side with an acrylic based pressure sensitive adhesive.

[0007] International Patent Publication No. WO2010/069800 to Tesa Se *et al.* describes a pressure sensitive adhesive consisting of a homogeneous mixture of at least one natural rubber component and at least one polyacrylate component in order to achieve improved properties in cohesion, aging and also in weathering resistance. The pressure sensitive adhesive may be utilised in a tape.

[0008] European Patent No. EP2283100 B1 to Tesa Se discloses a pressure sensitive adhesive mass comprising among others a mixture of a polymer blend of thermoplastic and/or non-thermoplastic elastomers with vinyl aromatic block copolymer and adhesive resin. The pressure sensitive adhesive may be utilised in a tape.

[0009] International Patent Publication No. WO2010/023229 to Loctite (R&D) Limited and Henkel Ag & Co. KGaA discloses curable cyanoacrylate based films dispensable from a release substrate. One particular film disclosed consists of a combination of a neopentyl cyanoacrylate and a rubber component. The production process associated with this particular film is expensive due to the vapour pressure of neopentyl cyanoacrylate.

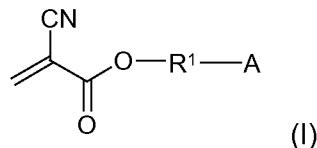
[0010] Notwithstanding the state of the art there remains a need for alternative adhesive tape formulations that exhibit improved coating properties on carrier and release substrates, exhibit high initial tack, and which show improved bonding strength. Accordingly, it would be desirable to provide an article, such as a (transfer) tape that has good storage stability, exhibits good adhesion to a wide variety of substrates, which is easy and cheap to manufacture, and which exhibits a combination of high initial tack and strong bond strengths.

Summary of the Invention

[0011] The present invention provides for adhesive articles such as adhesive tapes, transfer tapes, labels, laminates and the like.

[0012] In a first aspect the present invention provides for an article comprising a curable film on a release substrate and/or carrier substrate, wherein the film comprises:

(a) at least one cyanoacrylate monomer selected from compounds of formula (I)



wherein R^1 is a divalent linking group comprising 1 to 10 carbon atoms, and A represents an $\text{C}_5\text{-C}_{50}$ aryl residue or a $\text{C}_2\text{-C}_{50}$ heteroaryl residue; and

(b) at least one film forming (co)polymer.

[0013] As used herein, the term aryl residue refers to an aromatic carbocyclic structure which is monocyclic or polycyclic (unfused or fused). Similarly, the term heteroaryl refers to an aromatic heterocyclic structure having as ring members atoms of at least two different elements. The heteroaryl residue may be monocyclic or polycyclic (unfused or fused). The carbon atoms of

the aryl or heteroaryl residue may optionally be substituted one or more times, for example, with at least one of a cyano group, a nitro group, a halogen, C₁-C₁₀ alkyl, a C₁-C₁₀ ether, a C₁-C₁₀ thioether, a C₁-C₁₀ ester, C₁-C₁₀ ketone, C₁-C₁₀ ketimine, C₁-C₁₀ sulfone, C₁-C₁₀ sulfoxide, a C₁-C₁₀ primary amide or a C₁-C₂₀ secondary amide.

[0014] As used herein, the term release substrate refers to a material, which acts as protective covering for the curable film and prevents unwanted adhesion and contamination of the adhesive surface during shipping and handling. The release substrate may be coated on one or two sides with a release agent, and can be removed to release tacky materials such as pressure sensitive adhesives without deleteriously effecting the integrity of the curable film.

[0015] With reference to the article of the present invention, the release substrate may be paper, or plastic based (e.g. PET, PE, HDPE, PP) materials, which are optionally coated with a release agent.

[0016] Release agents allow the adhesive films of the article of the present invention to be easily transferred from the release substrate to the article of interest. The release agent may be selected from the group consisting of polyvinyl alcohol, clays, siloxanes, and combinations thereof. Suitable release agents, in particular siloxane-based release agents, are available under the trade name SILCOLEASE®.

[0017] As used herein, the term carrier substrate refers to a material onto which the curable film can be coated so as to stabilize the adhesive. The carrier substrate can add thickness to the article so as to improve handling. The carrier substrate differs from the release substrate in that it cannot be removed from the curable film without deleteriously effecting the integrity of the curable film.

[0018] The carrier substrate may be flexible, for example a flexible sheet. The carrier substrate may be selected from polymeric films, metal foils, foams, cloths, and combinations thereof. For example, the carrier substrate may be selected from the group consisting of polyester, polypropylene, polyethylene, foam and paper.

[0019] Within the context of this specification the term (co)polymer refers to either a polymer derived from a single monomeric species or a polymer derived from two (or more) monomeric species.

[0020] The term film forming (co)polymer refers to a (co)polymer material which when formulated with the cyanoacrylate monomer of formula (I) provides a curable film.

[0021] Advantageously, the curable films of the articles of the present invention exhibit pressure sensitive adhesion properties at 23 °C. Subsequent cure of the films can be initiated as appropriate. For example, an external stimulus such as heat or radiation (e.g. UV cure) may be applied to induce cure of the curable films when desired to do so.

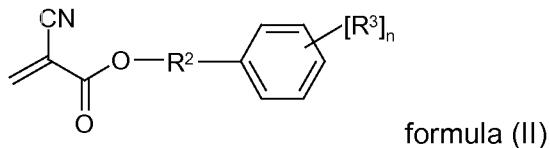
[0022] As used herein, the term “pressure sensitive adhesion properties” refers to materials and formulations that are permanently tacky and adhere under finger pressure. More particularly

said term is used for materials or formulations having a glass transition temperature (T_g) of less than 25 °C and a storage modulus G' of 3.3×10^5 Pa or less at 23 °C, wherein the glass transition temperature (T_g) is determined by Differential Scanning Calorimetry (DSC) and the storage modulus G' is determined by Dynamic Mechanical Analysis (DMA) at 1 Hz, and at 23 °C.

[0023] The term divalent linking group refers to a moiety which links the unsaturated oxygen of the ester functional group to the aryl residue.

[0024] With reference to the cyanoacrylate monomer of the article of the present invention the variable A may be C_5 - C_{50} aryl residue.

[0025] For example, the cyanoacrylate monomer may be selected from compounds of formula (II),



wherein n is 0 to 5, R^2 is a C_{1-5} alkylene group, and each R^3 , if present, is independently selected from C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, fluorine, chlorine, bromine, cyano and nitro.

[0026] As used herein, the term " C_x - C_y alkyl" embraces C_x - C_y unbranched alkyl, C_x - C_y branched alkyl and combinations thereof. The term " C_x - C_y alkylene group" should be construed as " C_x - C_y alkyl".

[0027] The cyanoacrylate monomer may have a melting point at 1013.25 mbar of more than 25 °C.

[0028] With reference to the compounds of formula (II), n may be 0 to 2, R^2 may be a C_{1-3} alkylene group, and each R^3 , if present, is independently selected from C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, fluorine, chlorine, bromine, cyano and nitro. For example, n may be 0 to 2, R^2 may be a C_{1-3} alkylene group, and each R^3 , if present, may be independently selected from fluorine, chlorine, bromine, cyano and nitro. In another embodiment, n may be 0, and R^2 may be a C_{1-5} alkylene group. For example, n may be 0, and R^2 may be a C_{1-3} alkylene group

[0029] The cyanoacrylate monomer may be (2-phenylethyl) 2-cyanoacrylate, *i.e.* in formula (II) R^2 is C_2H_4 , and n is 0.

[0030] The cyanoacrylate monomer of the general formula (I) may be present in an amount of at least 15 wt.%, based on the total weight of the film. For example, the cyanoacrylate monomer may be present in an amount from 20 wt.% to 80 wt.%, based on the total weight of the curable film.

[0031] The film forming (co)polymer may be present in an amount from 20 wt.% to 85 wt.%, based on the total weight of the film.

[0032] The film forming (co)polymer may be selected from the group consisting of poly(meth)acrylates, polyvinyl ethers, natural rubbers, polyisoprenes, polybutadienes, polyisobutylenes, polychloroprenes, butadieneacrylonitrile polymers, thermoplastic elastomers, styrene-isoprenes, styreneisoprene-styrene block copolymers, ethylene-propylene-diene polymers, styrene-butadiene polymers, poly-alpha-olefins, silicones, ethylene-containing copolymers, ethylene vinyl acetates, and combinations thereof. Preferably, the film forming (co)polymer may comprise poly(meth)acrylates and/or ethylene vinyl acetates.

[0033] The film forming (co)polymer may have a glass transition temperature (Tg), as determined by Differential Scanning Calorimetry (DSC), of less than 30 °C.

[0034] The film forming (co)polymer may be a (co)polymer having pressure sensitive adhesion properties at 23 °C.

[0035] The film forming (co)polymer may be a (co)opolymer of (meth)acrylic acid, (meth)acrylic acid esters and optionally other comonomers.

[0036] The film forming (co)polymer may have an acid number from about 0 to about 30. Preferably, the film forming (co)polymer has an acid number below 15. The acid number is the weight in milligrams of KOH required to neutralize the pendant carboxylate groups in one gram of the (co)polymer. The method of determining the acid number of the (co)polymer is described in the experimental section, *vide infra*.

[0037] The film forming (co)polymer may be an ethylene vinyl acetate copolymer. The ethylene vinyl acetate copolymer may have a vinyl acetate content of 50 wt.% to 98 wt.%, based on the total weight of the ethylene vinyl acetate copolymer.

[0038] The curable films of the articles of the present invention exhibit pressure sensitive adhesion properties at 23 °C. The curable film of the article of the present invention may have a storage modulus G', measured with Dynamic Mechanic Analysis (DMA) at 1 Hz and 23 °C, of about 3.3×10^5 Pa or less.

[0039] The curable film of the article of the present invention may return a tack value of at least 3 N in the standard loop tack test as measured by DIN EN 1719.

[0040] The curable film of the article of the present invention, may have a glass transition temperature (Tg) of less than 10 °C as determined by Differential Scanning Calorimetry (DSC). For example, the curable film may have a glass transition temperature as determined by DSC ranging from -60 to +10 °C.

[0041] The curable film of the article of the present invention may have a 180° peel strength of 3 N/25mm to 50 N/25mm after 10 min as measured by DIN EN 1939 (Afera 5001) on steel substrate at 23 °C.

[0042] The curable film utilised in the present invention may have, in its uncured state, a modulus G' at room temperature of about 3.3×10^5 Pa or less, measured with DMA at 1 Hz, and

may return a tack value of at least 3 N, preferably of at least 5 N, in the standard loop tack test as measured by DIN EN 1719.

[0043] The curable film utilised in the article of the present invention may have, in its uncured state, a modulus G' at room temperature of about 3.3×10^5 Pa or less, measured with DMA at 1 Hz, and may have a glass transition temperature (Tg) of less than 10 °C, for example from -60 to +10 °C as determined by Differential Scanning Calorimetry (DSC).

[0044] The curable film utilised in the article of the present invention may have, in its uncured state, a glass transition temperature (Tg) of less than 10 °C, for example from -60 to +10 °C as determined by Differential Scanning Calorimetry (DSC), and may return a tack value of at least 3 N, preferably of at least 5 N, in the standard loop tack test as measured by DIN EN 1719.

[0045] The curable film utilised in the article of the present invention may have, in its uncured state, a modulus G' at room temperature of about 3.3×10^5 Pa or less, measured with DMA at 1 Hz, a glass transition temperature (Tg) of less than 10 °C, for example from -60 to +10 °C as determined by Differential Scanning Calorimetry (DSC), and may return a tack value of at least 3 N, preferably of at least 5 N, in the standard loop tack test as measured by DIN EN 1719.

[0046] The curable film utilised in the article of the present invention may comprise, in addition to the solid cyanoacrylate of formula (I) a film forming (co)polymer matrix substance selected from the group consisting of poly(meth)acrylates, polyvinyl ethers, natural rubbers, polyisoprenes, polybutadienes, polyisobutylenes, polychloroprenes, butadieneacrylonitrile polymers, thermoplastic elastomers, styrene-isoprenes, styreneisoprene-styrene block copolymers, ethylene-propylene-diene polymers, styrene-butadiene polymers, poly-alpha-olefins, silicones, ethylene-containing copolymers, ethylene vinyl acetates, and combinations thereof. Preferably, the film forming (co)polymer matrix substance may comprise poly(meth)acrylates and/or ethylene vinyl acetates.

[0047] With reference to the article of the present invention, the film may comprise, based on the total weight of the film:

- (a) from 15 to 80 wt.% of one or more cyanoacrylate monomers selected from compounds of formula (I);
- (b) from 20 to 85 wt.% of one or more film forming (co)polymers; and
- (c) from 0 to 65 wt.% of one or more additives.

[0048] For example, the film may comprise, based on the total weight of the film:

- (a) from 40 to 60 wt.% of one or more cyanoacrylate monomers selected from compounds of formula (I);
- (b) from 40 to 60 wt.% of one or more film forming (co)polymers; and
- (c) from 0 to 20 wt.% of one or more additives.

[0049] The film of the article of the present invention may further comprise one or more additives selected from cyanoacrylate polymers, tackifiers, plasticizers, toughening agents, antioxidants, stabilizers, water absorbing agents and/or combinations thereof.

[0050] Examples of filler components include but are not limited to, for example, silicas, quartz, alumina, calcium, clays, talcs and other inorganic filler materials such as polycarbonates and other polymer powders, along with certain acrylate components.

[0051] Examples of stabiliser components which may be suitably used in the adhesive film of the present invention include hydroquinone, pyrocatechol, resorcinol or derivatives thereof, phenols, sulfur dioxide, sulfuric acid, alkyl sulfonic acids, aromatic sulfonic acids, boranes and combinations thereof. For example, the stabiliser may be selected from methanesulfonic acid (MSA), BF_3 , SO_2 and combinations thereof.

[0052] With reference to the article of the present invention, the weight ratio of cyanoacrylate monomers of the formula (I) to film forming (co)polymers in the film may be from 1:8 to 8:1. Suitably, the weight ratio of cyanoacrylate monomers of the formula (I) to film forming (co)polymers in the film may be from 1:4 to 4:1.

[0053] With reference to the article of the present invention the curable film may comprise, based on the total weight of the curable film:

- (a) from 15 to 80 wt.% of one or more cyanoacrylate monomers selected from compounds of formula (I);
- (b) from 20 to 85 wt.% of one or more film forming (co)polymers, wherein said film forming copolymer has pressure sensitive adhesion properties at 23 °C; and
- (c) from 0 to 65 wt.% of one or more additives.

[0054] With reference to the article of the present invention the curable film may comprise, based on the total weight of the curable film:

- (a) from 15 to 80 wt % of (2-phenylethyl) 2-cyanoacrylate;
- (b) from 20 to 85 wt% of one or more film forming (co)polymers; and
- (c) from 0 to 65 wt.% of one or more additives.

[0055] With reference to the article of the present invention the curable film may comprise, based on the total weight of the curable film:

- (a) from 15 to 80 wt % of (2-phenylethyl) 2-cyanoacrylate;
- (b) from 20 to 85 wt% of one or more film forming (co)polymers, wherein said film forming copolymer has pressure sensitive adhesion properties at 23 °C; and
- (c) from 0 to 65 wt.% of one or more additives.

[0056] With reference to the article of the present invention, the film may comprise, based on the total weight of the film:

- (a) from 15 to 80 wt.% of one or more cyanoacrylate monomers selected from compounds of formula (I);

- (b) from 20 to 85 wt.% of one or more film forming (co)polymers of (meth)acrylic acid, (meth)acrylic acid esters and optionally other comonomers; and
- (c) from 0 to 65 wt.% of one or more additives.

[0057] With reference to the article of the present invention, the film may comprise, based on the total weight of the film:

- (a) from 15 to 80 wt.% of one or more cyanoacrylate monomers selected from compounds of formula (I);
- (b) from 20 to 85 wt.% of one or more (co)polymers of (meth)acrylic acid, (meth)acrylic acid esters and optionally other comonomers, wherein said (co)polymer has pressure sensitive adhesion properties at 23 °C; and
- (c) from 0 to 65 wt.% of one or more additives.

[0058] With reference to the article of the present invention the curable film may comprise, based on the total weight of the curable film:

- (a) from 15 to 80 wt % of one or more cyanoacrylate monomers selected from compounds of formula (I);
- (b) from 20 to 85 wt% of one or more film forming ethylene vinylacetate copolymers; and
- (c) from 0 to 65 wt.% of one or more additives.

[0059] With reference to the article of the present invention the curable film may comprise, based on the total weight of the curable film:

- (a) from 15 to 80 wt % of (2-phenylethyl) 2-cyanoacrylate;
- (b) from 20 to 85 wt% of one or more film forming ethylene vinylacetate copolymers; and
- (c) from 0 to 65 wt.% of one or more additives.

[0060] With reference to the article of the present invention the curable film may comprise, based on the total weight of the curable film:

- (a) from 15 to 80 wt % of (2-phenylethyl) 2-cyanoacrylate;
- (b) from 20 to 85 wt% of one or more film forming (co)polymers of (meth)acrylic acid, (meth)acrylic acid esters and optionally other comonomers; and
- (c) from 0 to 65 wt.% of one or more additives.

[0061] Alternatively, the curable film may comprise, based on the total weight of the curable film:

- (a) from 15 to 80 wt % of (2-phenylethyl) 2-cyanoacrylate;
- (b) from 20 to 85 wt% of one or more (co)polymers of (meth)acrylic acid, (meth)acrylic acid esters and optionally other comonomers, wherein said (co)polymer has pressure sensitive adhesion properties at 23 °C; and
- (c) from 0 to 65 wt.% of one or more additives.

[0062] Suitable poly(meth)acrylate (co)polymers include DuroTAK® 2123. Suitable ethylene vinylacetate copolymers include Levamelt® 900.

[0063] Suitable additives may be selected from cyanoacrylate polymers, tackifiers, plasticizers, toughening agents, antioxidants, stabilizers, water absorbing agents and/or combinations thereof.

[0064] Suitable tackifiers are known to persons skilled in the art. Sources of tackifiers can be found in standard publications on pressure sensitive adhesives, for example, the "Handbook of Pressure Sensitive Adhesive Technology" from Donata Satas (van Niststrand, New York, 1989).

[0065] The article of the present invention may take the form of an adhesive transfer tape comprising:

a curable film according the present invention located on a release substrate, the curable film defining two adhesive surfaces, and optionally

a second release substrate on top of the curable film (the covering substrate), the release substrate(s) having a release function relative to the film.

[0066] The first and second release substrates may be a paper, cloth or plastic based material or a combination thereof, which are optionally coated with a release agent. Release agents allow the adhesive films of the article of the present invention to be easily transferred from the release substrate to the article of interest. The release agent may be selected from the group consisting of polyvinyl alcohol, clays, siloxanes, and combinations thereof. Suitable release agents, in particular siloxane-based release agents, are available under the trade name SILCOLEASE®.

[0067] Advantageously, an adhesive transfer film with first and second release substrates allows easy handling of the film and safe protection of the film between the two release layers.

[0068] When using first and second release substrates it is desirable that they should have different release properties relative to the film, such that it is clear which release layer should be removed first.

[0069] When using only a first release substrate and no second or covering release substrate the first release substrate should preferably have release properties on both sides. Preferably the release properties are different between the two sides. When winding the product (substrate and film) into a roll, there will be a clear differentiation between the release effects of the two sides. Consequently, the film will preferentially adhere to one side during unwinding of the roll.

[0070] The article of the present invention may also take the form of a single-sided adhesive tape comprising:

a curable film according the present invention located on a carrier substrate, and optionally

a release substrate on the curable film, the release substrate having a release function relative to the film.

[0071] The carrier substrate, which stabilizes the film, may be selected from paper, polymeric film, metal foil, foam, cloth, and combinations thereof. It may comprise several layers, for

example a primer layer versus the film in order to bind the film to the carrier substrate or a release layer on the opposite side of the film.

[0072] The article of the present invention may take the form of a double-sided adhesive tape comprising:

 a first curable film according the present invention located on a first side of a carrier substrate,

 a second curable film according the present invention located on a second side of the carrier substrate, such that the carrier substrate is disposed between the first film and the second film, and optionally

 a first release substrate on the first curable film, and/or

 a second release substrate on the second curable film,

the release substrate(s) having a release function relative to the film(s).

[0073] The first and second curable films may be the same of different, *i.e.* they may comprise the same or different combinations of one or more cyanoacrylates of the formula (I) and film forming (co)polymers. The first and second release substrates may have different release properties relative to the first and second curable films. The first and second curable films may be the same of different, *i.e.* they may comprise the same or different combinations of one or more cyanoacrylates of the formula (I) and film forming (co)polymers and the first and second release substrates may have different release properties relative to the first and second curable films.

[0074] The carrier substrate in between the two film layers may be selected from paper, polymeric film, metal foil, foam, cloth, viscoelastic materials and combinations thereof.

Examples of viscoelastic materials are poly(meth)acrylates, polyvinyl ethers, natural rubbers, polyisoprenes, polybutadienes, polyisobutylenes, polychloroprenes, butadiene acrylonitrile polymers, thermoplastic elastomers, styrene-isoprenes, styrene-isoprene-styrene block copolymers, ethylene-propylene-diene polymers, styrene-butadiene polymers, poly-alpha-olefins, silicones, ethylene-containing copolymers, ethylene vinyl acetates and/or combinations thereof. The carrier substrate may comprise tackifiers, plasticizers, toughening agents, antioxidants, stabilizers, water absorbing agents and/or combinations thereof. The carrier substrate may be a foamed form of these materials.

[0075] The first and second release substrates may be a paper, cloth or plastic based material or a combination thereof which is optionally coated with a release agent. Release agents allow the adhesive films of the article of the present invention to be easily transferred from the release substrate and to rewind the article as a roll. The release agent may be selected from the group consisting of polyvinyl alcohol, clays, siloxanes, and combinations thereof. Suitable release agents, in particular siloxane based release agents, are available under the trade name SILCOLEASE®.

[0076] The articles of the present invention, such as transfer films, single-sided tapes, double-sided tapes or labels may be protected from ambient conditions such as light, heat or moisture so as to prolong the shelf life thereof.

[0077] Articles according to the present invention may be produced by coating the curable film on a carrier substrate or release substrate and subsequently laminating it to further release substrates or carrier substrates. The coating process may be a hotmelt-process, a solid-based process (*i.e.*, solvent-free), a solvent-based process or a dispersion process.

[0078] In a hotmelt process the components of the film of the present invention are intermingled with a suitable mixing device, *e.g.* an extruder, the mixture is melted through the suitable device, *e.g.* an extruder, and the mixture is formed into a film and coated on substrates through the suitable device, *e.g.* an extruder, and a die to form the film in a suitable thickness. Such hotmelt mixing and coating processes are well-known in adhesive and tape industry.

[0079] In a solid-based process (*i.e.*, solvent-free) the curable film contains only solids, *i.e.* the film is 100% solid. In a dispersion process the components of the curable film are mixed in a liquid phase, for example, an aqueous liquid phase. The aqueous liquid phase may be water.

[0080] In a solvent process the components of the films of the present invention are mixed in one or more solvents, *e.g.* benzene, toluene, acetone, ethylacetate and other organic solvents or combinations thereof. After solving/dispersing and mixing the components together the mixture is coated to a release substrate or carrier substrate, the solvent is removed by drying and the film is wound into a roll. Such solvent mixing, coating and drying processes are well-known in adhesive and tape industry.

[0081] Desirably, the film of the present invention is produced in a solvent process. Preferably the solvent is ethylacetate.

[0082] Articles of the present invention may exhibit pressure sensitive adhesion properties at 23 °C such that they can initially be tacked to or attached to a target surface. Desirably, other stimuli are used to promote cure of the adhesive film, for example heat and/or radiation (*e.g.* UV radiation). Where radiation is utilised to initiate or promote further cure masking may be employed to selectively induce cure.

[0083] In a further aspect, the present invention provides for a method of attaching a curable film to a surface, comprising the steps of:

- (a) providing an article according to the present invention;
- (b) attaching the curable film of the article to at least one surface to form an assembly,
- (c) exposing the assembly to conditions sufficient to cure the curable film of the article, wherein the release substrate(s) of the article, if present, are removed before and/or after step (b).

[0084] The article of the present invention may be a transfer tape, a single-sided adhesive tape, or a double-sided adhesive tape. Articles of the present invention may exhibit pressure

sensitive adhesion properties at 23 °C, thus attaching the curable film of the article to at least one surface may be achieved through the application of pressure to the curable film on the surface.

[0085] The articles of the present invention, such as transfer films, single-sided tapes, double-sided tapes or labels may find utility in bonding a plurality of substrates and or surfaces, including, but not limited to metals, metal alloys, glasses, enamels, wood, natural or synthetic fabrics and fibres, leather, stone, ceramic, plastics, paper or card, plastics, composite materials, and living tissues and organs.

[0086] Conditions sufficient to cure the curable film of the article of the present invention may include heat and/or radiation (e.g. UV radiation).

[0087] In a further aspect, the present invention provides for a method of adhering components together, said method comprising:

- (i) providing an article according to the present invention;
- (ii) attaching the curable film of the article to at least one of the components;
- (iii) mating the components; and
- (iv) curing the adhesive film between the components to be adhered together, wherein the release substrate of the article, if present, is removed before and/or after step (ii).

[0088] Articles of the present invention may exhibit pressure sensitive adhesion properties at 23 °C, thus attaching the curable film of the article to at least one component may be achieved through the application of pressure to the curable film on the component.

[0089] Conditions sufficient to cure the curable film of the article of the present invention may include heat and/or radiation (e.g. UV radiation).

[0090] For example, the method of the present invention may comprise adhering components together using a transfer tape according to the present invention, said method comprising:

- (i) providing a transfer tape according to the present invention;
- (ii) attaching the curable film of the transfer tape to at least one of the components;
- (iii) mating the components; and
- (iv) curing the adhesive film between the components to be adhered together, wherein the release substrate(s) of the transfer tape, if present, are removed before and/or after step (ii).

[0091] Transfer tapes may comprise one or two release substrates as illustrated in Figures 3 and 4, *vide infra*. As used herein, the term transfer tape refers to an article in which a release substrate can be utilised to transfer the curable film to a target substrate or surface.

[0092] In a further embodiment, the method of the present invention may comprise adhering components together using a single-sided adhesive tape according to the present invention, wherein the single sided adhesive comprises one of the components, said method comprising:

- (i) providing a single-sided adhesive tape according to the present invention;
- (ii) attaching the curable film of the single-sided adhesive tape to the component;
and
- (iii) curing the adhesive film,

wherein the release substrate of the single-sided adhesive tape, if present, is removed before step (ii).

[0093] Normally, single-sided adhesive tapes are either absent a release substrate or have a single release substrate as illustrated in Figures 1 and 2, *vide infra*.

[0094] In yet a further embodiment, the method of the present invention may comprise adhering components together using a double-sided adhesive tape according to the present invention, said method comprising:

- (i) providing a double-sided adhesive tape according to the present invention;
- (ii) attaching a first curable film of the double-sided adhesive tape to at least one of the components;
- (iii) attaching a second curable film of the double-sided adhesive tape to the other component; and
- (iv) curing the curable films between the components so as to adhere the components together,

wherein the release substrate(s) of the double-sided adhesive tape, if present, are removed before and/or after step (ii).

[0095] Double-sided adhesive tapes may comprise one or two release substrates as illustrated in Figures 5 and 6, *vide infra*.

[0096] The articles of the present invention may more specifically find industrial applicability across a wide range of applications such as, but not limited to lamination, bookbinding, shoe assembly, assembly of parts of motor vehicles, of air conditioning systems, components of an electric or electronic device or other consumer durables, components used in building industries [for example, in insulation (thermal and acoustic)], packaging, die attachment applications, wound closure, surgical closures, medical device applications and all sorts of labelling. The components may be the ends of longitudinal materials that are adhered together, for example splicing two material rolls together.

[0097] The article of the present invention may be utilised to laminate or mask a substrate, to cover part or all of the substrate, to bind two sides of a gap together, to wrap the substrate or bundle parts together and/or combinations of thereof.

[0098] In industrial processes, the articles of the present invention, such as transfer films, single-sided tapes, double-sided tapes or labels may be employed in a continuous supply process. For example, the carrier or release substrate may be continuously fed into a device that transfers the adhesive film on to the carrier or release substrate, whereupon the article thus formed can be contacted with (component) parts for bonding thereof.

[0099] All numerical ranges and ratios disclosed herein are inclusive of the indicated end points.

[00100] Where suitable, it will be appreciated that all optional and/or preferred features of one embodiment of the invention may be combined with optional and/or preferred features of another/other embodiment(s) of the invention.

Brief Description of the Drawings

[00101] Additional features and advantages of the present invention are described in, and will be apparent from, the detailed description of the invention and from the drawings in which:

[00102] **Figure 1** illustrates a single-sided tape absent a release substrate according to the present invention;

[00103] **Figure 2** illustrates an embodiment of the article of the present invention that may correspond to a single-sided tape or a label with a release substrate;

[00104] **Figure 3** illustrates a transfer tape with one release substrate according to the present invention;

[00105] **Figure 4** illustrates a transfer tape with two release substrates according to the present invention;

[00106] **Figure 5** illustrates a double-sided tape with one release substrate according to the present invention; and

[00107] **Figure 6** illustrates a double-sided tape with two release substrates according to the present invention.

Detailed Description of the Invention

[00108] It should be readily apparent to one of ordinary skill in the art that the examples disclosed herein below represent generalised examples only, and that other arrangements and methods capable of reproducing the invention are possible and are embraced by the present invention.

[00109] In **Figure 1** a single sided tape 101 is shown. The single sided tape 101 consists of a carrier substrate 102 and a curable film 103, the curable film 103 comprising one or more cyanoacrylates of the formula (I) and a film forming (co)polymer (*supra*). The surface of the carrier substrate opposite the curable film may be a special release-treated surface.

[00110] The embodiment of the invention depicted in **Figure 2** could be either a single sided tape or a label 201. The single sided tape or label 201 consists of a carrier substrate 102 and a curable film 103; the curable film 103 comprising one or more cyanoacrylates of the formula (I) and a film forming (co)polymer. The curable film 103 is covered with a release substrate 104 to protect the curable film and prevent unwanted adhesion of the curable film 103.

[00111] **Figures 3 & 4** depict transfer tapes according to the present invention. Transfer tapes are particularly useful for transferring the curable film from a release substrate to a target surface. In **Figure 3**, the transfer tape 301 consists of a release substrate 104 coated with a curable film 103. The curable film 103 comprises one or more cyanoacrylates of the formula (I) and a film forming (co)polymer. The release substrate 104 should preferably have release properties on both sides. Preferably the release properties are different between the two sides. Thus, when winding and unwinding the transfer tape 301 into a roll, there will be a differentiation between the release effects on the two sides of the release substrate 104.

[00112] In **Figure 4** the transfer tape 401 consists of a curable film 103, comprising one or more cyanoacrylates of the formula (I) and a film forming (co)polymer, sandwiched between first and second release substrates 104 and 105. The first and second release substrates 104 and 105 may have different release properties relative to the curable film. This allows the first and second release substrates 104 and 105 to be removed independently of one another.

[00113] A double-sided adhesive tape 501 is shown in **Figure 5**. The tape 501 consists of a carrier substrate 102 having a first curable film 103 on a first side of the carrier substrate 102 and a second curable film 106 on a second side of the carrier substrate 102. The first and second curable films 103 and 106 may be the same or different, *i.e.* they may comprise the same or different combinations of one or more cyanoacrylates of the formula (I) and film forming (co)polymers. A release substrate 104 covers and protects the second curable film 106. The release substrate 104 should preferably have release properties on both sides. Preferably the release properties are different between the two sides. Thus, when winding and unwinding the double-sided tape 501 into a roll, there will be a differentiation between the release effects on the two sides of the release substrate 104.

[00114] A second embodiment of a double-sided adhesive tape 601 is provided in **Figure 6**. The tape 601 consists of a carrier substrate 102 having a first curable film 103 on a first side of the carrier substrate 102 and a second curable film 106 on a second side of the carrier substrate 102. The first and second curable films 103 and 106 may be the same or different, *i.e.* they may comprise the same or different combinations of one or more cyanoacrylates of the formula (I) and film forming (co)polymers. A first release substrate 104 covers and protects the first curable film 103. A second release substrate 105 covers and protects the second curable film 106. The first and second release substrates 104 and 105 may have different release properties relative to the curable films 103 and 106.

Examples

Materials

[00115] Levamelt® 900 is a film forming ethylene vinylacetate copolymer with a vinylacetate content of about 90 wt %, commercially available from Lanxess AG, Leverkusen, Germany.

[00116] Durotak® 2123 is a solution of a film forming (meth)acrylic acid ester copolymer in ethyl acetate, commercially available from Henkel AG & Co. KGaA, Düsseldorf, Germany

[00117] Neopentyl 2-cyanoacrylate (NCA) is a solid cyanoacrylate (melting point 41°C) and can be synthesized according to WO2010/023229.

[00118] (2-Phenylethyl) 2-cyanoacrylate (PheCA) is a solid cyanoacrylate (melting point 30-32°C) and can be synthesized according to the Knoevenagel method using 2-Phenylcyanacetate, Formaldehyde and a catalyst in a solvent followed by a cracking process. Suitable syntheses can be found in Sato, Mitsuyoshi, Okuyama and Toshio, *Jpn. Kokai Tokkyo Koho* (1994), and JP 06192202A.

[00119] Release substrate 1 (RS 1) is polyester film, thickness 50 µm, covered on both sides with a silicone coating.

[00120] Release substrate 2 (RS 2) is a polyethylene film, thickness 50 µm, covered on both sides with a silicone coating.

[00121] Super glue is a representative for a general cyanoacrylate adhesive. It is commercially available as Loctite 4062 from Henkel AG & Co. KGaA, Düsseldorf, Germany.

Tape preparation

[00122] Different curable film formulations were prepared in HDPE bottles in accordance with the following procedure: The film forming (co)polymer was solved in ethyl acetate to give a 50 wt.% solution. The cyanoacrylate monomer and additional ethyl acetate were added to give a 50 wt.% (cyanoacrylate monomer + film forming (co)polymer) solution in ethyl acetate.. All formulations were stable in the presence of sulfonic acids, BF₃ or SO₂ as stabilizers.

[00123] To produce a tape, the curable film formulation was coated on a release substrate using a draw-down coater with blade. The wet curable film was left at 22°C for 10 min. The release liner and the curable film were further dried in an oven with air-flow for 5 min at 90 °C or as otherwise indicated to remove the ethyl acetate to a level of less than 1 wt.% residual solvent. The following tapes were prepared:

[00124] Tape 1 (PheCA + Levamelt® 900)

Curable film formulation: 25 wt % PheCA, 25 wt % Levamelt® 900, 49.957 wt.% ethyl acetate, 0.04 wt.% hydrochinone, 0.003% camphor-10-sulfonic acid;

Substrates: RS 1 and RS 2;

Grammage of curable film: 40 g/m²

[00125] Tape 2 (PheCA + Durotak® 2123)

Curable film formulation: 35 wt % PheCA, 15 wt % Durotak 2123 (polymer), 49.957 wt.% ethyl acetate, 0.04 wt.% hydrochinone, 0.003 wt.% camphor-10-sulfonic acid;

Substrates: RS 1 and RS 2;

Grammage of curable film: 40 g/m²

[00126] Comparative Tape 1 (NCA + Levamelt® 900)

Curable film formulation: 25 wt % NCA, 25 wt % Levamelt® 900, 49.957 % Ethyl acetate, 0.04% Hydrochinone, 0.003% Camphor-10-sulfonic acid.

Substrates: RS 1 and RS 2

Grammage of curable film: 40 g/m²

[00127] Comparative Tape 2 (Durotak® 2123)

Curable film formulation: Durotak® 2123 (68.7 wt.% Durotak 2123 polymer in 31.3 wt.% ethyl acetate);

Substrates: RS 1 and RS 2;

Grammage of curable film: 40 g/m²

The properties of the different tapes were evaluated by using the following test methods.

Test methods

Loop tack

[00128] The loop tack is determined in accordance with DIN EN 1719: The curable film is laminated on aluminium and cut into strips with a width of about 25mm and a length of about 300 mm. The strips are immediately measured in a "Zwick" tensile testing machine Z010 with a velocity of 100 mm/min.

[00129] To determine the loop tack after curing a specimen is prepared as described above. Before the specimen is placed in a "Zwick" tensile testing machine Z010 the curable film is cured under the described conditions, wherein the loop tack is determined as described above.

Shear resistance

[00130] The film is laminated on a polyester film and cut into strips with a width of about 25mm and a length of about 50mm. The strip is put on a steel plate to cover an area of about 25 mm x

25 mm at the edge of the steel plate. Immediately after preparation the steel plate is positioned vertically in a suitable device and stressed with loads between 1 N to 160 N. The shear value is the maximum stress (in Newton) at which the strip still sticks to the plate after 4 hours.

[00131] To determine the shear resistance after curing a specimen is prepared as described above. Before the shear resistance is measured as described above, the curable film is cured under the described conditions.

Lap shear tests

[00132] Grit blasted mild steel (GBMS) panels: The GBMS panels consist of grit blasted mild steel. The grit blasting must be done < 24h before the test. Blasting medium: Corundum, diameter 0.21-0.3 mm, blasting pressure 3 bar. The curable film is transferred to GBMS steel panels (25 mm width) to cover an area of 25 mm x 12, 5 mm (312,5 mm²) at the edge of the first steel panel. A second steel panel is put on the first panel in such a way that a complete overlap of the covered area is achieved. Two clamps (load each of them 45-90N) are used to press the steel panels together. The resulting specimen is then stored under defined temperature and time conditions.

[00133] The lap shear strength was measured using a "Zwick" tensile testing machine Z010. Velocity: 2 mm/min; initial load: 5 N. The resulting value is the maximum force before specimen breaks.

[00134] To determine the lap shear strength after curing a specimen is prepared as described above. Before the lap shear strength is measured as described above, the curable film is cured under the described conditions

Differential Scanning Calorimetry (DSC)

[00135] For the DSC measurements a NETZSCH DSC204F1 instrument is used, wherein the measurement conditions are the following: Scanning temperature range from -80°C to 200°C with 10 K/ min, sample weight: 5 mg.

Dynamic Mechanical Analysis (DMA)

[00136] For the DMA measurements a METTLER TOLEDO DMA/SDTA861e instrument is used, wherein the measurement conditions are the following: harmonic shear load with 1 Hz, max. force 1.5 N, max. distance 10 µm, Scanning temperature range from -150°C to 200°C. The storage modulus G` was determined from the DMA results.

Example 1

[00137] The curable film of Tape 1 exhibits a high initial tackiness and shows good pressure sensitive adhesion properties at 23 °C. The curable film can be fully cured by exposing said film

to a temperature of 65 °C for 1 hour followed by a temperature of 23 °C for 24 hours. The glass transition temperature (T_g) of the curable film is –40 °C whereas the glass transition temperature (T_g) of the cured film is 15 °C. For the curable film a storage modulus G' of $3 \cdot 10^3$ Pa was observed.

In Table 1 several material properties of Tape 1 are given.

Table 1

	Substrate	Uncured state	Cured state
Loop-Tack	Steel	7 N	none
Shear resistance	Steel	< 10 N	> 160 N
Lap Shear strength	GBMS	< 15 N / 312.5 mm ² < 0.05 MPas	1966 N / 312.5 mm ² 6.3 MPas

[00138] The importance of the curing process is further shown in Table 2, where different curing conditions were used. High shear strengths were only observed for cases where the samples were exposed to conditions which could cause the curing of the curable film.

Table 2

Curing conditions	F-max [N/312,5mm²]	MPas
23 °C/30min	< 30	< 0.1
23 °C/1 hour	150	0.48
23 °C/ 3 hours	590	1.89
23 °C/ 10 hours	930	2.98
23 °C/ 24 hours	1550	4.96
23 °C / 72 hours	1510	4.83
65 °C / 5 minutes	< 30	< 0.1
65 °C / 30 minutes	438	1
65 °C / 1 hour	935	3
65 °C / 1 hour + 24h RT post curing	2281	7.3

Example 2

[00139] The curable film of Tape 2 exhibits a very high initial tackiness and shows very good pressure sensitive adhesion properties at 23 °C. The curable film can be fully cured by exposing said film to a temperature of 65 °C for 1 hour followed by a temperature of 23 °C for 24 hours.

In Table 3 several material properties of Tape 2 are given.

Table 3

	Substrate	Uncured state	Cured state
Loop-Tack	Steel	9 N	none
Lap Shear strength	GBMS	< 15 N / 312.5 mm ² < 0.05 MPas	525 N / 312.5 mm ² 1.68 MPas

Example 3 (comparative example)

[00140] Curing of the curable film at a temperature of 65 °C for 1 hour followed by a temperature of 23 °C for 24 hours does not sufficiently increase the lap shear strength on GBMS, which means that this tape could be unsuitable for a variety of structural bonding applications.

In Table 4 several material properties of Comparative Tape 1 are given.

Table 4

	Substrate	Uncured status	Cured status
Loop-Tack	Steel	7 N	8 N
Shear resistance	Steel	< 10 N	< 20
Lap Shear strength	GBMS	< 15 N / 312.5 mm ² < 0.05 MPas	80 N / 312.5 mm ² 0.25 MPas

Example 4 (comparative example)

[00141] The film of Comparative Tape 2 exhibits a high initial tackiness and shows pressure sensitive adhesion properties at 23 °C. However, exposing the film to different conditions (see Table 5) does not lead to a significant increase of the bonding strength on GBMS, which means that this tape is unsuitable for all structural bonding applications.

Table 5

Temperature/Time	F-max [N/312,5mm²]	MPas
23°C/30min	< 15	< 0,05
23°C/1 hour	30	0.1
23°C/ 3 hours	50	0.16
23°C/ 10 hours	50	0.16
23°C/ 24 hours	48	0.15

Procedure for Determining (Co)Polymer Acid Number

[00142] Check if sample is at room temperature by replacing the lid of the sample container by a lid with thermometer. Determine the temperature. If the temperature is between 20 and 30 °C, the analyses can start in the sequence specified. If the temperature is not within the above range, place the sample in a water bath at 25 °C and check the temperature regularly until it reaches a value between 20 and 30 °C. Some (co)polymers will contain volatile compounds, so it is recommended to start with the analyses of the most critical parameters.

Method:

1. Weigh in a sample bottle of 250 cc X g of the (co)polymer.
2. Add acetone. Prior to use, neutralize the acetone with 0.05 N KOH, using phenolphthalein.
3. Shake the sample bottle until the (co)polymer is dissolved.
4. Cool the sample bottle (0 – 5 °C) and titrate with 0.05 N KOH from clear to light pink. The change of colour has to stay for 30 seconds.
5. Where the (co)polymer has a low acid number (1.0 mg KOH/g dry resin max), a small 10 ml burette should be used.

[00143] The acid number of the (co)polymer is determined according to the following equation:

$$\text{acid number (in mg KOH/g dry resin)} = \frac{(\text{ml of KOH}) \times (\text{N of KOH}) \times 56 \times 100}{(\text{g sample}) \times (\text{Total Solids in Sample})}$$

[00144] Total solids in sample refers to the % dry polymer in the (co)polymer. Normally, (co)polymers are solvent based. The typical value of total solids in the sample is 30 – 60%.

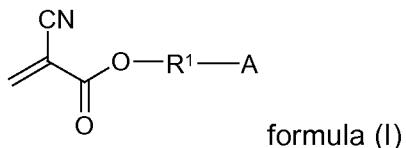
[00145] The words “comprises/comprising” and the words “having/including” when used herein with reference to the present invention are used to specify the presence of stated features, integers, steps or components but do not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

[00146] It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

Claims

1. An article, comprising a curable film on a release substrate and/or carrier substrate, wherein the curable film comprises:

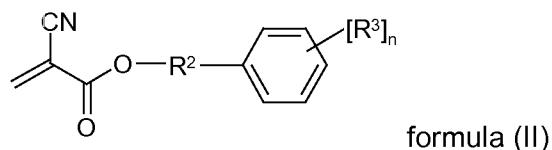
(a) at least one cyanoacrylate monomer selected from compounds of formula (I)



wherein R^1 is a divalent linking group comprising 1 to 10 carbon atoms, and A represents an $\text{C}_5\text{-C}_{50}$ aryl residue or a $\text{C}_2\text{-C}_{50}$ heteroaryl residue; and

(b) at least one film forming (co)polymer.

2. The article according to claim 1, wherein the cyanoacrylate monomer is selected from compounds of formula (II),



wherein n is 0 to 5, R^2 is a C_{1-5} alkylene group, and each R^3 , if present, is independently selected from $\text{C}_1\text{-C}_{10}$ alkyl, $\text{C}_1\text{-C}_{10}$ alkoxy, fluorine, chlorine, bromine, cyano and nitro.

3. The article according claim 1 or 2, wherein the cyanoacrylate monomer has a melting point at 1013.25 mbar of more than 25 °C.

4. The article according to any preceding claim, wherein the cyanoacrylate monomer is (2-phenylethyl) 2-cyanoacrylate.

5. The article according to any preceding claim, wherein the cyanoacrylate monomer is present in an amount of at least about 15 wt.%, based on the total weight of the curable film.

6. The article according to any preceding claim, wherein the cyanoacrylate monomer is present in an amount from about 20 wt.% to about 80 wt.%, based on the total weight of the curable film.

7. The article according to any preceding claim, wherein the film forming (co)polymer is selected from poly(meth)acrylate (co)polymers, polyvinyl ethers, natural rubbers, polyisoprenes, polybutadienes, polyisobutylenes, polychloroprenes; butadiene-acrylonitrile polymers,

thermoplastic elastomers, styrene-isoprene copolymers, styrene-isoprene-styrene block copolymers, ethylene-propylene-diene polymers, styrene-butadiene polymers, poly-alpha-olefins, silicones, ethylene vinyl acetate copolymers and/or combinations thereof.

8. The article according to any preceding claim, wherein the film forming (co)polymer has a glass transition temperature (T_g), as determined by Differential Scanning Calorimetry (DSC), of less than 30 °C.

9. The article according to any preceding claim, wherein the film forming (co)polymer is a (co)polymer having pressure sensitive adhesion properties at 23 °C.

10. The article according to any preceding claim, wherein the film forming (co)polymer is a copolymer of (meth)acrylic acid, (meth)acrylic acid esters and optionally other comonomers.

11. The article according to any preceding claim, wherein the film forming (co)polymer has an acid number from about 0 to about 30.

12. The article according to any one of claims 1 to 8, wherein the film forming (co)polymer is an ethylene vinyl acetate copolymer.

13. The article according to claim 12, wherein the ethylene vinyl acetate copolymer has a vinyl acetate content of 50 wt.% to 98 wt.%, based on the total weight of the ethylene vinyl acetate copolymer.

14. The article according to any preceding claim, wherein the film forming (co)polymer is present in an amount from about 20 wt.% to about 80 wt.%, based on the total weight of the curable film.

15. The article according to any preceding claim, wherein the weight ratio of the total amount of cyanoacrylate monomers to the total amount of film forming (co)polymers in the curable film is from 1:8 to 8:1.

16. The article according to any preceding claim, wherein the curable film further comprises one or more additives selected from cyanoacrylate polymers, tackifiers, plasticizers, toughening agents, antioxidants, stabilizers, water-absorbing agents and/or combinations thereof.

17. The article according to any preceding claim, wherein the curable film has a storage modulus G' , measured with Dynamic Mechanic Analysis (DMA) at 1 Hz and 23 °C, of about 3.3×10^5 Pa or less.

18. The article according to any preceding claim, wherein the curable film has a tack value of at least about 3 N in the standard loop tack test as measured by DIN EN 1719.

19. The article according to any preceding claim, wherein the curable film has a 180° peel strength from about 3 N/25mm to about 50 N/25mm after 10 min as measured by DIN EN 1939 on steel substrate at 23°C.

20. The article according to any preceding claim, wherein the curable film has a glass transition temperature (T_g), as determined by Differential Scanning Calorimetry (DSC), of less than 10 °C.

21. The article according to any preceding claim, wherein the carrier substrate is selected polymeric films, foams, metal foils, cloths, and combinations thereof.

22. The article according to any preceding claim, wherein the release substrate is a paper or plastic-based material, which is optionally coated with a release agent.

23. The article according to any preceding claim, wherein the article is a label, a single-sided tape, a transfer tape or a double-sided tape.

24. A method of attaching a film to a curable surface, comprising the steps of:

- (a) providing an article according to any one of claims 1 to 23;
- (b) attaching the curable film of the article to at least one surface to form an assembly,
- (c) exposing the assembly to conditions sufficient to cure the curable film of the article, wherein the release substrate of the article, if present, is removed before and/or after step (b).

25. A method of adhering components together, said method comprising:

- (i) providing an article according to the present invention;
- (ii) attaching the curable film of the article to at least one of the components;
- (iii) mating the components; and
- (iv) curing the adhesive film between the components to be adhered together, wherein the release substrate of the article, if present, is removed before and/or after step (ii).

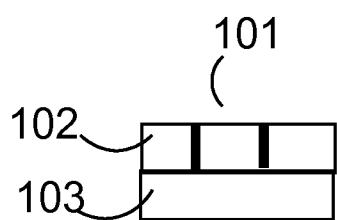


Figure 1

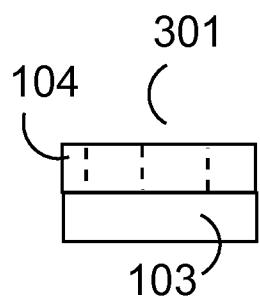


Figure 3

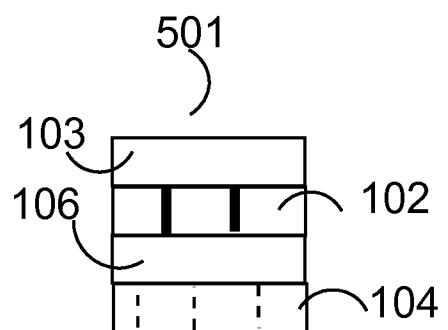


Figure 5

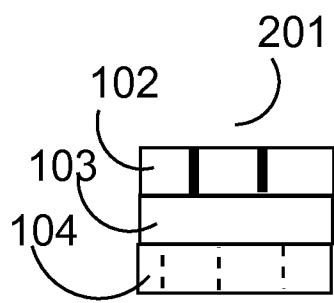


Figure 2

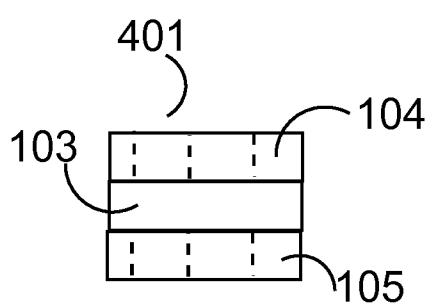


Figure 4

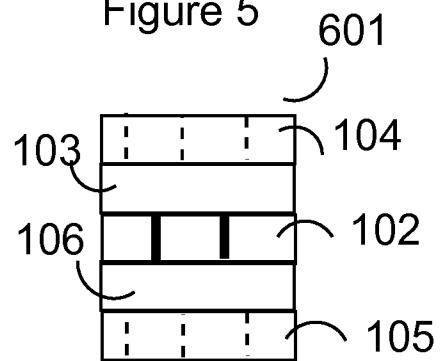


Figure 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/059630

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09J4/00 C09J7/00 C09J7/02
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09J

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

Electronic data base consulted during the international search (name of data base and, where practicable, 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.
A	EP 2 154 214 A2 (THREE BOND CO LTD [JP]) 17 February 2010 (2010-02-17) paragraphs [0011], [0012] -----	1-25
A	US 5 902 443 A (KANAKUBO MASARU [US] ET AL) 11 May 1999 (1999-05-11) column 2, line 40 - column 3, line 15 -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

12 March 2013

19/03/2013

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

Trauner, H

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/059630

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2154214	A2 17-02-2010	EP 2154214 A2 JP 2010059405 A	17-02-2010 18-03-2010
US 5902443	A 11-05-1999	NONE	