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(54) DISPENSER, KIT AND METHOD FOR APPLYING AN ACTIVATOR FOR A CURABLE CYANOACRYLATE-BASED COMPONENT

(57) A device for activating a curable cyanoacrylate-based material comprising a source of activator component in gaseous form. The device has a chamber for holding the gaseous form of the activator; and either a dispensing arrangement for dispensing the gaseous form of the activator from the chamber onto the curable material or a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable material by contact with the gaseous form of the activator component within the chamber. A kit form includes the curable component and said device comprising the source of the activator component in gaseous form.

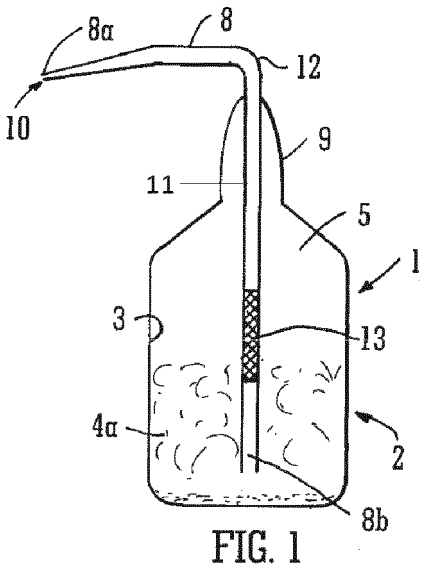

FIG. 1

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Description

Background of the Invention

Field of the Invention

[0001] The present invention is concerned with a method of activating curable or otherwise activatable cyanoacrylate-based materials, typically adhesive compositions. This activation may be performed alone or in combination with the priming of the surfaces for the application of cyanoacrylate based materials, as desired.

[0002] The invention, in particular, relates to a device suitable for applying an activator for activating a curable cyanoacrylate-based materials; and, a kit comprising a curable cyanoacrylate-based material and such a device.

Brief Description of Related Technology

[0003] The problem of activating cyanoacrylate-based adhesives while achieving a neat cure is well established. Activating cyanoacrylate-based materials with conventional, known activators - such as solvent-based activators - oftentimes results in a "bloom" on the surface on which the product to be activated resides. The bloom is often manifested by an amount of white-coloured, cured curable component; in some instances a white cloudy appearance is observed in a normally colourless and transparent cured curable product; in other cases, a white "halo" (or ring of discoloured material) may be visible on the substrate surface around the cured curable product. Thus, while good cure properties can be achieved there may nonetheless be an undesired aesthetic appearance of the cured product and/or the substrate to which it is applied.

[0004] It is thought that undesirable discoloration, such as blooms, may be caused by the application of the activator. The activator is generally provided in a delivery vehicle which may be a solvent or a solvent/propellant mix in the case aerosols, and is typically applied subsequent to the application of a "bead" or other amount of the curable materials on the surface concerned.

[0005] Since discolouration impairs the appearance of the product/article on which it forms, it is highly desirable to avoid such blooms, halo effects or indeed any such other discolouration. Discolouration effects on the surface on which the activated cyanoacrylate-based product resides is aesthetically unpleasing. Therefore it would be desirable to achieve activation without impairing either the appearance of the cured cyanoacrylate-based material or the substrate to which it is applied in circumstances where activation is desirable to achieve advantageous cure speeds and bond strengths.

[0006] Activator compositions may also be flammable, generally on account of the carrier vehicle for the activator; common carrier vehicles include, for instance, n-heptane, acetone, and ethyl acetate. In production plants and the like, it is necessary to provide specialised zones, such as "explosion-proof" areas, where flammable products can be handled safely.

[0007] Other downsides of conventional, solvent-based activators can be the deformation of the adhesive "bead" or other shape caused when an activator is applied onto a pre-applied adhesive. This effect may be caused by the partial mixing of the activator and the adhesive, resulting in turbulence and stress in the adhesive as it undergoes hardening. It may also arise due to evaporation of solvent. As a consequence, the cured material may have a porous structure or a visibly rough surface (owing to convection, exothermic reactions and resulting evaporation) which does not give an aesthetically pleasing cured bead. Moreover, the bead can also readily crumble apart.

[0008] Still further downsides of conventional activators are:

- Environmental concerns surrounding the use of high VOC (volatile organic carbons), including olfactory irritation where such VOCs have strong smells;
- Problematically long dry-off-times between either activator application and adhesive application or the mating of parts;
- Corrosion or softening of substrates, in particular plastics, caused by the solvent of the activator;
- Contamination of skin and clothes caused by spillage during handling of liquid activator formulations; and,
- Difficulties in the neat application of liquid activator formulations in an upward direction, against gravity.

[0009] Activators that may be suitable for the cure of cyanoacrylate adhesives are disclosed in Japanese Patent Document No. JP-A-62 022 877, which document specifically speaks to the use of *N,N*-dimethylbenzylamine and *N,N*-diethyltoluidine as activators.

[0010] Japanese Patent Document No. JP-A-59 066471 discloses the use of *N,N*-dimethylaniline; *N,N*-diethylaniline; *N,N*-dimethyl-p-toluidine; *N,N*-dimethyl-m-toluidine; *N,N*-dimethyl-o-toluidine; dimethylbenzylamine; pyridine; picoline; and, vinyl pyridine as suitable activators for cyanoacrylate adhesives.

[0011] EP 0 100 063 A discloses the use of low boiling point (<200°C) aromatic heterocycles as suitable activators for cyanoacrylate adhesives. Examples of the disclosed activators include: 2-acetylpyridine; 4,7-dichloroquinoline; 5-

nitroquinoline; 5-chloropyridine; 5-bromopyridine; 3,5-dichloropyridine; 3,5-dibromopyridine; and, 3-cyanopyridine.

[0012] As previously mentioned, activators for cyanoacrylate adhesives are generally applied to a substrate in liquid form, which may require that they be dispersed in a carrier vehicle such as a solvent. For instance, aerosol spray can deliver fine droplets of an activator onto the desired surface (as well as into the atmosphere); larger volumes can be applied by dripping or dropping an activator solution onto a curable product such as an adhesive already present on a substrate. Such methods of application do not allow for sufficiently controlled dispensing of the activator. With the spray method, it may be necessary to mask areas of the substrate which should be protected from excess/misdirected activator. Masking the substrate may be time consuming and the masking material may leave residual marks on the substrate which will then require cleaning. Masking and/or cleaning the substrate obviously adds additional steps to the production of a product and will also increase the costs involved in manufacturing the product. The dropping application method also has the disadvantage of misdirected activator, for example the activator solution may drip or run onto an undesired location on the substrate. Again subsequent cleaning may be required. In addition, it may be difficult to control the amount of activator solution that is dispensed. Accordingly there is need to provide a dispenser and a method of dispensing activators in a controlled manner.

Summary of the Invention

[0013] In one aspect the present invention relates to a device for activating a curable cyanoacrylate-based material, said device comprising:

(i) a source of activator component in gaseous form; and
(ii) a chamber for holding the gaseous form of the activator;

said device further comprising at least one of:

(iii) a dispensing arrangement for dispensing the gaseous form of the activator from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and
(iv) a product pathway for allowing introduction of the curable cyanoacrylate-based material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber.

[0014] The present invention thus provides alternative contacting arrangements. The contacting arrangement may be an enclosure in which the curable material may be placed and the activator component in gaseous form is disposed within the enclosure. The enclosure may have a stationary atmosphere including activator component in gaseous form. Alternatively the activator component may be provided as a moving volume of gas, such as a continuous or intermittent flow-through gas stream within the enclosure. The process can be carried out on an as needed basis or be employed within an industrial process for example a (continuous) line production process or a batch process.

[0015] In one arrangement the device is a dispenser for dispensing an activator component and the contacting arrangement is a dispensing arrangement for dispensing activator onto the material to be cured. A conduit from a chamber to a dispensing nozzle to dispense the gaseous form when force is applied to the contents of the container is one appropriate arrangement.

[0016] The device of the invention has the advantage of allowing contacting/dispensing of the activator in a controlled manner. The activator used will generally be solvent-free and, desirably, also non-flammable so that the device will not release solvent vapours.

[0017] Where the device is a dispenser it will generally comprise an enclosed chamber such as a container comprising an enclosed chamber. This allows for the retention of activator until dispensing is desired.

[0018] The activator will generally be provided initially in solid or liquid form. Generally for those activators which are in solid form, it is desirable that the materials are volatile (including materials which sublimate) to generate the desired gaseous activator. Where the activator is in solid form it may be provided in particles of any desired size, e.g. powder, pellets, and lumps.

[0019] The solid activator may equally be provided in a predetermined shaped format, for example cast (at least partially) to a given shape or to the shape of a container in which it is to be held. For example, the activator material may be shaped to follow an inner wall of a reservoir. This is particularly of interest where the device is a dispenser.

[0020] The activator may be attached to the inner wall, e.g. melted-on or glued-on. A mass of activator material may thus be provided in any predetermined shape. If desired a retainer, holder or other barrier may be employed to hold the activator material within a desired position within the container. This may also help to prevent non-gaseous forms from being inadvertently blown out during operation of the device.

[0021] Where the activator is provided in fluid form, for example in liquid form, it is desirable to further provide a retainer

of a type which is adapted to retain the activator component by adsorption and/or absorption. In such a case, the activator component will generally be adsorbed onto and/or absorbed into the retainer. Where the device is a dispenser the retainer will generally be located within the dispenser such as in an enclosed chamber thereof.

[0022] Generally speaking the activator will be expelled as a vapour (gaseous) to activate the curable component. It is the vapour which will generally be dispensed, for example as an air/activator mixture. It will be appreciated that a carrier gas other than air may be employed if desired. A controlled stream of air or gas may be passed over/through the activator to produce the desired gaseous form of activator.

[0023] Generally the activator and any retainer present will occupy only part of the enclosed chamber of the device so that a portion of the chamber unoccupied by the retainer and/or activator (which may be referred to as a "head-space") of the chamber becomes filled with vapour-saturated gas, for example air. This vapour/gas-mix is then contactable with the curable product/surface for example by being dispensable utilising a dispensing arrangement of the dispenser. Sufficient activator is present in the gas stream to allow activation of the curable product.

[0024] The activator components particularly useful with a device of the present invention will generally be solids or liquids of considerable volatility. This will generally provide a sufficient saturation of activator vapour in a head-space of the device.

[0025] In a simple construction, a mixture of the gaseous form of the activator and air is employed; the air is desirably taken from the environment although pressurised sources of carrier gases are also useful. If desired, the device could either have all air evacuated from it, or an isolated activator supply so that substantially only the gaseous form of the activator is employed. A gas other than air could also be used as a carrier gas for carrying activator. Any mixture of gases may be employed also including mixtures with air. A gas stream may be provided by a pump, e.g., a manual or motorised pump. A pressurised container may also be used.

[0026] It is desirable that the retained activator component is in a form which is not easily spilled. This may be achieved by providing an activator and/or retainer which is in solid form or is absorbed or adsorbed according to the alternative arrangements described above. Activator which is adsorbed or absorbed on or in the retainer will then be held on and/or within the retainer and spillages will not easily occur. This is of greatest importance where the activator is in a liquid form. In this respect, it is desirable that the retainer is constructed of a material which can adsorb or absorb relatively high amounts of activator.

[0027] Generally open-structured materials are desirable. Adsorptive and absorptive (solid) materials may be employed. Such materials include natural and artificial materials an exemplary list of which include inert fillers such as beads for example glass or plastic beads, paper, sponge, silicates, sand, gravel, alumina, vermiculite, pumice, wood, fabric including fibers and for example felt, Raschig rings and the like and/or combinations thereof.

[0028] The material selected will also be inert to the activator. While it may be desirable in certain circumstances to have the retainer as one (solid) piece, for example a block of material with an open structure which allows adsorption or absorption, other forms of materials such as particulate matter, e.g. finely divided materials may be employed. In certain instances it may be desirable to employ a flexible or rigid holder to hold the retainer against movement. The activator may, for example, be provided in a porous holder such as a compartment for example a pouch made from fabric or paper or a cartridge.

[0029] It is additionally desirable to avoid overdosing of activator directly onto a curable material which is to be activated and this is achieved by the device of the present invention.

[0030] It is desirable that the activator component induces a fast cure and it is desirable to also induce a good cure-through-volume (CTV) in the curable composition to which it is applied. In a desired aspect of the invention solvent-free activator materials are employed. A skilled person will know which solvent-free activator materials are suitable for use.

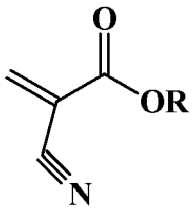
[0031] In embodiments where the activator is sensitive to either air or the humidity contained in air, a drying agent or oxygen scavenger or both may be employed. An example of a suitable oxygen scavenger is Cu_2O and an example of a suitable humidity absorber is $CaCl_2$. The oxygen scavenger or humidity absorber may be placed between a gas source and the chamber. Alternatively, gas may be supplied from a dried gas source. If necessary the device may be sealed to protect the activator substance from air or humidity and/or evaporation. The device may also be equipped with valves in order to prevent humidity of the air or respectively the oxygen of the air from coming through the outlet/nozzle into the device.

[0032] Desirably the activator substances have a vapour pressure of around (at least) about 0.1 mBar at room temperature.

[0033] Some exemplary activators which may be used with the present invention (desirably in solvent-free form) include: *N,N*-dimethylbenzylamine; *N,N*-diethyltoluidine; *N,N*-diethyl-*p*-toluidine; *N,N*-dimethylaniline; *N,N*-diethylalinine; *N,N*-dimethyl-*p*-toluidine; *N,N*-dimethyl-m-toluidine; *N,N*-dimethyl-*o*-toluidine; *N*'-benzyl-*N,N*-dimethylethylenediamine; *N*-benzylethylenediamine; *N,N*-diethyl-*N*'-phenylethylenediamine; *N,N'*- dibenzyi-*N,N*'-dimethylethylenediamine; *N,N*'-dibenzylethylenediamine; *N,N*-diethyl-*N',N'*-dimethylethylenediamine; *N,N,N',N*'-tetrakis(2-hydroxyethyl)ethylenediamine; *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine; *N,N,N',N'*-tetraallylethylenediamine; *N,N,N',N*'-tetraethylethylenediamine; dimethylbenzylamine; pyridine; picoline; vinyl pyridine; 2-acetylpyridine; 4,7-dichloroquinoline; 5-nit-

roquinoline; 5-chloropyridine; 5-bromopyridine; 3,5-dichloropyridine; 3,5-dibromopyridine; 3-cyanopyridine and combinations thereof. Combinations of (solvent-free) activator materials, such as a combination of activator monomers, may be employed in the present invention.

[0034] The cyanoacrylate adhesive compositions include cyanoacrylate monomers, such as those represented by the structure:



wherein R is selected from alkyl, alkoxyalkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, aryl, allyl and haloalkyl groups each having from 1 to 16 carbon atoms. Preferably, the cyanoacrylate monomer is selected from methyl cyanoacrylate; ethyl-2-cyanoacrylate; propyl cyanoacrylates; butyl cyanoacrylates (such as n-butyl-2-cyanoacrylate); hexyl cyanoacrylate; octyl cyanoacrylates; allyl cyanoacrylate; ß-methoxyethyl cyanoacrylate and combinations thereof.

[0035] A particularly desirable cyanoacrylate monomer is ethyl-2-cyanoacrylate.

[0036] The curable compositions of the present invention may also contain one or more additives such as stabilizers, accelerators (e.g. crown ethers, calixarenes, cyclodextrins, oligo- and poly- ethers), plasticizers, fillers, opacifiers, thickeners, viscosity modifiers, inhibitors, thixotropy conferring agents, dyes, pigments, perfumes, fluorescence markers, thermal degradation reducers and adhesion promoters. These additives are known to those of skill in the art.

[0037] The present invention also provides a coating method comprising the steps of:

(i) applying a curable cyanoacrylate-based material to a substrate,
(ii) exposing the curable material to a gaseous form of an activator to form a first layer of cured material;
(iii) applying a further amount of curable cyanoacrylate-based material to the cured material; and optionally
(iv) exposing the further amount of curable material to a gaseous form of an activator to form a further layer of cured material.

[0038] The type of substrate is not intended to be limited and encompasses those substrates which are conventionally bonded with curable cyanoacrylate based materials and adhesive compositions; said substrates may optionally be primed or otherwise surface treated to raise the surface energy of the substrate to a suitable level for coating or adhesion with the cyanoacrylate based material concerned. In one interesting embodiment, the optionally primed substrate to which a curable cyanoacrylate based material is applied is a so-called "difficult-to-bond" or non-polar substrate selected from the group consisting of: polyolefins, for example linear homo- or copolymers of simple olefins, such as polyethylene, polypropylene, polybutene, polymethylpentene, and polytetrafluoroethylene; polyacetals; some polyurethanes; some polyamides; EPDM (ethylene-propylene-diene terpolymer) some elastomers; and, thermoplastic rubbers based on vulcanised polyolefins.

[0039] The invention also relates to a method of bonding which includes applying a cyanoacrylate-based curable material onto one or two of parts to be glued together, subsequently applying the gaseous activator by directing the activating gas jet onto one or both applied amounts of curable material e.g. an adhesive beads, (respectively adhesive-wetted surfaces), and subsequently mating the parts.

[0040] Suitably each time an amount of curable cyanoacrylate-based material is laid down it is activated before application of a subsequent amount. In this way layers of material can be built up as desired by repeating the application and activation. The present inventors have found that they can build up coatings on substrates quite easily using such a process. It will be appreciated in this respect that the term "layer" is used to identify separately applied amounts of curable cyanoacrylate-based material rather than being limited to any particular type of physical arrangement. This could also be done in a continuous process: the cyanoacrylate may be continuously dispensed onto the substrate surface while the beam of liquid adhesive is being brought into contact with activator-enriched air (gas), so that the entire fillet / bead of adhesive is thoroughly activated during dispensing. This technique is suitable for coating, doming, encapsulation and potting.

[0041] Of particular interest within the present invention is the ability to coat or encapsulate objects, in particular fragile objects, where more robust handling may be desired.

[0042] The inventors have found that the coatings of the invention cure to be dry (hard) to the touch and in many cases remain transparent. The substrate which is so coated, e.g. encapsulated, is protected from damage such as environmental damage arising from mechanical and chemical stresses. The discoloration which arises with other methods of activation

does not occur to any substantial extent with the present invention and thus the coatings of the invention may be used for many applications and in particular those applications where the coated article is visible during use and for which aesthetics are important. The invention is suitable for potting applications, doming and encapsulating techniques including fragile components such as electronic components.

[0043] The invention thus allows a method to efficiently build up transparent layers of polycyanoacrylate on substrates. The polymerised material will have high transparency, be potentially colourless, and will be bubble-free (as compared to materials activated by more conventional methods). Glossy and smooth coatings can also be achieved. The cyanoacrylate can be applied as a liquid and quickly cured in comparatively thick layers of up to 3-5 mm, without compromising the neat appearance of the coating. Good cure through volume is achieved so that encapsulation or coating of unmounted components, or components mounted on a substrate, can easily be achieved by doming or casting.

[0044] The material provides sufficiently hard protection to avoid scratching etc. from mechanical stresses and additionally provides protection from environmental soiling.

[0045] The dispensing arrangement of the dispenser allows the end user to dispense the activator component onto a curable cyanoacrylate-based material in a controlled manner.

[0046] In the present invention "solvent-free" as it pertains to the activator(s), means an activator material, or combination of activator materials, which is not provided in a liquid solution by dissolution in a carrier solvent. This does not preclude the possibility of small or trace amounts of solvent, up to 1 wt.% by weight of the activator material, being present in an activator.

[0047] To ensure that unwanted amounts of in particular solid activator do not get dispensed a dispensing arrangement can be provided with a retaining barrier such as a mesh or cotton wool or rock wool *etc.;* this will act as a filter for the undesired material while not interfering to any substantial extent with the dispensing of gaseous activator.

[0048] Where the device of the invention is a contacting arrangement in which the curable cyanoacrylate-based material is placed within an enclosure for contact with the activator, it is desirable nonetheless to have a dispensing arrangement for dispensing the activator into the enclosure so that the dispensing arrangement for a dispenser can be employed in this alternative arrangement also.

[0049] The dispensing arrangement may be any suitable arrangement that allows for collection of a gaseous form of the activator from within a dispenser and for its delivery to a desired application site. The dispensing arrangement may thus include a dispensing path defined by a conduit. For example the dispensing arrangement may include a dispensing nozzle. Generally the dispensing arrangement will not collect, for dispensing, substantial amounts of activator which is in liquid or solid form. Instead the dispensing arrangement will generally be arranged to collect a vapour form of the activator, such as activator alone or an activator/air mixture and to dispense that vapour form.

[0050] It has been surprisingly found that using such an applicator for a gaseous form of activator substantially reduces blooming and other such undesirable discolorations and, in some circumstances, deformation of the adhesive bead where the curable product is cyanoacrylate; the surface of the bead of cyanoacrylate adhesive is cured in a neat way, without formation of surface roughness and with the bead retaining both its transparency and its original shape. In this case, no drying time is required: the time allowed for the solvent to evaporate from traditional forms of activator is substantially reduced or completely eliminated.

[0051] If desired a carrier gas for carrying the activator may be passed through the dispenser and/or an enclosure. In this embodiment the dispenser/enclosure may be provided with a port or conduit for introduction of the carrier gas.

[0052] The carrier gas can be any desired gas such as air or other gases (inert to the activator) like noble gases, nitrogen gas (N_2), nitrous oxide (N_2O), halogenated hydrocarbons and halogenated carbons such as CFC-propellants or mixtures thereof. Use of an introduced carrier gas in this way can lead to greater amounts of activator being picked up as a result of a moving gas stream. The dispenser can be provided with a manually operated device such as a pump which can be manipulated (e.g. squeezed) by the use to apply activator. Alternatively the carrier gas can be supplied from a source such as from a pressurised container, a pump-up spray container, a (compression) pump or indeed any other suitable supply. A pump-up spray container is one in which the expulsion pressure for expelling material can be increased by a pumping action prior to expulsion of material. It is recommended to choose a design where the pressure of the carrier gas/air above the activator species is fairly low because at lower pressures the vapour pressure of the substance is relatively high; in certain cases, where the vapour pressure of the activator species is relatively low, a high pressure of the carrier gas/air would possibly lower the activator's vapour pressure too much.

[0053] One simple embodiment of the present invention is a hand-squeezable dispensing bottle having a dispensing arrangement thereon.

[0054] Alternatively the parts on which the adhesive to be activated has been applied can be put into a chamber containing air or a carrier gas enriched with activator. Such a chamber may contain a reservoir of activator component or the gaseous carrier gas/activator mixture is fed into it. The chamber may also contain a blower such as a fan which may facilitate mixing of the gas/activator mixture.

[0055] In the case of a chamber adapted to accommodate one or more substrates to which the curable cyanoacrylate-based material to be activated has been or is applied, it is desirable to have a dispensing arrangement as described

above arranged to dispense the activator into the chamber.

[0056] Generally a device of the invention will not have an amount of activator in liquid form, which is not retained by the retainer, that is an excess of liquid activator above that which is absorbed into or adsorbed onto the retainer.

[0057] In another aspect the present invention provides a kit comprising;

(i) an activatable curable cyanoacrylate-based component, and
(ii) a device as described above having therein the activator material for activating the curable component.

[0058] The kits of the invention may be used for fast and durable curing of curable cyanoacrylate-based products. Good adhesion on difficult-to-bond surfaces may also be achieved. By providing the kit, an end-user has both a curable material and its activator, which allows for quick and reliable use, for example, secure fixing of substrates bonded together.

[0059] Any suitable cyanoacrylate material may be used. The skilled person will know which cyanoacrylate materials are suitable for use. Of particular interest in relation to the present invention are liquid cyanoacrylate adhesives for example those of low to high density. Combinations of cyanoacrylate materials (such as cyanoacrylate monomers) are included within cyanoacrylate materials suitable for activation by the present invention.

[0060] Any suitable solvent-free activator material may be used. A skilled person will know which solvent-free activator materials are suitable for use. Illustrative examples include: *N,N*-dimethylbenzylamine; *N,N*-diethyltoluidine; *N,N*-diethyl-*p*-toluidine; *N,N*-dimethylaniline; *N,N*-diethylalinine; N,N-dimethyl-*p*-toluidine; *N,N*-dimethyl-m-toluidine; *N,N*-dimethyl-o-toluidine; *N*'-benzyl-*N,N*-dimethylethylenediamine; *N*-benzylethylenediamine; *N,N*-diethyl-*N*'-phenylethylenediamine; *N,N'*-dibenzyl-*N,N*'-dimethylethylenediamine; *N,N*'-dibenzylethylenediamine; *N,N*-diethyl-*N',N'*-dimethylethylenediamine; *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine; *N,N,N',N*-tetrakis(2-hydroxypropyl)ethylenediamine; *N,N,N',N*'-tetraallylethylenediamine; *N,N,N*',*N*'-tetraethylethylenediamine; dimethylbenzylamine; pyridine; picoline; vinyl pyridine; 2-acetylpyridine; 4,7-dichloroquinoline; 5-nitroquinoline; 5-chloropyridine; 5-bromopyridine; 3,5-dichloropyridine; 3,5-dibromopyridine; 3-cyanopyridine; and, combinations thereof. Combinations of solvent-free activators are included within solvent-free activator materials useful in the present invention.

[0061] The present invention also provides a method for activating a curable cyanoacrylate-based component, said method comprising the steps of:

(i) applying a curable cyanoacrylate-based material to a substrate on which it is to be cured; and
(ii) dispensing a gaseous form of an activator component onto the curable material to activate the curable component.

[0062] The step of applying the curable cyanoacrylate-based material to the surface to be bonded, coated or sealed may be performed by the end user prior or subsequent to dispensing the activator though the former is likely to give best activation in most circumstances. For example the activator material may then be dispensed over the curable material by the end user.

[0063] By utilising a dispenser or the method of the present invention the activator component may be dispensed in a controlled manner, which, on the one hand allows sufficient application of activator material onto the curable material whilst also preventing overdosing of the activator component onto the curable material.

[0064] Commercially available activators may contain liquid solvents: the solvent contacting the adhesive causes turbulence, convection and stress in the adhesive bead during hardening, resulting in rugged, sometimes bubbly surface. The cure triggered by an activator system according to this invention results in a hardened adhesive bead which is indistinguishable, or almost indistinguishable in appearance from the liquid bead before cure; that is the bead is neat in shape, transparent and colorless. Combinations of solvent-free activators are included within the term solvent-free activator materials.

[0065] Some of the advantages of the present invention are that a very neat cure is achievable, for example of cured adhesive beads, as compared to those compositions activated by conventional activators. Depending on the choice of the activator chemical the product will generally be non-flammable. The device and cured product are solvent-free. The cured product may have relatively lower toxicity. Generally spillage of liquid activator can be avoided and there is no need to equip production with explosion-proof areas. There will be no corrosive attack or softening of (plastic) substrates since the process is solvent-free.

[0066] The device of the invention will be relatively low weight since the formulation is simple and does not require other components such as solvent; this may lead to lower transport and storage costs. Activation of curable compositions according to the present invention will allow for tack-free surfaces on the cured product within a relatively short period. Other benefits are reduced odour, since the novel system is not based on solvents, as well as virtually zero VOC emissions.

[0067] It is also possible to co-dispense the curable material and the gaseous activator so that, upon dispensing, the curable material is already activated by having been mixed with the activator. The advantage is that the adhesive has been activated without bringing in any solvent, noting that a solvent brought into the adhesive could be detrimental to the adhesives characteristics and performance, e.g. looks, material properties, adhesion, and durability. The present

invention includes such a co-dispensing system.

[0068] In an embodiment, it may be it is possible to provide: i) a dispenser including a reservoir for curable cyanoacrylate-based product; and, ii) a reservoir for activator component alone or activator component with a carrier gas such as air, for activating the curable product, wherein the dispenser is arranged upon dispensing action to mix the curable product with activator component in gaseous form to activate the product for curing. The dispenser may be arranged as described above to dispense the mixture into an enclosed chamber in which the curable product to be activated is disposed. For instance, the dispenser may be a double chamber dispenser such as a double chamber cartridge.

[0069] In such an arrangement separate chambers may be employed to separately retain the curable product and the activator component. Dispensing is then utilised to mix the two components. For example, a common dispensing path may be provided to mix the two components; a dispensing nozzle may be employed to mix the components, for instance. A static mixer may be disposed along the dispensing path or at the dispensing nozzle. Sufficient mixing is easily achieved so as to efficiently activate the curable product.

[0070] In one arrangement the dispenser is a squeezable bottle for retaining activator with a multi aperture diffusor head for applying the gaseous form of the activator. The diffusor head may be formed in two or more interconnected parts which may be taken apart for cleaning purposes etc.

[0071] The present invention does provide a versatile two-part system which includes a curable cyanoacrylate-based product and an activating vapour. The curable product can be considered Part A, and the vapour Part B of the two-part system.

Brief Description of the Drawings

[0072] The invention will be more clearly understood from the following description of some embodiments thereof, given by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of one embodiment of a dispenser in accordance with the present invention for dispensing activator.

Figure 2 is a schematic representation of an alternative dispenser to that of Figure 1;

Figure 3 is a schematic representation of a still further alternative embodiment of the dispenser of the present invention, in which embodiment the activator is cast onto the walls of the dispenser;

Figure 4 illustrates dispensing onto a bead of adhesive;

Figure 5 shows a schematic representation of an alternative device for dispensing activator;

Figure 6 is an image of a pump type dispenser which may be employed; and,

Figure 7 illustrates a side view (Figure 7a) and a front view (Figure 7b) of a yet further dispensing device of the present invention.

Figure 8 shows photographic images of: i) in the left column, samples (adhesive beads on black ABS-plastic strips) activated by conventional activator application methods; and, ii) in the right column, samples activated using the dispenser and method of the present invention.

Detailed Description of the Invention

[0073] Referring to Figure 1, the dispenser 1 is for dispensing an activator component for activating an activatable material and comprises a container 2 - usually constituted by an elastically deformable structure such as a squeezable wash bottle type - having an enclosed chamber 3. The enclosed chamber or reservoir 3 houses an amount of solid volatile activator 4a. In the embodiment the activator 4a takes the form of a particulate material (which may be considered a disintegrated solid) for example a powder or pellets or the like.

[0074] In the embodiment of Figure 1, the activator component 4a is desirably of high volatility and provides sufficient saturation of a head-space 5 of the enclosed chamber 3. Alternatively, solid activator component 4b may be cast into the shape of the (internal) sidewalls of the dispenser 1, as shown in Figure 3.

[0075] In the case of use of a liquid activator, the solid activator material 4a/4b is replaced by a retainer, onto and/or into which the liquid activator is absorbed or adsorbed. As described above this will avoid spillage. The retainer can take any suitable form and it too may be shaped to conform to the shape of the container. For example, material 4a/4b may alternatively be a solid material which is impregnated with the activator.

[0076] Desirably the activator component is highly volatile so that the head-space 5 of the container contains gaseous activator. As the head-space 5 of the dispenser 1 accommodates only a certain volume of gas at any given time, the risk of overdosing of the activator substance directly onto a curable cyanoacrylate-based composition 6 located between two substrates 7 is reduced (see Figure 4). In the embodiment of Figure 4, the cyanoacrylate material is for bonding the substrates together and the activation by gaseous activator dispensed from dispenser 1 provides suitable activation to achieve effective cure including good cure-through volume.

[0077] The dispenser 1 of Figure 1 illustrates one embodiment of the invention. The general principle of the invention resides in the activator substance itself being either a solid or a liquid. Air or gas in, or fed into, the dispenser 1 takes up small quantities of the activator in gaseous form if the activator is in liquid or solid form.

[0078] In the case of a solid activator, chunks or crystals or powders of the activator can be put into the dispenser 1. Alternatively, the inner wall of the dispenser may be coated (as shown in Figure 3). In the embodiments utilising a liquid activator (Figure 1), the liquid activator may be adsorbed onto or absorbed into a porous material.

[0079] An alternative arrangement with an external gas feed is shown in Figure 5 where a gas stream indicated by arrow 21 - which may be air - is passed into a chamber 17 with activator 4a therein. The stream of gas enters through a first port 15 and over the activator 4a and exits through port 16. Within this exits pipe it is desirable to place a filter 13 to prevent particles from being blown out of the device. The exiting gas includes a gaseous form of the activator. It will be appreciated that the devices of the invention can be employed to generate an atmosphere in a container which has sufficient activator to achieve the desired function. The chamber can be dimensioned to accommodate the material to be activated. In such a case, it may be desirable to arrange the construction so that a dispenser is arranged to dispense the gaseous form into the chamber. Generally the dispenser will be external to the chamber but it could be accommodated within the chamber if desired.

[0080] The dispenser 1 of the present invention (which takes the form of a wash-bottle type container) also comprises a dispensing arrangement in the form of a nozzle 8 having two spaced apart ends 8a and 8b. In the embodiment of Figures 1-4 the nozzle 8 protrudes from the neck 9 of the container. The nozzle 8 has an outlet 10 at its first end 8a and an elongate body 11. The elongate body extends from the outlet 10 through the neck 9 of the container 2 such that the second end 8b is positioned within the bottle 1 proximate the activator 4a/4b. This arrangement allows air entering the end 8b of the nozzle 8 to pass over and/or through the activator 4a/4b and thereby take up activator vapour. The device 1 can thus dispense air/activator in a gaseous form.

[0081] The nozzle 8 may be equipped with a bendable area 12 analogous to a bendable or flexible drinking straw, such that the angle of the nozzle can be adjusted. (This bendable feature 12 is also present in the embodiment of Figures 6A and 6B.) In embodiments where the activator component is retained on and/or in a retainer, preferably porous retainer is soaked with liquid activator component(s). The activator component(s) may evaporate from the retainer to form a gaseous activator mix in the head space 5 of the dispenser 1. The nozzle 8 may also be provided with a stop filter or mesh 13 to prevent unwanted material (e.g. liquid droplets or solid particulate material activator component) from being dispensed.

[0082] Desirably, the activator vapourwill be dispensed onto the surface of the curable cyanoacrylate-based material by a stream of gas. This will usually be achieved by squeezing of the dispenser 1. The emitted gas will contain gaseous activator material. Gas, such as air, that is present in the head-space 5 of the container 2 above the activating material takes up the activating material vapour and the activator/gas mixture may be dispensed over the curable material 6 as shown in Figure 4. Desirably, the gas in the head-space 5 of the container 2 will be air but can be any suitable gas. Desirably, the activator/gas mixture will be dispensed in a stream produced by the end user squeezing the container 2 with manual pressure.

[0083] In the embodiment of Figure 3, the activator material 4b is cast on the inner wall of the container 2. The head space 5 of the container 2 again takes up the activating material vapour. As with all embodiments the head space contains air but can contain any suitable gas. As in the embodiment of Figure 1 the activator/gas mixture will be dispensed in a stream produced by the end user squeezing the container with manual pressure.

[0084] In another embodiment of the dispenser 1 such as that illustrated in Figure 5, (pressurised) dispensing or carrier gas is supplied to the dispenser as indicated by arrow 21. In the embodiment the supply is an air or gas supply from an external source. In this embodiment manual pressure on the container 2 is not required. Instead, dispensing may be controlled by controlling the amount of dispensing, or carrier, gas provided into the dispenser 1.

[0085] In the embodiment of Figure 2, the gas supplied into the dispenser is pumped by squeezing a squeezable reservoir or bulb 15. The gas taken into the reservoir 15 can be contained by a one-way valve 16. A further, optionally one-way, valve 20 may be provided to prevent air/activator from the dispenser 1 from re-entering the bulb 15.

[0086] Gas, such as air from the reservoir 15, enters the headspace 5 and mixes with activator material vapour while moving over or through the activator material or retainer 4a retained in the dispenser 1. The activator material can be a disintegrated solid such as pellets, or it can be cast on top of the inner wall of the dispensing container.

[0087] Alternatively, the activator material may be retained on a retainer 4a which is made of a porous material or a material having a high surface area, such as paper, sponge, silicates, fabric, wood or any suitable porous or large-surface material known to a person skilled in the art to avoid spillage of the activator material and overdosing onto the curable cyanoacrylate-based material 6.

[0088] The nozzle 8 of the container 2 will desirably allow the end user to dispense the activator material in a controlled manner. Desirably, the means of dispensing the activator material will be through a nozzle 8 or by any other means of controlled release of a vapour.

[0089] In a further aspect of the present invention a kit is provided which comprises a dispenser of the type described

above and a curable cyanoacrylate-based material which will usually be held in a container. Any suitable cyanoacrylate material may be used. In particular liquid cyanoacrylate adhesives of low to high viscosity may be easily activated utilizing the present invention.

[0090] The kit of the invention may be used for fast and durable adhesion of surfaces. Having the curable material and the corresponding activator allows for quick and secure fixing of surfaces to be bonded. The container holding the curable cyanoacrylate-based material and/or the dispenser 1 containing the activator material can be colour coded to designate the types of surfaces that can be bonded by the activated curable material to assist selection of the correct activator material by the end user.

[0091] Figure 6 shows an image of a spray dispenser 30 of a type which can be utilized to dispense activator through nozzle 31 by pressing on a button within nozzle 31. In this type of arrangement a manual pump of the dispenser may be pumped until primed and/or until a desired level of pressure is achieved and then used to blow out activator-saturated air (or carrier gas) at that pressure. In this embodiment, it is important to select an activator material of sufficiently high volatility to compensate for the reduced volatility caused by the elevated internal pressure of the device.

[0092] Figures 7a and 7b provide different views of a device 1 according to the present invention and of which the interior chamber may be of similar construction to that shown in Figure 1 or Figure 3. The device of Figure 7 includes a screw-on cap 35 which allows for the container to be re-filled. The nozzle 8 extends through the cap 35 and may come away with the cap 35. The nozzle 8 is provided with a diffusor head 36 with apertures 37 defined therein in a predetermined pattern; depending on requirements, the diffuser and apertures can provide a more or less turbulent gas jet. The device is manually squeezed to eject the activator-saturated carrier gas from the nozzle.

[0093] It will be appreciated that sufficient amounts of the gaseous form of the activator pressure may be generated by, for example, a pumping action (Figure 6), a squeeze ball/valve system (Figure 2), a pressurised container or a motor driven pump. In embodiments where the activator is hygroscopic, a suitable dessicant may be employed.

[0094] It is desirable that, upon application to a curable cyanoacrylate-based material, the activator material promotes a fast cure and a good cure through volume. Any suitable solvent-free activator material may be used including all those activators referenced above. A skilled person will know which solvent-free activator materials are suitable for use.

[0095] Suitably the activator will have a relatively low boiling point, for instance a boiling point less than 250 °C at ambient pressure).

[0096] The above description applies to activator material. Primer material may be utilised in an analogous fashion.

Examples

[0097] Table 1 shows a comparison of activation according to the technique of the present invention as against existing (solvent-based) techniques.

Conventional Method

[0098] The activator product which is available from Henkel Ireland Ltd, Dublin 24, Ireland under the product name Loctite® 7455 was post-applied (three drops) on-top of a bead of adhesive (created using three drops of adhesive placed on an ABS surface). The adhesive in question is identified in Table 1. (All Loctite® products are available commercially from Henkel Ireland Limited, Dublin, Eire).

Method of the Present Invention

[0099] A squeezable bottle (wash bottle type, LDPE total volume ~ 260 ml) such as shown in Figure 1, had placed therein about 50 g of the activator 3,5-dichloropyridine. The dispensing nozzle was fitted with a paper filter in order to avoid particles been blown out of nozzle. Hardening of adhesive was achieved by positioning the nozzle of bottle a few (~3) centimeters above the adhesive bead and squeezing the bottle 5 times (in the same manner as one would do with a wash bottle).

[0100] Skin formation and CTV were checked by means of a wooden applicator stick as well as visually: when the bead is manually pressed one may judge whether or not a skin has formed and whether liquid adhesive is left within the bead. The visual results achievable on plastics material can be seen in Figure 8. The right column of Figure 8 shows the effects post-application of compositions of the invention; the left column of Figure 8 shows post-application of a conventional liquid activator (Loctite ® Product No. 7445). The latter exhibits significant cratering of the cured bead in addition to whitening on top of the bead, and white halos around it. Such undesired effects are not visible under the conditions of the system of the present invention as shown in the right column. It is to be noted, in aside, that any visible white spots in the right hand column of Figure 8 are caused by light reflection due in turn to the glossy appearance of the cured material.

Table 1

Adhesive	Skin Formation - time elapsed secs		CTV - time elapsed in seconds		Appearance of cured bead	
	7455	Gaseous activator*	7455	Gaseous activator*	7455	Gaseous activator*
Loctite® 401	6	4	20	25	w, h, c	slight c
Loctite® 406	7	6	25	25	w, h, c	slight c
Loctite® 407	6	7	30	30	w, h, c	slight c
Loctite® 416	9	11	30	40	w, h	
Loctite® 424	7	9	25	25	h, c	
Loctite® 431	6	6	20	25	w, h	
Loctite® 480	20	25	180	180	h, c	
(h= white halo around cured bead; w = whitening of adhesive surface; c = *'cratering' of adhesive surface, means surface is rugged after cure* * = *The gaseous activator utilized in Table 1 is 3,5-Dichloropyridine)*						

[0101] Table 2 shows the results of comparative tests carried out by applying activator to a bead of cyanoacrylate adhesive (3 drops) utilizing various combinations of activators and retainers within a dispenser as shown in Figure 1. The tack-free time was evaluated by touching the bead's surface with a paper.

Table 2

Activator and State Thereof at 25°C, 1atm	Device like Figure 1 Retainer material/ Bottle filling:	Tack free time of Loctite® 401 (secs)	Tack free time of Loctite® 416 (secs)
2-Methoxy pyridine, liquid	Wooden sticks	2	3
2,6-Dimethoxy pyridine, liquid	Wooden sticks	3	3
3-Cyanopyridine, solid	Large Crystals (no retainer required)	2	3
2-(Methylmercapto)benzthiazol, solid	Coated inner wall	4	4
2,6-Dimethyl pyrazine, solid	Large Crystals (no retainer required)	2	3
Pyrazine, solid	Large Crystals (no retainer required)	2	3
N,N-Dimethyl-p-toluidine, liquid	Paper roll	6	9

Co-Dispensing Curable Product and Activator

[0102] Here a dual chamber reservoir, in this case a dual syringe, was provided in which the syringe is of the type typically used for two-part adhesive dispensing. The syringe had two chambers where the volume capacity was in a ratio of 4:1 (curable product: activator). One gram of cyanoacrylate adhesive (Loctite® 401, available from Henkel Ireland Ltd, Dublin 24, Ireland) was placed in the smaller syringe barrel. 2 g of 3,5-dichloropyridine was placed in the second (larger) chamber. A paper filter was provided to prevent dispensing of the solid activator. The activator was arranged at the dispensing end of the syringe so that air could be pushed through it when the plunger was depressed. Air in the syringe between the plunger and the activator could thus be pushed past and through the activator so that air exiting the larger chamber provided a gaseous stream containing activator.

[0103] A static mixer (a dispensing nozzle with a tortuous mixing path provided by a baffle arrangement) was provided to mix the curable material and the activator on dispensing from the respective chambers. The cyanoacrylate and the

activator were thus mixed before dispensing from the static mixing nozzle. The 1 gram of adhesive and was dispensed had cured fully in just 90 seconds. Without such activation, the hardening of 1 gram of cyanoacrylate adhesive, if dispensed as a bead, would require at least several hours or even a day or more to cure. The experiment thus demonstrates that activation by co-dispensing curable product plus a gaseous stream containing activator is possible.

[0104] 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. 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 does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

Claims

1. A device for activating a curable cyanoacrylate-based material, said device comprising:

i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:

a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber.

2. The device according to claim 1, wherein said source of the activator component is solvent-free.

3. The device according to claim 1 or claim 2, wherein said source of the activator component is a volatile solid or liquid.

4. The device according to claim 1 or claim 2, wherein said source of the activator component is provided in solid, particulate form.

5. The device according to claim 1 or claim 2, wherein said source of the activator component is provided in a solid form which is cast in a predetermined shape, which shape preferably conforms, at least partially, to the shape of the chamber.

6. The device of claim 1 or claim 2, wherein said source of the activator component is provided in liquid form and the device further comprises a retainer for the liquid, preferably wherein the retainer is adapted to retain the liquid by adsorption and/or absorption.

7. A device according to any one of claims 1 to 6, wherein the activator component is selected from the group consisting of: *N,N*-dimethylbenzylamine; *N,N*-diethyltoluidine; *N,N*-diethyl-*p*-toluidine; *N,N*-dimethylaniline; *N,N*-diethylalinine; *N,N*-dimethyl-*p*-toluidine; *N,N*-dimethyl-m-toluidine; *N,N*-dimethyl-o-toluidine; *N*'-benzyl-*N*,*N*-dimethylethylenediamine; *N*-benzylethylenediamine; *N,N*-diethyl-*N*'-phenylethylenediamine; *N,N'*- dibenzyl-*N,N'*-dimethylethylenediamine; *N*,*N*'-dibenzylethylenediamine; *N,N*-diethyl-*N*',*N'*-dimethylethylenediamine; *N*,*N*,*N*',*N*'-tetrakis(2-hydroxyethyl)ethylenediamine; *N,N,N',N*'-tetrakis(2-hydroxypropyl)ethylenediamine; *N,N,N',N'*-tetraallylethylenediamine; *N*,*N*,*N*',*N*'-tetraethylethylenediamine; dimethylbenzylamine; pyridine; picoline; vinyl pyridine; 2-acetylpyridine; 4,7-dichloroquinoline; 5-nitroquinoline; 5-chloropyridine; 5-bromopyridine; 3,5-dichloropyridine; 3,5-dibromopyridine; 3-cyanopyridine and combinations thereof.

8. The device according to any one of claims 1 to 7, wherein a retaining barrier, preferably a mesh or a filter, is provided to retain the source of activator component.

9. The device according to any one of claims 1 to 8 further comprising a source of carrier gas for carrying the activator component.

10. The device according to any one of claims 1 to 9 further comprising a propulsion system for applying a force to allow application of said activator component, said propulsion system preferably being selected from a squeezable container, a pump, a plunger arrangement, a pressurised propellant or a connection to a pressurised air-line.

11. The device according to any one of claims 1 to 10, wherein the dispensing arrangement or the product pathway includes a diffuser for diffusing the gaseous form of the activator component.

12. A method of coating or encapsulating a substrate comprising the steps of:

i) applying a cyanoacrylate-based curable material to said substrate,
ii) exposing the curable material to a gaseous form of an activator component to form a first layer of cured material;
iii) applying a further amount of curable material to the cured material; and optionally
iv) exposing the further amount of curable material to a gaseous form of an activator component to form a further layer of cured material.

13. A kit comprising:

i) a curable cyanoacrylate-based material; and,
ii) a device as defined in any one of claims 1 to 11.

14. A method for activating a curable cyanoacrylate-based material comprising the steps of:

i) applying a curable material to a substrate on which it is to be cured; and, either
ii)a) dispensing a gaseous form of an activator component onto the curable cyanoacrylate-based material to activate said curable material; or
ii)b) introducing the substrate and the curable cyanoacrylate-based material into a chamber holding a gaseous form of an activator component through a product pathway in the chamber so as to activate the curable material by contact with the gaseous form of the activator component within the chamber.

15. A method of bonding two substrates comprising the steps of:

i) applying curable cyanoacrylate-based material to at least one of the substrates;
ii) dispensing an activator component in a gaseous stream onto the curable material to activate the curable material; and
iii) bonding the two substrates utilising the activated curable material.

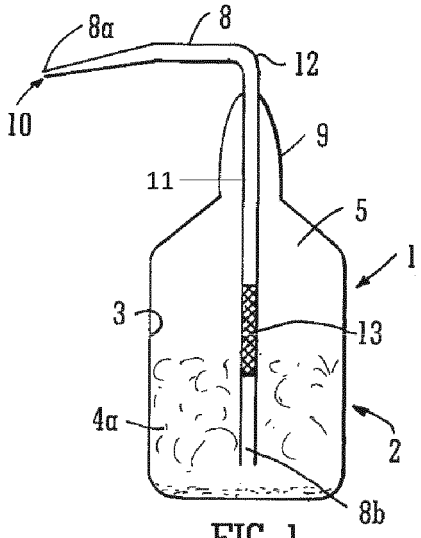


FIG. 1

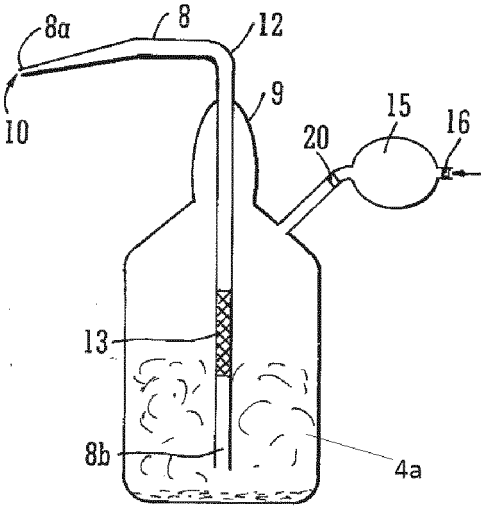


FIG. 2

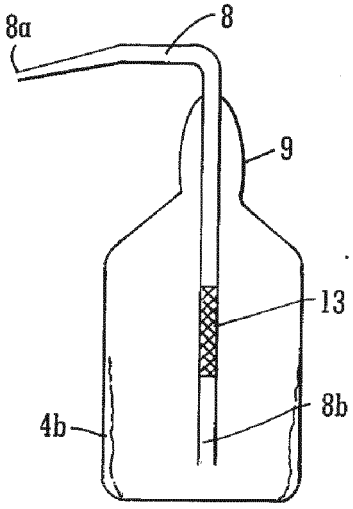


FIG. 3

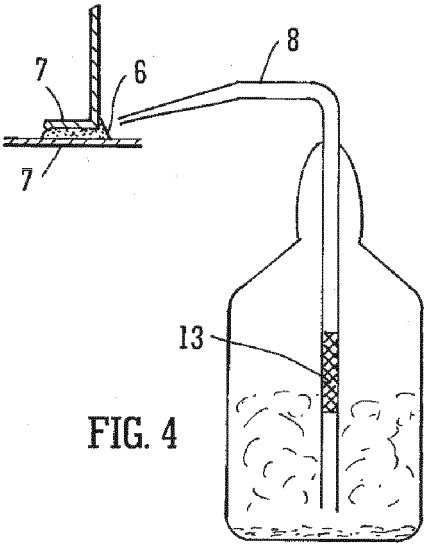


FIG. 4

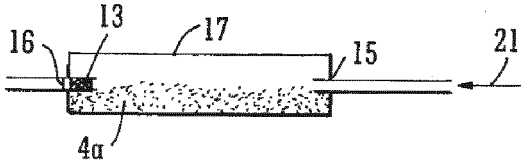


FIG. 5

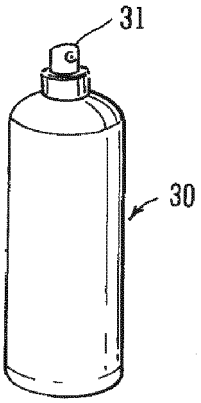


FIG. 6

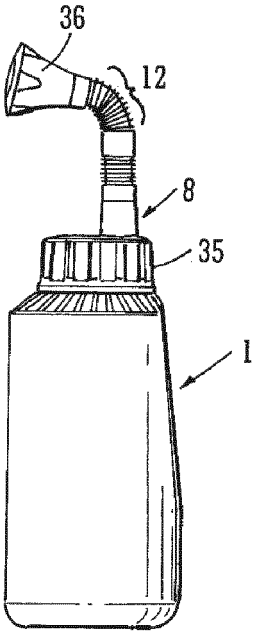


FIG. 7A

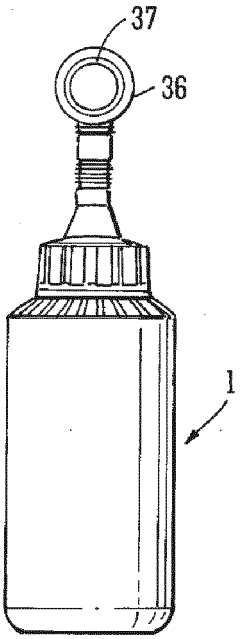


FIG. 7B

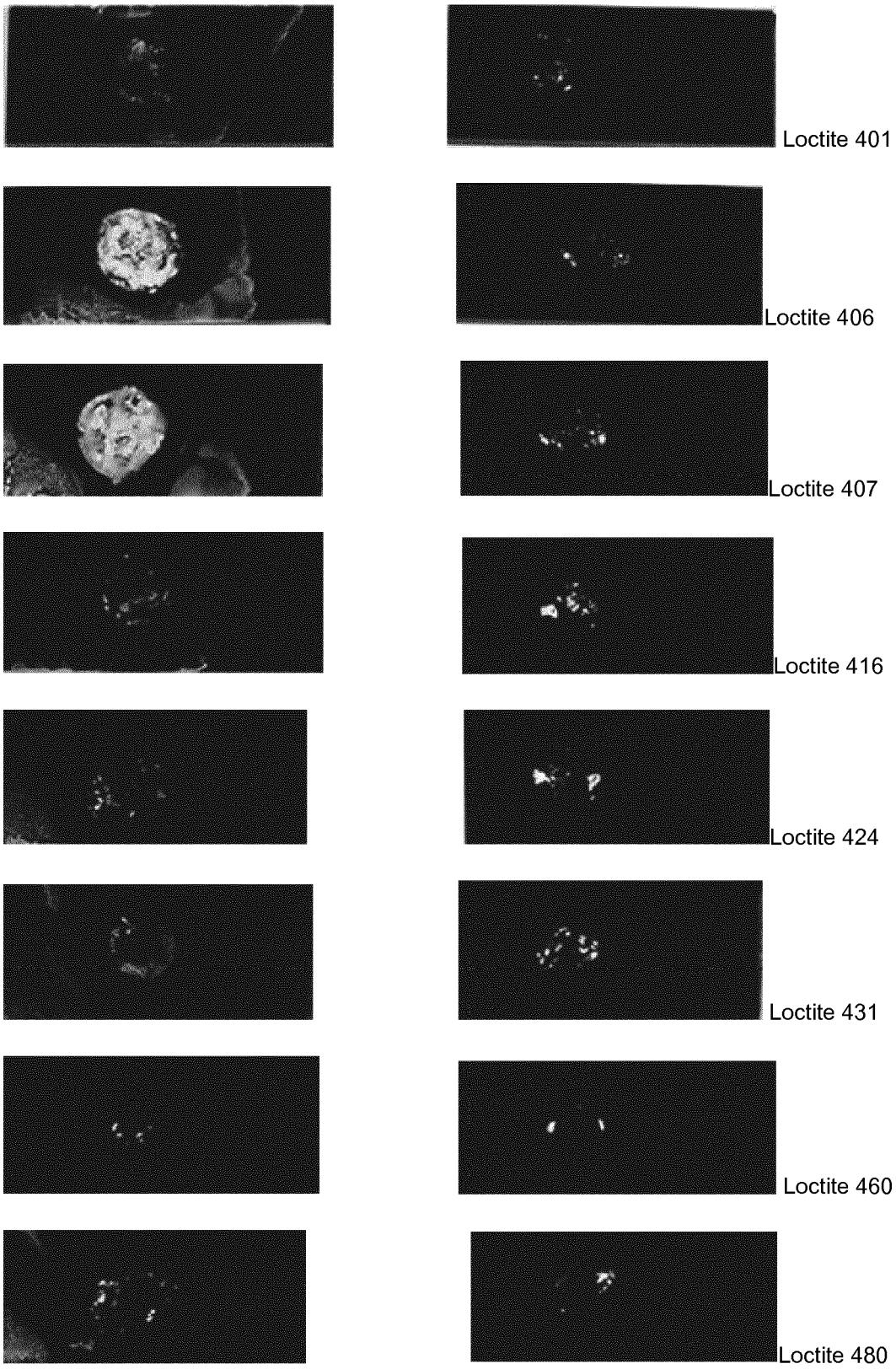

Loctite 401
Loctite 406
Loctite 407
Loctite 416
Loctite 424
Loctite 431
Loctite 460
Loctite 480

Fig. 8

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EUROPEAN SEARCH REPORT

Application Number
EP 15 18 5668

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 4 634 644 A (IRVING EDWARD [GB] ET AL) 6 January 1987 (1987-01-06) * example 2 *	1-3,13, 14	INV. B05D3/04
X	JP S57 23666 A (TAOKA CHEMICAL CO LTD) 6 February 1982 (1982-02-06) * abstract *	1	
X	WO 2010/149733 A1 (BASF SE [DE]; CRANFILL DAVID [US]; GUTOWSKI KEITH E [US]; CAMPBELL DON) 29 December 2010 (2010-12-29) * claims; figures; examples *	1	
X	GB 291 839 A (ERNEST WILLIAM MAYER) 5 June 1928 (1928-06-05) * figures *	1	
X	US 2 227 536 A (FRANCESCO D AGOSTINO) 7 January 1941 (1941-01-07) * claims; figure 1; examples *	1-3,6, 9-11	
X	US 2007/196579 A1 (NECKERS DOUGLAS C [US] ET AL) 23 August 2007 (2007-08-23) * claims; figures; examples *	1	TECHNICAL FIELDS SEARCHED (IPC) B05D
A	WO 91/07446 A1 (LOCTITE CORP [US]) 30 May 1991 (1991-05-30) * example 3 * * page 16, line 18 - line 21 *	1,13,14	

~~The present search report has been drawn up for all claims~~

Place of search	Date of completion of the search	Examiner
The Hague	12 April 2016	Slembrouck, Igor

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

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European Patent Office
Office européen des brevets

Application Number
EP 15 18 5668

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

2, 3, 6, 9-11, 13, 14(completely); 1(partially)

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 15 18 5668

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 2, 3, 6, 9-11, 13, 14(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:
a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber;
a kit comprising:
i) a curable cyanoacrylate-based material; and,
ii) a device as defined in any one of claims 1 to 11;
a method for activating a curable cyanoacrylate-based material comprising the steps of:
i) applying a curable material to a substrate on which it is to be cured; and, either
ii)a) dispensing a gaseous form of an activator component onto the curable cyanoacrylate-based material to activate said curable material; or
ii)b) introducing the substrate and the curable cyanoacrylate-based material into a chamber holding a gaseous form of an activator component through a product pathway in the chamber so as to activate the curable material by contact with the gaseous form of the activator component within the chamber;

1.1. claims: 2(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:
a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber;
wherein said source of the activator component is solvent-free;

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1.2. claims: 3(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:
a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber;
wherein said source of the activator component is a volatile solid or liquid;

1.3. claims: 6(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:
a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber,
wherein said source of the activator component is provided in liquid form and the device further comprises a retainer for the liquid;

1.4. claims: 9(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:
a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber, further comprising a source of carrier gas for carrying the activator component;

1.5. claims: 10(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:
a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber, further comprising a propulsion system for applying a force to allow application of said activator component, said propulsion system preferably being selected from a squeezable container, a pump, a plunger arrangement, a pressurised propellant or a connection to a pressurised air-line;

1.6. claims: 11(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:
a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber, wherein the dispensing arrangement or the product pathway includes a diffuser for diffusing the gaseous form of the activator component;

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1.7. claim: 13

a kit comprising:
i) a curable cyanoacrylate-based material; and,
ii) a device D;

1.8. claim: 14

a method for activating a curable cyanoacrylate-based material comprising the steps of:
i) applying a curable material to a substrate on which it is to be cured; and, either
ii)a) dispensing a gaseous form of an activator component onto the curable cyanoacrylate-based material to activate said curable material; or
ii)b) introducing the substrate and the curable cyanoacrylate-based material into a chamber holding a gaseous form of an activator component through a product pathway in the chamber so as to activate the curable material by contact with the gaseous form of the activator component within the chamber;

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2. claims: 4, 5(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:
a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber wherein said source of the activator component is provided in solid form;

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3. claims: 7(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:

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Application Number
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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber, wherein the activator component is selected from the group consisting of: N,N-dimethylbenzylamine; N,N-diethyltoluidine; N,N-diethyl-p-toluidine; N,N-dimethylaniline; N,N-diethylalinine; N,N-dimethyl-p-toluidine; N,N-dimethyl-m-toluidine; N,N-dimethyl-o-toluidine; N'-benzyl-N,N-dimethylethylenediamine; N-benzylethylenediamine; N,N-d iethyl-N-phenylethylenediamine; N,N = dibenzyl-N,N'-dimethylethylenediamine; N,N = dibenzylethylenediamine; N,N -diethyl- N',N' -dimethylethylenediamine; N,N,N',N'- tetrakis(2-hyd roxyethyl)ethylened iam ine; N, N, N', N' -tetrakis(2-hydroxypropyl)ethylenediamine; N, N, N?N'-tetraallylethylenediamine; N, N, N' , N' tetraethylethylenediamine; dimethylbenzylamine; pyridine; picoline; vinyl pyridine; 2-acetylpyridine; 4,7-dichloroquinoline; 5-nitroquinoline; 5-chloropyridine; 5-bromopyridine; 3,5-dichloropyridine; 3,5-dibromopyridine; 3-cyanopyridine and combinations thereof;

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4. claims: 8(completely); 1(partially)

a device for activating a curable cyanoacrylate-based material, said device comprising:
i) a source for an activator component in gaseous form; and
ii) a chamber for holding the gaseous form of the activator component; and
iii) at least one of:
a) a dispensing arrangement for dispensing the gaseous form of the activator component from the chamber onto the curable cyanoacrylate-based material comprising a conduit connecting the chamber and a dispensing outlet; and,
b) a product pathway for allowing introduction of the curable material into the chamber so as to activate the curable cyanoacrylate-based material by contact with the gaseous form of the activator component within the chamber, wherein a retaining barrier, preferably a mesh or a filter, is provided to retain the source of activator component;

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5. claim: 12

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

a method of coating or encapsulating a substrate comprising the steps of:
i) applying a cyanoacrylate-based curable material to said substrate,
ii) exposing the curable material to a gaseous form of an activator component to form a first layer of cured material;
iii) applying a further amount of curable material to the cured material; and optionally
iv) exposing the further amount of curable material to a gaseous form of an activator component to form a further layer of cured material;

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6. claim: 15

a method of bonding two substrates comprising the steps of:
i) applying curable cyanoacrylate-based material to at least one of the substrates;
ii) dispensing an activator component in a gaseous stream onto the curable material to activate the curable material; and
iii) bonding the two substrates utilising the activated curable material;

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 15 18 5668

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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