(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 144 073 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.03.2017 Bulletin 2017/12

(51) Int Cl.:
B05D 3/04 *(2006.01)*

(21) Application number: **15185669.7**

(22) Date of filing: **17.09.2015**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA

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(54) DISPENSER, KIT AND METHOD FOR APPLYING AN ACTIVATOR FOR A CURABLE MATERIAL

(57) A device for activating a curable material comprising a source of an 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 material and the activator.

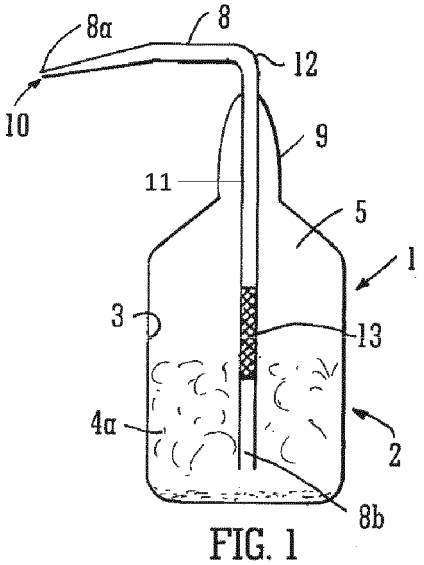

FIG. 1

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Description

Background of the Invention

Field of the Invention

[0001] The present invention relates to the field of activating activatable or curable (reactive) materials, such as the curable components of adhesive, sealant and coating compositions. The invention in particular relates to a device for applying an activator for activating a curable material, a kit comprising a curable material or component and said device, and a method of activating a curable material. Of particular interest are anaerobically curable products. Novel activators and a device comprising said activators is also disclosed.

Brief Description of Related Technology

[0002] The problems of activating curable components, in particular anaerobically curable products, are well known.

[0003] The activator is generally provided in a delivery vehicle which may be a solvent or a solvent / propellant mix in the case of aerosols and is either applied prior to dispensing of the adhesive or applied subsequent to the application of a bead or other amount of curable material on the surface concerned.

[0004] Activator compositions may also be flammable, generally on account of the carrier vehicle for the activator compounds. In production plants and the like, it is necessary provide specialised zones, such as "explosion-proof" areas, in which flammable products can be handled safely.

[0005] Further downsides of conventional activators are:

- Environmental and health and safety concerns surrounding the use of high VOC (volatile organic carbons), including olfactory irritation where such VOC's have strong smells.
- Problematically long dry-off-time between activator application and adhesive application or the mating of parts.
- Corrosion, softening and deformation of any plastic substrates - which may be disposed adjacent to the metal substrates being bonded using the anaerobically curable adhesives - can be caused by the solvent for the activator.
- Contamination of skin and clothes caused by spillage of liquid activator formulations during handling.
- Difficulties in the (neat) application of liquid activator formulations in an upward direction, against gravity.

[0006] Anaerobic adhesive compositions are well known for their ability to remain in a liquid, un-polymerized state in the presence of oxygen and to cure to a solid state upon the exclusion of oxygen. Early work on anaerobic adhesive compositions concentrated on developing a cure system which improved the speed and/or bond strength of the adhesive composition. Various cure systems for anaerobic adhesive compositions have been developed to primarily focus on efficiently performing the redox reaction, which is the basis for anaerobic chemistry.

[0007] Typically one-part anaerobic adhesive compositions have been used to provide fixture between components were there is a sufficiently small gap between the components to be bonded together to create substantially anaerobic conditions during mating which in turn allows curing of the anaerobic formulation. Good fixture speed and torque strength has been achieved on various components, for example on the threaded fasteners such as steel fasteners, on lap shears, and pin and collar arrangements. Typical anaerobic compositions include acetyl phenylhydrazine, saccharin and cumene hydroperoxide as the primary cure components. Anaerobic compositions have however had problems in bonding passive substrate such as those constructed of nylon or titanium.

[0008] Anaerobic adhesive compositions generally are well-known as documented in R. D. Rich, "Anaerobic Adhesives" in Handbook of Adhesive Technology, 29,467-79, A. Pizzi and K. L. Mittal, eds., Marcel Dekker, Inc., New York (1994), and in the references cited therein. Their uses are many and new applications continue to be developed.

[0009] Conventional anaerobic adhesives ordinarily include a free-radically polymerizable acrylate ester monomer, together with a peroxy initiator and an inhibitor component.

[0010] Desirable anaerobic cure-inducing compositions to induce cure may include saccharin, toluidines, such as *N,N*-diethyl-*p*-toluidine and *N,N*-dimethyl-*o*-toluidine, acetyl phenylhydrazine ("APH"), maleic acid, and quinones, such as naphthaquinone and anthraquinone. See e.g., Loctite® (now part of Henkel Corporation) U. S. Patent Nos. 3,218,305 (Krieble), 4,180,640 (Melody), 4,287,330 (Rich) and 4,321,349 (Rich). In addition, other curatives for anaerobic adhesives include thiocaprolactam and thioureas, such as tetramethyl thiourea as disclosed in US Patent No. 3,970,505 (Hauser).

[0011] Hydroperoxides were found to serve as a catalyst for the generation of a free radical. For example, U. S. Patent No. 2,895,950 (Kriebel), discloses the inclusion of hydroperoxides in amounts of 0.1 to 10% by weight in anaerobic adhesive compositions to achieve faster cure times. Amines, used in amounts up to about 10% by weight, are also disclosed in this reference as accelerators to generate free radicals from the peroxide.

[0012] Activators for curing anaerobic materials are known and include those described in Irish Patent Application No.

2001/0905 (Wrobel, assigned to the present Applicants). This document discloses washing solutions for surfaces to which an anaerobic material is to be applied; the washing solutions contain soluble activators. Mentioned as potential activators are transition metal salts of copper and iron such as an acetate of copper; copper naphthenate; dihydropyridine; mercaptobenzylthiazole; and, dihydroxyethyl-*p*-toluidine.

[0013] US Patent No. 4,990,281 and US Patent No. 4,731,146 (Paul J. Clark assigned to Loctite® Corporation, now Henkel Corporation) describe an activator - for curable acrylic monomer formulations, particularly anaerobic curable formulations - which comprises a solution in a volatile organic solvent of a Cu(II), Co(II), Mn(II), Mn(III), or Cr(III) salt of an acid phosphate acrylic monomer.

[0014] US Patent No. 3,855,040 (Malofsky assigned to Loctite® Corporation, now Henkel Corporation) describes anaerobic compositions containing a polymerizable acrylate ester monomer; an activator containing a ferrocene moiety, such activator being preferably selected from the group consisting of ferrocene, polymers incorporating ferrocene, the acyl, alkyl, hydroxyalkyl, alkenyl, and aryl derivatives of ferrocene, and mixtures thereof; and, a peroxy polymerisation initiator for said monomer selected from the group consisting of hydroperoxide and perester compounds.

[0015] A known technical problem is the fact that anaerobic adhesives do not cure on all substrates. Only certain metals, mainly the transition metals, and alloys containing said metals can be bonded. Other materials like plastics, ceramics, wood or main group metals or early d-group metals either cannot be bonded or they are difficult to bond in that the curing speed of the adhesive is slow or inadequate. In order to bond such inactive substrates, an activator is required.

[0016] State-of-the-art activators for the curable compositions described above are applied to a substrate in liquid form, which may require that they are dispersed in a carrier vehicle such as a solvent. For instance, an aerosol spray can deliver the activator onto the desired surface (as well as into the atmosphere); larger volumes can be applied by dropping an activator solution onto a curable product, such as an adhesive already present on a substrate. It is considered that such methods of application do not allow for sufficiently controlled dispensing of the activator. With the spray method of application it may be necessary to mask areas of the substrate which it is desirable to protect 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 or other parts adjacent to the metal part to be bonded may be negatively impacted - corroded or softened in the case of plastics - by the solvent part of the activator. In addition it may also be difficult to control the amount of activator solution that is dispensed. Accordingly, there is a clear need to provide a dispenser and a method of dispensing activators in a controlled manner.

[0017] Activators often suffer from the problem of high VOC content where it is typically desirable to have low or substantially zero VOC. It is desirable therefore to provide a composition in a user-friendly manner to allow for ease of handling. Presenting activator compositions in user friendly forms and/or packages can be a difficult task as the component must not have its cure-promoting capabilities deleteriously affected by the form, or package, in which it is presented for use. Furthermore solvents have all the draw-backs set out above for activators, including: flammability; the requirement for special equipment and clothing for handling, including the provision of explosion proof areas; spillages; and, the difficulty in their application in an upwards direction (against gravity).

Summary of the Invention

[0018] In one aspect the present invention relates to a device for activating a curable material comprising:

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

a) a dispensing arrangement for dispensing the gaseous form of the activator from the chamber onto the curable 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 material by contact with the gaseous form of the activator component within the chamber.

[0019] The enclosure may have a stationary atmosphere including the activator component in gaseous form. Alternatively, the activator component may be provided in a moving volume of gas, such as a continuous or intermittent flow-through 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.

[0020] In one arrangement the device is a dispenser for dispensing an activator component and the contacting ar-

rangement 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.

[0021] 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 the device will not release solvent vapours.

[0022] 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.

[0023] 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 in particles of any desired size, e.g. powder, pellets, large crystals and lumps.

[0024] A solid source of activator may, however, 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.

[0025] 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 being blown out during operation of the device.

[0026] Where the activator is initially 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.

[0027] Generally speaking the activator will be expelled as a vapour (or gas) 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.

[0028] Generally the source of 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 can become 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 or priming of the substrate.

[0029] 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.

[0030] In a simple construction, a mixture of the gaseous form of the activator and air is employed and the air is taken from the environment, although pressurised sources of carrier gases are also useful. If desired the device could 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, and this might indeed be required where the activator is sensitive to oxygen: inert gases such as the Nobel gases and in particular Argon might be mentioned in this regard. Mixtures of gases, including gas mixtures with air, are not precluded. A gas stream may be provided by a pump, e.g., a manual or motorised pump. A pressurised container may also be used.

[0031] It is desirable that the retained activator component is in a form that is not easily spilled. This may be achieved by providing an activator and/or retainer that 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.

[0032] 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 fibres and for example felt, Raschig rings and the like and/or combinations thereof.

[0033] 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 or compartment, for example a pouch made from fabric or

paper or a cartridge.

[0034] 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.

[0035] 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. Exemplary solvent free activators are disclosed herein.

[0036] In embodiments where the activator is sensitive to either air or the humidity contained in air, a drying agent or oxygen scavenger 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 (gas inlet) 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 the humidity of the air or, respectively, the oxygen of the air from coming through the outlet / nozzle into the device.

[0037] Desirably the activator substances have a vapour pressure of around (at least) about 0.1 mBar at room temperature.

[0038] Without intention to limit the present invention, exemplary solvent-free activators for anaerobically curable compositions, which may be used in the defined device or dispenser include those compounds of transition metals which are volatile at 25°C and of which compounds the transition metal can exist in at least two oxidation states of similar stability. Volatile compounds of those transition metals within subgroups 4, 5, 6, 7, 8 and 11 of the Periodic Table (d-group elements), more desirably members of subgroups 5, 6, 7, 8 and 11 might be mentioned. Further, suitable compounds include trifluorophosphanes, halogenides, alkoxides, hexafluoroacetylacetonates, alkyls, amides and nitrosyls.

[0039] Specific examples of such compounds are given below:

Trifluorophosphane complexes: $Fe(PF_3)_5$, $Ni(PF_3)_4$, $Ru(PF_3)_5$, $Pt(PF_3)_4$, $Rh_2(PF_3)_8$, $HMn(PF_3)_5$, $HRe(PF_3)_5$, $H_2Fe(PF_3)_4$, $H_2Ru(PF_3)_4$, $H_2Os(PF_3)_4$, $HCo(PF_3)_4$, $HRh(PF_3)_4$, $HIr(PF_3)_4$, $Mo(PF_3)_6$, $Cr(PF_3)_6$, $W(PF_3)_6$, $HCo(PF_3)_3(CO)$, $HFe(PF_3)_3(NO)$, $HMn(PPh_3)_2(NO)_2$, $Co(PF_3)_3(NO)$, $Rh(PF_3)_3(NO)$, $Fe(PF_3)_2(NO)_2$, Cr(C6H6)(PF3)3, and $Co(C_5H_5)(PF_3)_2$

Halogenides: VF_5, VBr_4, NbF_5, $NbCl_5$, TaF_5, $TaCl_5$, CrF_5, CrF_4, MoF_5, WCl_5, WF_6, WBr_5, WI_4, WBr_6, ReF_7, ReF_5, ReF_6, OsF_6, OsF_4, RhF_6, RhF_5, IrF_6, IrF_5, PtF_6, $PtCl_4$, $PtBr_4$, $VOCl_3$, $VOBr_3$, $VOCl_2$, $ReOF_5$, $ReOF_4$, ReO_2F_3, ReO_3F, $ReOCl_4$, ReO_3Cl, ReO_3Br, RuF_5 and RuF_6.

Alkoxides: $OV(OCH_2CH_3)_3$, $OV(OCH(CH_3)_2)_3$, $OV(OCH_2CH_2CH_3)_3$, $Cr(OCH_3)_4$, $Cr(OCH_2CH_3)_4$, and $Cr(O(CH(CH_3)_2)_4$

Hexafluoroacetylacetonates: Cu(hfac)(DMB)

Alkyls: $Cr(CH_2Si(CH_3)_3)_4$

Aminocomplexes: Cr(N(CH3)3)4, and Cr(N(CH2CH3)2)4

Nitrosyls: $Cr(NO)_4$, and $Mn(CO)(NO)_3$

Cyclopentadienyls: $Mn(ethylcyclopentadienyl)_2$, and $Ni(ethylcyclopentadienyl)_2$

[Ph=phenyl-; C_6H_6=benzene ligand; C_5H_5=cyclopentadienyl-; hfac=1,1,1,5,5,5-hexafluoroacetylacetone; DMB=3,3-dimethyl-1-butene ligand]

[0040] Metal carbonyls may also be used, but they are generally less desirable due to their often high toxicity and often high flammability.

[0041] Combinations of activator materials such as combinations of activator monomers may be employed in the present invention.

[0042] Anaerobic compositions are based on a (meth)acrylate component, together with an anaerobic cure inducing composition, such as one including the trithiadiaza pentalene materials of WO 00/40664, the disclosure of which is herein incorporated by reference.

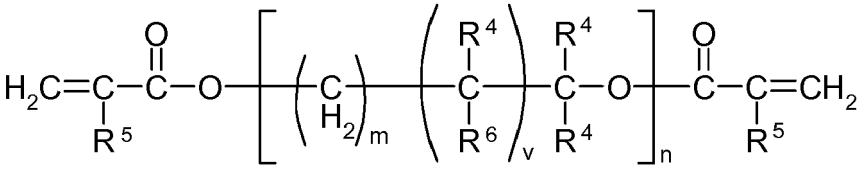
[0043] (Meth)acrylate monomers suitable for use as the (meth)acrylate component in the present invention may be chosen from a wide variety of materials, such as those represented by the general formula:

$H_2C=CGCO_2R^1$

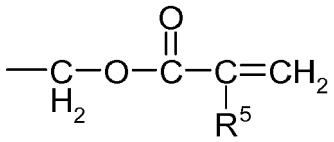
Wherein: G may be hydrogen, halogen or an alkyl group having from 1 to 4 carbon atoms; and, R^1 may be selected from alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, alkaryl, aralkyl or aryl groups having from 1 to 16 carbon atoms, any of which may be optionally substituted or interrupted as the case may be with silane, silicon, oxygen, halogen, carbonyl, hydroxyl, ester, carboxylic acid, urea, urethane, carbonate, amine, amide, sulfur, sulfonate, sulfone and the like.

[0044] Additional (meth)acrylate monomers suitable for use herein include polyethylene glycol di(meth)acrylates, tetrahydrofuran (meth)acrylates and di(meth)acrylates, hydroxypropyl(meth)acrylate ("HPMA"), hexanediol di(meth)acrylate, trimethylol propane tri(meth)acrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, di(pentamethylene glycol)dimethacrylate, tetraethylene diglycol diacrylate, diglycerol tetramethacrylate, tetramethylene dimethacrylate, ethylene dimethacrylate, neopentyl glycol diacrylate, trimethylol propane triacrylate and bisphenol-A di(meth)acrylates, such as ethoxylated bisphenol-A (meth)acrylate ("EBIPMA").

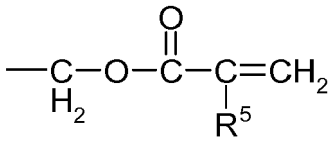
[0045] Other (meth)acrylate monomers may also be used, such as reaction products of the diglycidylether of bisphenol-A with methacrylic acid and a (meth)acrylate ester corresponding to structure as shown below:



wherein: R^4 may be selected from hydrogen, alkyl groups having from 1 to 4 carbon atoms, hydroxyalkyl groups having from 1 to about 4 carbon atoms or



R^5 may be selected from hydrogen, halogen, and alkyl groups of from 1 to 4 carbon atoms; R^6 may be selected from hydrogen, hydroxy and



m is an integer equal to at least 1, e.g., from 1 to 8 or higher, for instance, from 1 to 4; v is 0 or 1; and, n is an integer equal to at least 1, e.g., 1 to 20 or more.

[0046] Still further (meth)acrylate monomers that may be used herein include silicone (meth)acrylate moieties ("SiMA"), such as those taught by and claimed in U. S. Patent No. 5,605,999 (Chu), the disclosure of which is expressly incorporated herein by reference.

[0047] Of course, combinations of these (meth)acrylate monomers may also be used.

[0048] The (meth)acrylate component should comprise from about 10 to about 90 percent by weight of the composition, such as about 60 to about 90 percent by weight.

[0049] The curable compositions of the present invention may also contain additives such as stabilizers, plasticizers, fillers, opacifiers, thickeners, viscosity modifiers, thixotrophy conferring agents, dyes, pigments, perfumes, fluorescence markers, thermal degradation reducers, adhesion promoters, and combinations thereof, and the like. These additives are known to those of ordinary skill in the art.

[0050] The dispensing arrangement of the device of the present invention allows the end user to dispense the activator component onto a curable material or onto the substrate, prior to adhesive dispensing, in a controlled manner.

[0051] In the present invention, "solvent-free" as it pertains to the activator(s), means an activator material, or combination of activators, 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 being present in an activator composition.

[0052] To ensure that unwanted amounts of activator - in particular of solid activator particles - do not get dispensed, the dispensing arrangement can be provided with a retaining barrier, such as a mesh, that acts as a filter for the undesired material. The barrier or mesh should not interfere to any substantial extent with the issue of the gaseous activators.

[0053] Where the device of the invention is a contacting arrangement - in which the curable material or the surface to be activated 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; the dispensing arrangement for a dispenser can thus also be employed in this alternative arrangement.

[0054] 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 said vapour form.

[0055] It has been surprisingly found that using such an applicator for a gaseous form of activator can successfully activate the surface in question, particularly that of an adhesive bead. In these cases, no drying time is required; the time which would be required to allow solvent to evaporate from traditional forms of activator is substantially reduced or completely eliminated.

[0056] 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.

[0057] 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), carbon dioxide (CO_2), 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) to apply activator. Alternatively, the carrier gas can be supplied from a source such as from a pressurised container, a pump-up dispensing container, a (compression) pump or indeed any other suitable supply. A pump-up dispensing container is one in which the expulsion pressure for expelling material can be increased by a pumping action prior to expulsion of material.

[0058] One simple embodiment of the present invention is a hand-squeezable dispensing bottle having a dispensing arrangement thereon.

[0059] In an alternative embodiment, 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 the activator component or the gaseous carrier gas/activator is fed into it. The chamber may also contain a blower such as a fan which may facilitate mixing of the gas/activator mixture.

[0060] In the case of a chamber adapted to accommodate one or more substrates to which the curable material to be activated is applied, it is desirable to have a dispensing arrangement as described above which is arranged to dispense the activator into the chamber.

[0061] Generally a device of the invention will not have any amount of activator in liquid form, which is not retained by the retainer; in other words, there is no excess of liquid activator over that which is absorbed into or adsorbed onto the retainer.

[0062] In another aspect the present invention provides a kit comprising;

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

[0063] The kits of the invention may be used for fast and durable curing of curable product. By providing the kit, an end-user has both a curable material and its activator, which allows for quick and reliable use, for example, in the secure fixing of substrates bonded together.

[0064] Desirably the curable material will be any suitable curable material that will benefit from activation, such as an adhesive material, in particular an anaerobically curable adhesive material, such as a (meth)acrylate-based material. The skilled person will know which materials are suitable for use for any given application. Combinations of curable materials are also included within the present invention.

[0065] The present invention also provides a method for activating a curable material comprising the steps of:

i) applying a curable 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 said curable material.

[0066] The step of applying the curable material to the surface to be bonded, coated or sealed may be performed by

the end user either prior or subsequent to dispensing the activator though the former is likely to give best activation in most circumstances. For example the activator component may then be dispensed over the curable material by the end user.

[0067] By utilising a dispenser or the method of the present invention, the activator may be dispensed in a controlled manner which, on the one hand, allows sufficient application of activator onto the curable material whilst also preventing overdosing of said activator onto the curable material. Combinations of solvent-free activator monomers are included within the term solvent-free activator materials.

[0068] 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 the production site with explosion-proof areas. There will be no attack of (plastic) substrates since the process is solvent-free.

[0069] The device of the invention will be of relatively low weight since the formulation is simple and does not require other components such as solvents; this will also lead to lower costs. Other benefits are reduced odour, since the novel system is not based on solvents, as well as nearly zero VOC emissions.

[0070] It is also possible to co-dispense the curable material and a gas containing gaseous activator species so that, upon dispensing, the curable material is already activated by having been mixed with the gaseous activator. The present invention includes such a co-dispensing system.

[0071] For example, it may be it is possible to provide: a dispenser including a reservoir for curable product; and a reservoir for activator component, for activating the curable product, the dispenser being 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 or surface to be primed is locatable.

[0072] In such an arrangement, separate chambers may be employed to retain (separately and) respectively 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. For example, a dispensing nozzle may be employed to mix the components. The dispensing path, for example the dispensing nozzle, may include a static mixer; sufficient mixing is thus easily achieved so as to efficiently activate the curable product.

[0073] In one arrangement the dispenser is a squeezable bottle for retaining activator and comprise 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.

[0074] The present invention provides a versatile two-part system which includes a curable 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

[0075] 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 an activatable adhesive composition, such as an anaerobic adhesive composition, which is disposed between two substrates which are intended to be mated together;

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.

Detailed Description of the Invention

[0076] Referring to Figure 1, the dispenser 1 is for dispensing an activator component for activating an activatable component and comprises a container 2 - usually constituted as 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 or primer 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.

[0077] 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.

[0078] In the case of use of a liquid activator, the solid source 4a/4b of the activator component 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, liquid material 4a/4b may alternatively be a solid material which is impregnated with the activator.

[0079] 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 composition 6 located between two substrates 7 is reduced (see Figure 4). In the embodiment of Figure 4, the curable material is a curable adhesive, desirably a curable material 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.

[0080] 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.

[0081] 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.

[0082] An alternative arrangement with an external gas feed is shown in Figure 5 where a gas stream indicated by arrow 21 - and 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. The exiting gas includes a gaseous form of the activator and the outlet pipe is provided with a filter 13 to prevent the egress off particles. 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 or the substrate to be primed. 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.

[0083] 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.

[0084] The nozzle 8 has a bendable area 12 analogous to a bendable or flexible drinking straw, such that the angle of the nozzle can be adjusted. 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 or solid material activator component) from being dispensed.

[0085] Desirably, the activator component will be dispensed either onto the surface of the curable material or on top of the substrate by a stream of gas. This will usually be achieved by squeezing of the dispenser 1. The emitted gas will contain volatile activator component. 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.

[0086] In the embodiment of Figure 3, the source 4b of the activator component 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.

[0087] 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 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.

[0088] 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.

[0089] Gas, such as air from the reservoir 15, enters the headspace 5 and mixes with activator vapour while moving over or through the activator source material or retainer 4a retained in the dispenser 1. The source of the activator component can be a disintegrated solid such as pellets or large crystals, or it can be cast on top of the inner wall of the dispensing container.

[0090] Alternatively, the activator may be retained on a retainer 4a which is made of a porous material 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 material 6.

[0091] The nozzle 8 of the container 2 will desirably allow the end user to dispense the activator vapour in a controlled manner. Desirably, the means of dispensing said activator will be through a nozzle 8 or by any other means of controlled release of a vapour.

[0092] In a further aspect of the present invention a kit is provided which comprises a dispenser of the type described above and a curable material which will usually be held in a container. The present invention is particularly useful for activating curable material such as those described above and in particular liquid adhesives of low to high viscosity may be easily activated utilizing the present invention.

[0093] 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 material and/or the dispenser 1 containing the activator component 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 component by the end user.

[0094] Figure 6 shows an image of a dispenser 30 of a type which can be utilized to dispense activator through nozzle 31 by pressing on a button disposed in said nozzle 31. In one arrangement of this dispenser, the button may be pumped to prime the device and/or until a desired level of pressure is achieved in the device which is then used to dispense activator at that pressure. In an alternative arrangement, the dispenser 30 is an industrial spray bottle which already contains a pressurized gas within its headspace in addition to the gaseous activator component. Here one has to consider the fact that in such a pressurized device the evaporation of the active species is reduced; this could be compensated for by either selected an activating compound of higher volatility or by applying the activator over an extended duration.

[0095] Figures 7a and 7b provide different views of a device 1 according to the present invention which is of similar construction to that shown in Figure 1. 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. A bendable section 12 may be disposed within the device - analogous to the section of a bendable straw - to allow for adjustment of the nozzle 8 position. That nozzle 8 is provided with a dispensing head 36 with dispensing apertures 37 defined therein in a predetermined pattern; the design of the apertures 37 can influence the turbulence of the emitted gas jet. The device is simply squeezed to eject the activator-enriched gas.

[0096] It will be appreciated that sufficient amounts of the gaseous form of the activator pressure may be generated by, for example, a spray bottle that may be pumped or primed (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 desiccant may be employed.

[0097] It is desirable that, upon application to a curable material, the activator component promotes a fast cure and a good cure through volume. Whilst any suitable solvent-free activator source material may be used, of particular relevance to the present invention are those activators referenced above. Suitably the activator will have a relatively low boiling point, for instance a boiling point less than 250°C at ambient pressure, or a relatively high volatility at room temperature, so that mentionable quantities of it evaporate.

[0098] The above description applies to activator material.

Examples

Examples 1 to 29:

[0099] Table 1 includes results showing the comparative data obtained when bonding passive substrates - i.e. those inactive substrates which do not trigger anaerobic curing - with conventional anaerobic adhesive compositions as compared to those utilizing the novel activator system of the present invention. The formulations of the present invention display good anaerobic cure with faster and stronger fixture on passive threadlocking assemblies and passive lap shears assemblies. Comparative examples utilized within this experimental work include typical anaerobic based formulations which include acetyl phenylhydrazine, saccharin and cumene hydroperoxide as the primary cure components such as Loctite® 243 and Loctite® 326 (available commercially from Henkel Ireland Ltd., Dublin, IE).

Table 1

Sample No.	Activator Substance	Substrate	Adhesive	Layout of Activator Device	Curing Time (green strength)
1	None (control)	PMMA	Loctite® 638	None (control)	No cure after 1 week
2	None (control)	PVC	Chester Molecular D-36	None (control)	No cure after 1 week
3	None (control)	PC	Chester Molecular D-36	None (control)	No cure after 1 week
4	Vanadium(V) oxide triethoxide	PMMA	Loctite® 638	Squeezable PE bottle (as shown in Fig. 4) Activator absorbed into porous paper	6 min
5	Vanadium(V) oxide triisopropoxide	PMMA	Loctite® 638	As in entry 4	20 min.
6	Tungsten(V) bromide	PVC	Chester Molecular D-36	Dispensing Bottle with pump ball (see Figure 2) with $CaCl_2$ drying stage between ball and bottle	3 hours
7	Vanadium(V) oxide triethoxide	PVC	Chester Molecular D-36	As in entry 4	2.5 min.
8	Vanadium(V) oxide triethoxide	PC	Chester Molecular D-36	As in entry 4	6 min.
9	Vanadium(V) oxide triethoxide	PMMA	Loctite® 243	As in entry 4	10 minutes
10	None (control)	PMMA	Loctite® 243	None (control)	No cure after 1 week
11	Vanadium(V) oxide triethoxide	PMMA	Chester Molecular D-36	As in entry 4	6 minutes
12	None (control)	PMMA	Chester Molecular D-36	None (control)	No cure after 1 week
13	Vanadium(V) oxide tripropoxide	PMMA	Loctite® 243	As in entry 4	90 minutes
14	Vanadium(V) oxide trichloride	PMMA	Loctite® 243	As in entry 4	2 minutes
15	Molybdenum (V) chloride	PMMA	Loctite® 243	Loose crystals in wash bottle, with filter paper in pipe	3 hours
16	Vanadium(V) oxide triisopropoxide	PC	Penloc	As in entry 4	5 hours
17	None (control)	PC	Penloc	None (control)	No cure after 1 week

(continued)

Sample No.	Activator Substance	Substrate	Adhesive	Layout of Activator Device	Curing Time (green strength)
18	Vanadium(V) oxide triisopropoxide	Nylon	Penloc	As in entry 4	13 minutes
19	None (control)	Nylon	Penloc	None (control)	No cure after 1 week
20	Vanadium(V) oxide triisopropoxide	Nylon	Loctite® 638	As in entry 4	40 seconds
21	None (control)	Nylon	Loctite® 638	None (control)	No cure after 1 week
22	Vanadium(V) oxide triisopropoxide	Glass	Loctite® 638	As in entry 4	30 seconds
23	None (control)	Glass	Loctite® 638	None (control)	No cure after 1 week
24	Vanadium(V) oxide triisopropoxide	Glass	Penloc	As in entry 4	90 minutes
25	None (control)	Glass	Penloc	None (control)	No cure after 1 week
26	Vanadium(V) oxide triisopropoxide	Aluminium	Loctite® 638	As in entry 4	2 minutes
27	None (control)	Aluminium	Loctite® 638	None (control)	No cure after 1 week
28	Vanadium(V) oxide triisopropoxide	Aluminium	Chester Molecular D-36	As in entry 4	3 minutes
29	None (control)	Aluminium	Chester Molecular D-36	None (control)	No cure after 1 week

[0100] Table 1 demonstrates that the novel activator concept does result in an activation of the anaerobic adhesive, facilitating fast bonding even of inactive substrates. All controls, where no activation had been done, did not cure at all. These controls are identified in Column 5 of Table 1.

[0101] 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 material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or
b) 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.

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

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

4. The device according to any one of claims 1 to 3, wherein a retaining barrier such as a mesh or filter is provided to retain said source of the activator component in gaseous form.

5. The device according to any one of claims 1 to 4 further comprising a source of carrier gas for carrying the activator component in gaseous form.

6. The device according to any one of claims 1 to 5 further comprising a propulsion system for applying a force to allow application of activator, preferably said propulsion system being a squeezable container, a pump, a plunger arrangement, a pressurised propellant or a connection to a pressurised air- or gas-line.

7. The device according to any one of claims 1 to 6, wherein said source of the activator component is provided in solid, particulate form.

8. The device according to any one of claims 1 to 6, wherein said source of the activator component is provided in solid form which is cast, at least partially, to the shape of the chamber.

9. The device according to any one of claims 1 to 6, wherein said source of the activator component is provided in liquid form and the device further comprises a retainer for the liquid.

10. The device according to claim 9, wherein the retainer is adapted to retain the liquid by adsorption and/or absorption.

11. The device according to any one of claims 1 to 6 for activating an anaerobically curable material, wherein the activator component is selected from transition metal compounds which are volatile at 25°C and of which compounds the transition metal can exist in at least two oxidation states of similar stability.

12. The device according to claim 11 for activating an anaerobically curable material, wherein the transition metal is selected from subgroups 4, 5, 6, 7, 8 and 11 of the Periodic Table and combinations thereof.

13. The device according to claim 11 or claim 12 for activating an anaerobically curable material, wherein the activator component is selected from the compounds of the group comprising trifluorophosphanes, halogenides, alkoxides, hexafluoroacetylacetonates, alkyls, amides, nitrosyls, cyclopentadienyls and combinations thereof.

14. The device according to any one of claims 1 to 6 for activating an anaerobically curable material, wherein the activator component is selected from compounds of the group comprising: $Fe(PF_3)_5$; $Ni(PF_3)_4$; $Ru(PF_3)_5$;$Pt(PF_3)_4$;$Rh_2(PF_3)_8$; $HMn(PF_3)_5$; $HRe(PF_3)_5$; $H_2Fe(PF_3)_4$; $H_2Ru(PF_3)_4$; $H_2Os(PF_3)_4$; $HCo(PF_3)_4$; $HRh(PF_3)_4$; $HIr(PF_3)_4$; $Mo(PF_3)_6$; $Cr(PF_3)_6$;$W(PF_3)_6$; $HCo(PF_3)_3(CO)$; $HFe(PF_3)_3(NO)$; $HMn(PPh_3)_2(NO)_2$; $Co(PF_3)_3(NO)$; $Rh(PF_3)_3(NO)$; $Fe(PF_3)_2(NO)_2$; $Cr(C6H6)(PF3)3$; $Co(C_5H_5)(PF_3)_2$; VF_5 ; VBr_4 ; NbF_5 ; $NbCl_5$; TaF_5 ; $TaCl_5$; CrF_5 ; CrF_4 ; MoF_5 ; WCl_5 ; WF_6 ; WBr_5 ; WI_4 ; WBr_6 ; ReF_7 ; ReF_5 ; ReF_6 ; OsF_6 ; OsF_4 ; RhF_6 ; RhF_5 ; IrF_6 ; IrF_5 ; PtF_6 ; $PtCl_4$; $PtBr_4$; $VOCl_3$; $VOBr_3$; $VOCl_2$; $ReOF_5$; $ReOF_4$; ReO_2F_3 ; ReO_3F ; $ReOCl_4$; ReO_3Cl ; ReO_3Br ; RuF_5 ; RuF_6; $OV(OCH_2CH_3)_3$; $OV(OCH(CH_3)_2)_3$; $OV(OCH_2CH_2CH_3)_3$; Cr(OCH3)4 ; Cr(OCH2CH3)4 ; $Cr(O(CH(CH_3)_2)_4$ Cu(hfac)(DMB) ; $Cr(CH_2Si(CH_3)_3)_4$; $Cr(N(CH_3)_3)_4$; $Cr(N(CH_2CH_3)_2)_4$; $Cr(NO)_4$; $Mn(CO)(NO)_3$; Mn(ethylcyclopentadienyl)$_2$; Ni(ethylcyclopentadienyl)$_2$ and combinations thereof, wherein in said selection Ph=phenyl-; C_6H_6=benzene ligand; C_5H_5=cyclopentadienyl-; hfac=1,1,1,5,5,5-hexafluoroacetylacetone; and, DMB=3,3-dimethyl-1-butene ligand.

15. A dispenser for dispensing an activator component for activating an activatable material, comprising:

i) a container comprising an enclosed chamber;
ii) a retainer in the enclosed chamber, the retainer being adapted to retain the activator component by adsorption and/or absorption;
iii) a dispensing arrangement for dispensing gaseous activator component from the enclosed chamber, said arrangement comprising a conduit connecting the chamber and a dispensing outlet; and
iv) an activator component adsorbed onto or absorbed into the retainer.

16. The dispenser according to claim 15, wherein the dispensing arrangement includes a diffuser for diffusing the gaseous activator component.

17. A method for activating a curable material comprising the steps of:

i) applying a curable 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 material.

18. A method for activating a curable material comprising the steps of:

i) applying a curable material to a substrate on which it is to be cured;
ii) introducing the substrate and the curable 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.

19. Use of activators selected from the group consisting of volatile complexes or salts of transition metals and combinations thereof, preferably volatile complexes or salts of transition metals within subgroups IV B, V B, VI B, VIIB, VIII B and I B (according to IUPAC nomenclature) or subgroups 4-11 (according to CAS nomenclature) of the Periodic Table and combinations thereof, for the activation of anaerobically curable products.

20. An activator composition for activating an anaerobically curable product comprising an activator component selected from the group consisting of volatile complexes or salts of transition metals and combinations thereof, preferably volatile complexes or salts of transition metals within subgroups IV B, V B, VI B, VIIB, VIII B and I B (according to IUPAC nomenclature) or subgroups 4-11 (according to CAS nomenclature) of the Periodic Table and combinations thereof.

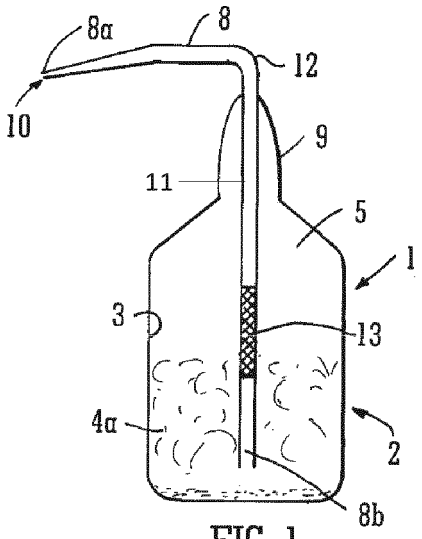


FIG. 1

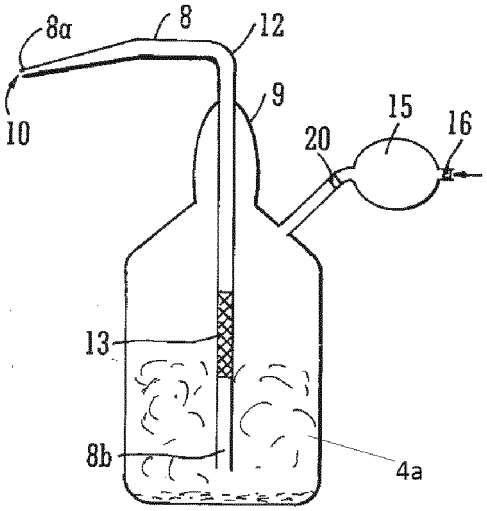


FIG. 2

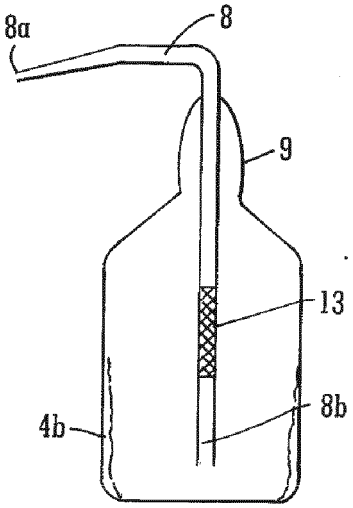


FIG. 3

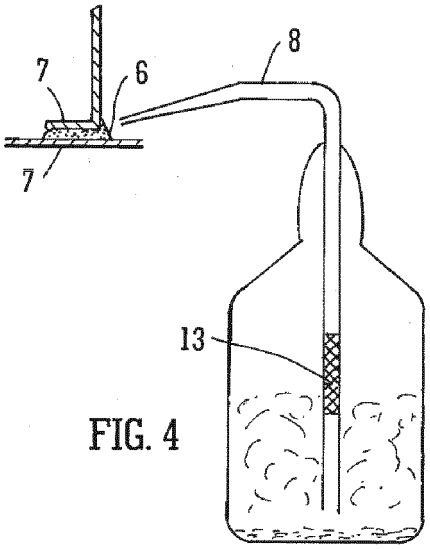


FIG. 4

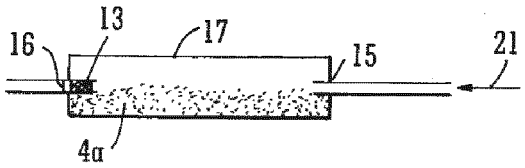


FIG. 5

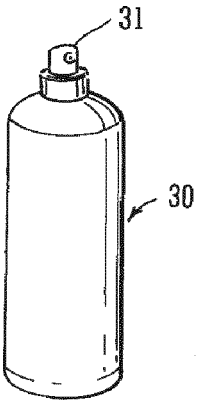


FIG. 6

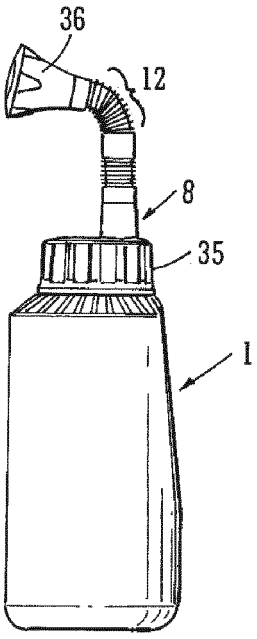


FIG. 7A

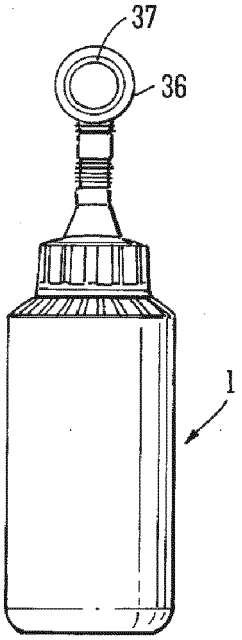


FIG. 7B

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EUROPEAN SEARCH REPORT

Application Number
EP 15 18 5669

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 2007/196579 A1 (NECKERS DOUGLAS C [US] ET AL) 23 August 2007 (2007-08-23) * paragraphs [0044], [0046], [0047], [0050], [0059] - [0061], [0063], [0072]; figure 1; tables 1,2,3, 5,9 *	1,3,5,17	INV. B05D3/04
X	WO 2010/149733 A1 (BASF SE [DE]; CRANFILL DAVID [US]; GUTOWSKI KEITH E [US]; CAMPBELL DON) 29 December 2010 (2010-12-29) * claims 1,2; figures *	1,2,18	

TECHNICAL FIELDS SEARCHED (IPC)

B05D
A61M

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

Place of search	Date of completion of the search	Examiner
The Hague	11 April 2016	Slembrouck, Igor

CATEGORY OF CITED DOCUMENTS

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Application Number
EP 15 18 5669

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, 5, 17, 18(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 5669

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, 5, 17, 18(completely); 1(partially)

a device for activating a curable material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or
b) 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

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

a device for activating a curable material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or
b) 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,
wherein said source of activator component is solvent-free;

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

a device for activating a curable material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or
b) 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,
wherein said source of activator component in gaseous form is either a volatile solid or a liquid;

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 15 18 5669

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:

1.3. claims: 5(completely); 1(partially)

a device for activating a curable material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or
b) 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,
further comprising a source of carrier gas for carrying the activator component in gaseous form;

1.4. claim: 17

a method for activating a curable material comprising the steps of:
i) applying a curable 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 material;

1.5. claim: 18

a method for activating a curable material comprising the steps of:
i) applying a curable material to a substrate on which it is to be cured;
ii) introducing the substrate and the curable 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(completely); 1(partially)

a device for activating a curable material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or

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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:

b) 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,
wherein a retaining barrier such as a mesh or filter is provided to retain said source of the activator component in gaseous form;

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

a device for activating a curable material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or
b) 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,
further comprising a propulsion system for applying a force to allow application of activator, preferably said propulsion system being a squeezable container, a pump, a plunger arrangement, a pressurised propellant or a connection to a pressurised air- or gas-line;

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4. claims: 7, 8(completely); 1(partially)

a device for activating a curable material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or
b) 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,
wherein said source of the activator component is provided in solid form;

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5. claims: 9, 10(completely); 1(partially)

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 15 18 5669

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 device for activating a curable material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or
b) 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,
wherein said source of the activator component is provided in liquid form and the device further comprises a retainer for the liquid;

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6. claims: 11-13(completely); 1(partially)

a device for activating a curable material 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 material comprising a conduit connecting the chamber and a dispensing outlet; or
b) 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,
for activating an anaerobically curable material, wherein the activator component is selected from transition metal compounds which are volatile at 25°C and of which compounds the transition metal can exist in at least two oxidation states of similar stability;

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7. claims: 14(completely); 1(partially)

a device for activating a curable material 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 material comprising a conduit connecting the chamber and a

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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:

dispensing outlet; or
b) 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,
for activating an anaerobically curable material, wherein the activator component is selected from compounds of the group comprising: Fe(PF 3)5 ; Ni(PFs)4 ; Ru(PFs)5 ;Pt(PF3)4 ;Rh2 (PF3)8 ; HMn(PF3)5 ; HRe(PFs)5 ; H2 Fe(PF3)4 ; H2 Ru(PF3)4 ; H2 0S (PF3)4 ; HCo(PF3)4 ; HRh(PFs)4 ; Hlr(PF3)4 ; Mo(PF3)6 ; Cr(PF3)6 ;W(PF3)6; HCo(PF3)3(CO) ; HFe(PF3)3 (NO); HMn(PPh3)2 (NO)2 ; Co(PF3)3(NO); Rh(PF3)3(NO); Fe(PF3)2(NO)2; Cr(C6 H6)(PF3)3 ; Co(C5 H5)(PF3)2 ; VF5; VBr4 ; NbF5; NbCl5 ; TaF5; TaCl5 ; CrF5; CrF4; MoF5; WC15 ; WF6 ; WBr5; WI4 ; WBrs ; ReF7 ; ReF5; ReFs; OsF6 ; OsF4 ; RhF6 ; RhF5; IrFs ; IrF5 ; PtF6 ; PtCl4 ; PtBr4; VOCl3 ; VOBr3 ; VOCl2 ; ReOF5 ; ReOF4; Re02F3; Re03F ; ReOCl4 ; Re03CI ; Re03Br; RuF5; RuFs; OV(OCH2 CH3)3 ; OV(OCH(CH3)2)3 ; OV(OCH2 CH2 CH3)3 ; Cr(OCH3)4 ; Cr(OCH2 CH3)4 ; Cr(O(CH(CH3)2)4 ; Cu(hfac)(DMB) ; Cr(CH2 Si(CH3)3)4 ; Cr(N(CH3)3)4 ; Cr(N(CH2 CH3)2)4 ; Cr(NO)4 ; Mn(CO)(NO)3 ; Mn(ethylcyclopentadienyl)2 ; Ni(ethylcyclopentadienyl)2 and combinations thereof, wherein in said selection Ph=phenyl-; C6 H6 =benzene ligand; C5 H5 =cyclopentadienyl-;
hfac=1,1,1,5,5,5-hexafluoroacetylacetone; and,
DMB=3,3-dimethyl-1-butene ligand;

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8. claims: 15, 16

a dispenser for dispensing an activator component for activating an activatable material, comprising:
i) a container comprising an enclosed chamber;
ii) a retainer in the enclosed chamber, the retainer being adapted to retain the activator component by adsorption and/or absorption;
iii) a dispensing arrangement for dispensing gaseous activator component from the enclosed chamber, said arrangement comprising a conduit connecting the chamber and a dispensing outlet; and
iv) an activator component adsorbed onto or absorbed into the retainer;

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9. claim: 19

use of activators selected from the group consisting of volatile complexes or salts of transition metals and combinations thereof, preferably volatile complexes or salts of transition metals within subgroups IV B, V B, VI B, VIIB,

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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:

VIII B and I B (according to IUPAC nomenclature) or subgroups 4-11 (according to CAS nomenclature) of the Periodic Table and combinations thereof, for the activation of anaerobically curable products;

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10. claim: 20

an activator composition comprising an activator component selected from the group consisting of volatile complexes or salts of transition metals and combinations thereof, preferably volatile complexes or salts of transition metals within subgroups IV B, V B, VI B, VIIB, VIII B and I B (according to IUPAC nomenclature) or subgroups 4-11 (according to CAS nomenclature) of the Periodic Table and combinations thereof;

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 5669

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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11-04-2016

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REFERENCES CITED IN THE DESCRIPTION

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