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(71) Applicant: **BAE SYSTEMS plc**
London SW1Y 5AD (GB)

(72) Inventor: **The designation of the inventor has not yet been filed**

(74) Representative: **BAE SYSTEMS plc**
Group IP Department
Farnborough Aerospace Centre
Farnborough
Hampshire GU14 6YU (GB)

(54) RESONANT ACOUSTIC MIXING (RAM) OF AN EXPLOSIVE COMPOSITION

(57) The invention relates to a cast explosive composition, particularly to a pre-cure castable explosive composition comprising an explosive material, a polymerisable binder, a microencapsulated cross linking reagent, said microencapsulated cross linking reagent, comprising a cross linking agent encapsulated in a microcapsule. Providing a process for formulating a homogenous crosslinked polymer bonded explosive composition comprising the steps of:

i) forming an admixture of pre-cure castable explosive composition, said composition comprising an explosive material, a polymerisable binder, a microencapsulated cross linking reagent, said microencapsulated cross linking reagent, comprising a cross linking reagent encapsulated in a microcapsule;

wherein the microcapsule, comprises at least one shell wall polymer, wherein the microcapsule's shell wall polymer comprises at least one resonant acoustic stimulus labile linkage,

ii) applying resonant acoustic stimulus to the admixture, causing the microcapsule to rupture and release said cross linking reagent, to cause the cure process to start.

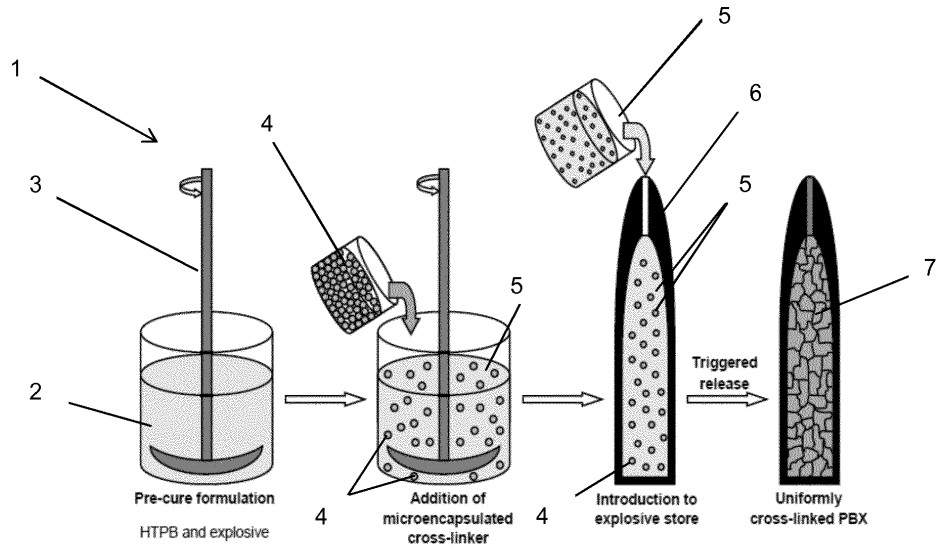

Fig 1

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Description

[0001] This invention relates to cast explosive compositions, their preparation and use. In particular, the invention relates to the use of resonant acoustic stimulus to formulate polymer-bonded explosive compositions.

[0002] Explosives compositions are generally shaped, the shape required depending upon the purpose intended. Shaping can be by casting, pressing, extruding or moulding; casting and pressing being the most common shaping techniques. However, it is generally desirable to cast explosives compositions as casting offers a greater design flexibility than pressing.

[0003] Polymer-bonded explosives (also known as plastic-bonded explosives and PBX) are typically explosive powders bound into a polymer matrix. The presence of the matrix modifies the physical and chemical properties of the explosive and often facilitates the casting and curing of high melting point explosives. Such explosives could otherwise only be cast using melt-casting techniques. Melt casting techniques can require high processing temperatures as they generally include a meltable binder. The higher the melting point of this binder, the greater the potential hazard. In addition, the matrix can be used to prepare polymer-bonded explosives which are less sensitive to friction, impact and heat; for instance, an elastomeric matrix could provide these properties.

[0004] The matrix also facilitates the fabrication of explosive charges which are less vulnerable in terms of their response to impact, shock, thermal and other hazardous stimuli. Alternatively, a rigid polymer matrix could allow the resulting polymer-bonded explosive to be shaped by machining, for instance using a lathe, allowing the production of explosive materials with complex configurations where necessary.

[0005] Conventional casting techniques require the polymerisation step to have commenced during the fill stage which often results in a solidified composition which retains air bubbles introduced during mixing of the material, non-homogenous cross linking, and in certain cases solidification of the "pot" of explosive before all munitions or moulds have been filled... These voids, non-homogenous cross linking can reduce the performance of the composition as less explosive is present per unit volume. In addition, these defects may affect the shock sensitivity of the composition, making the composition less stable to impact or ignition from a shock wave.

[0006] The invention seeks to provide a cast explosive composition in which the stability of the composition is improved. Such a composition would not only offer improved stability, but also a reduced sensitivity to factors such as friction, impact and heat. Thus, the risk of inadvertent initiation of the explosive is diminished.

[0007] According to a first aspect of the invention there is provided a process for formulating a homogenous crosslinked polymer bonded explosive composition comprising the steps of:

i) forming an admixture of pre-cure castable explosive composition, said composition comprising an explosive material, a polymerisable binder, a microencapsulated cross linking reagent, said microencapsulated cross linking reagent, comprising a cross linking reagent encapsulated in a microcapsule wherein the microcapsule, comprises at least one shell wall polymer, wherein the microcapsule's shell wall polymer comprises at least one resonant acoustic stimulus labile linkage;

ii) applying a resonant acoustic stimulus to the admixture, causing the microcapsule to rupture and release said cross linking reagent, to cause the cure process to start; optionally

iii) filling a munition with the admixture; allowing the cure process to go to completion in the munition.

[0008] Current processes used in the production of composite rubber materials involve mixing a hydroxy-terminated aliphatic polymer with a cross linking reagent. Upon addition, an immediate polymerisation reaction occurs, leading to the formation of an inhomogeneous crosslinked rubber matrix. Formation of an inhomogeneous matrix leads to material being rejected or the mixture fully polymerising before all munitions or moulds have been filled. This leads to the rejected material requiring disposal, a process that has both cost and hazard associated.

[0009] Confining the cross linking reagent within microcapsules allows uniform distribution of the microcapsule encapsulated cross linking reagent within the pre-cure composition, thereby allowing control of when the curing reaction may be initiated. Upon application of a resonant acoustic stimulus, the microcapsule contents may be released allowing the formation of a uniform polymeric matrix, when desired.

[0010] The enhanced control of the cross linking reactions allows the recovery of the pre-cure compoistion in the event of process equipment failure, which in a conventional cure technique would result in many tonnes of material solidifying in the reaction vessel.. Further, the delay of the start of cure reaction allows product quality to be confirmed, before the reaction commences, therby a poor quality composition, is not filled into mould, pots or munitions. The confinement of the cross linking reagent within a microcapsule may reduce the exposure to operators of hazardous cross linking reagents.

[0011] WO2017/006110 describes the use of microcapsules to encapsulate cross linking reagents, wherein the microcapsules are thermally labile, such that the mixture when heated may cause rupture of the microcapsule and con-

comitant release of the cross linking reagent.

[0012] The use of resonant acoustic stimulus technique allows the pre cure composistion to be mixed to form a homogenous mixture. The action of the resonant acoustic stimulus causes the rupture of the microcapsules to allow the release of the encapsulated cross linking reagent. The continued application of resonant acoustic stimulus to the precure composition with released cross linking reagent, allows for facile continued mixing of the composition to ensure a homogeneous mixture and a homogenous cured mixture.

[0013] The precure composition may be mixed in a large batch process of >100Kg to provide a homogenous mixture and the resonant acoustic stimulus applied directly to the mixing container. The resonant acoustic stimulus will cause the micropsheres to rupture allowing the crosslinking reagent to come into contact with the polymerisable binder, such that cure process starts within the large batch mixer. The curing composition may then be transferred to the munitions or pots for filling.

[0014] According to a further aspect of the invention there is provided a process for filling a munition with a homogenous crosslinked polymer bonded explosive composition comprising the steps of:

i) forming an admixture of pre-cure castable explosive composition, said composition comprising an explosive material, a polymerisable binder, a microencapsulated cross linking reagent, said microencapsulated cross linking reagent, comprising a cross linking reagent encapsulated in a microcapsule wherein the microcapsule, comprises at least one shell wall polymer, wherein the microcapsule's shell wall polymer comprises at least one resonant acoustic stimulus labile linkage;

ii) filling a munition,

iii) applying resonant acoustic stimulus to the munition, causing the microcapsule to rupture and release said cross linking reagent, to cause the cure process in the munition.

[0015] The precure composition may be first formed to an admixture using conventional mixing techniques in a large batch mixer, and transfered to a munition or pot for incorporation into a muniton. Using conventional mixing techniques, it may be extremely difficult to provide continuous mixing to the pre cure compostion once it is inside a munition or pot. This would require a plurlity of mixing blades to stir the precure composition, in the muntion or pot. The fill level on munitions may be tightly controlled, so the use of mixing blades or probes that are inserted into the precure composition in a munition may cause removal of material, spillages or even accidental insertion of foreign objects, debris. The use of resonant acousitc stimuls allows for mixing and rupture of the microcapsules to occur whilst the pre cure composition is in the munition or pot. The munitions or pots may be individually brought into contact with a resonant acousitc stimulus, or more preferably a plurality of munitions or pots may be arrnaged in a rack and the rack subjected to the resonant acoustic stimulus.

[0016] The resonant acoustic stimulus cure process may be carried out under vacuum, so as to remove volatiles and degas ie remove air, to prevent the formation of voids in the final cured formualtion.

[0017] The resonant acoustic stimulus process may be affected at different frequencies, at a first frequency the resonant acoustic stimulus may provide only homogeneous mixing of the formulation, but is insufficent to cause rupture of the microcapsules. At an second frquency the resonant acoustic stimulus process provides both homogenous mixing of the precure composition and concomitant rupture of the resonant acoustic stimulus labile microcapsules.

[0018] In a highly preferred arrangement the resonant acoustic stimulus labile microcapsules may be caused to at a frequency in the range of from 20 HZ to 100Hz, more preferably in the range of from 50Hz to 70Hz, yet more preferably 58Hz to 60hz.

[0019] Typically the resonant acoustic stimulus may apply an acceleration force of up to 100g.

[0020] The mixing time for typical shear force mixers may be in the order of several hours to ensure homogenous mixing, in resonant acoustic mixing the stimulus may cause the time to be reduced to less than hour, more preferably less than 20 mins or even less than 5 minutes. The period of time may depend on the size of the munition or pot that needs to be subjected to the resonant acoustic stimulus. The resonant acoustic stimulus will be applied until the rupture of the microcapsules has occurred.

[0021] The process of using a resonant acoustic stimulus will generate some heat within the precure composition that comprising the microcapsules, however the temperature will be significantly lower than the temperature required to thermally rupture the microcapsules. The rupture of the resonant acoustic stimulus labile microcapsules is due to primarily the vibrational ie mechanical forces, rather than a pure thermal stimulus. This allows for the precure composition to be processed at temperatures below that in WO2017/006110.

[0022] The curing step, after the release cross linking reagent, is exothermic and will generate further heat. It may be desirable to provide cooling jackets to a batch mixer or munitions or pots, to ensure the temperature does not increase towards the ignition temperature of the energetic material.

[0023] The rupture of the microcapsules using a resonant acoustic stimulus occurs below the ignition temperature of the explosive and may not require external heating to be applied to the precure composition to cause the thermal rupture of the microcapsules.

[0024] Polymer-bonded explosives include a polymeric polymerisable binder which forms a matrix bonding explosive particles within. The polymerisable binder thus may be selected from a wide range of polymers, depending upon the application in which the explosive will be used. However, in general at least a portion of the polymerisable binder will be selected such that when cross linked, with a cross linking reagent, to form polyurethanes, cellulosic materials such as cellulose acetate, polyesters, polybutadienes, polyethylenes, polyisobutylenes, PVA, chlorinated rubber, epoxy resins, two-pack polyurethane systems, alkyd/melanine, vinyl resins, alkyds, , thermoplastic elastomers such as butadiene-styrene block copolymers, and blends, copolymers and/or combinations thereof.

[0025] Energetic polymers may also be used either alone or in combination, these include polyNIMMO (poly(3-nitratomethyl-3-methyloxetane), polyGLYN (poly glycidyl nitrate) and GAP (glycidyl azide polymer). It is preferred that the polymerisable binder component be entirely selected from the list of polymerisable binders above either alone or in combination.

[0026] In some embodiments the polymerisable binder will comprise at least partly polyurethane, often the polymerisable binder will comprise 50 - 100 wt% polyurethane, in some instances, 80 - 100 wt%. In some embodiments the polymerisable binder will consist of polyurethane.

[0027] The cross linking reagents may be selected from a variety of commonly known, cross linking reagents, the selection of which depends on the functionality of the polymerisable binders.

[0028] Polyurethanes are a highly preferred polymerisable binder for PBX formation. The polyurethanes may typically be prepared by reacting polyols and polyisocyanates. In a preferred arrangement a monomer or polymer diol may be crosslinked with a cross linking reagent such as diisocyanate. The diisocyanate may be such as, for example, MDI (methylene diphenyl diisocyanate) and TDI (toluene diisocyanate) and IPDI (isophorone diisocyanate). IPDI is generally preferred as it is a liquid and hence easy to dispense; it is relatively slow to react, providing a long pot-life and slower temperature changes during reaction; and it has a relatively low toxicity compared to most other isocyanates. It is also preferred that, where the polymerisable binder comprises polyurethane, the polyurethane polymerisable binder includes a hydroxyterminated polybutadiene. The polyisocyanate may be dissolved in a minimal aliquot of solvent.

[0029] The explosive component of the polymer-bonded explosive may, in certain embodiments, comprise one or more heteroalicyclic nitramine compounds. Nitramine compounds are those containing at least one N-NO_2 group. Heteroalicyclic nitramines bear a ring containing N-NO_2 groups. Such ring or rings may contain for example from two to ten carbon atoms and from two to ten ring nitrogen atoms. Examples of preferred heteroalicyclic nitramines are RDX (cyclo-1,2,3-trimethylene-2,4,6-trinitramine, Hexogen), HMX (cyclo-1,3,5,7-tetramethylene-2,4,6,8-tetranitramine, Octogen), and mixtures thereof. The explosive component may additionally or alternatively be selected from TATND (tetranitrotetraminodecalin), HNS (hexanitrostilbene), TATB (triaminotrinitrobenzene), NTO (3-nitro-1,2,4-triazol-5-one), HNIW (2,4,6,8,10,12-hexanitrohexaazaisowurtzitane), GUDN (guanyldylurea dinitride), FOX-7 (1,1-diamino-2, 2-dinitroethene), and combinations thereof.

[0030] Other highly energetic materials may be used in place of or in addition to the compounds specified above. Examples of other suitable known highly energetic materials include picrite (nitroguanidine), aromatic nitramines such as tetryl, ethylene dinitramine, and nitrate esters such as nitroglycerine (glycerol trinitrate), butane triol trinitrate or pentaerythritol tetranitrate, DNAN (dinitroanisole), trinitrotoluene (TNT), inorganic oxidisers such as ammonium salts, for instance, ammonium nitrate, ammonium dinitramide (ADN) or ammonium perchlorate, and energetic alkali metal and alkaline earth metal salts.

[0031] The microcapsule may comprise at least one cross linking reagent or at least two independently selected cross linking reagents. The microcapsule may comprise a solvent, or other processing aids. In a preferred arrangement the microcapsule contains only a cross linking reagent, and a substantial absence of solvent.

[0032] The microcapsule may have a wall thickness in the range of from 0.5microns to 5 microns, more preferably 0.9 microns to 4.5 microns, preferably in the range of from 2 microns to 4 microns.

[0033] The microcapsule may have a diameter in the range of from 1 micron to 1000microns, preferably in the range of from 20-500 microns.

[0034] The microcapsule may comprise at least one shell wall polymer, selected from polyurethane, cellulosic materials such as cellulose acetate, polyesters, polybutadienes, polyethylenes, polyisobutylenes, PVA, chlorinated rubber, epoxy resins, two-pack polyurethane systems, alkyd/melanine, vinyl resins, alkyds, , butadiene-styrene block copolymers, polyNIMMO, polyGLYN, GAP, and blends, copolymers and/or combinations thereof.

[0035] The microcapsule wall polymer may preferably comprise nitro groups, to provide increased exothermic energy to the explosive composition.

[0036] In a preferred arrangement the microcapsule wall polymer and polymerisable binder (that is used to from the polymer bonded explosive) may be selected from substantially the same polymer class, such that both may be a polyurethane, or a polyester etc. This reduced the likelihood of incompatibility with the explosive material.

[0037] The polymer backbone (repeat unit) for the polymerisable binder and the wall polymer of the microcapsule may be independently selected.

[0038] The microcapsule shell wall polymer that forms the microcapsule may comprise at least one labile linkage. The labile linkage may allow a more facile rupture of the microcapsule, when subjected to resonant acoustic stimulus

[0039] In a further arrangement there may be provided a further stimulus, such as, for example a further chemical stimulus and/or further physical stimulus, is applied. The ruptured microcapsule will then allow the encapsulated contents to be released, when exposed to a specific stimulus.

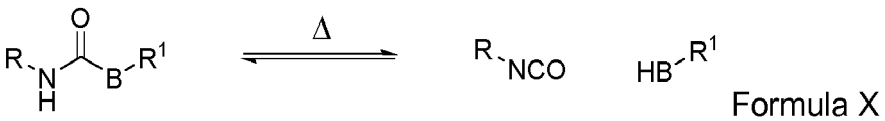
[0040] The further stimulus may be one or more of, such as, for example, pressure, heat, ultrasound, UV radiation, catalyst, or a shear force.

[0041] In a preferred arrangement the labile linkage is a resonant acoustic stimulus labile linkage, one that ruptures when subjected to elevated temperatures. The linkage may be selected from, acetals, blocked isocyanates, diels alder linkages.

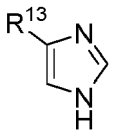
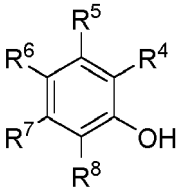
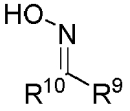
[0042] For PBX formulations it has been found that the selection of blocked isocyanates as the labile linkage group in the microcapsule shell wall polymer provide robust microcapsules, which can withstand the mixing, processing and handling during production of an explosive composition. Furthermore blocked isocyanates may be selected to provide de-blocking and hence rupture temperatures in a range that occurs below the temperature of initiation of high explosive materials and a de-blocking temperature that is above the temperatures that are generated during the mixing of the pre-cure reagents.

[0043] Thereby, there is a specific stimulus of heat which must be applied to the pre-cure to cause the rupture of the microcapsule walls, and thereby allow the release of the encapsulated cross linking reagent, such that the formation of the PBX may be realised.

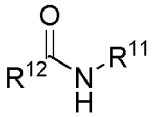
[0044] The blocked isocyanate labile linkages may be selected from aromatic heterocycles, secondary amines, substituted phenols, oximes and amides.



Formula X

Blocking Group	Deblocking Temperature Range (°C)
 **i) Aromatic heterocycles**	110 - 160
 **ii) Amines**	40-130
 **iii) Phenols**	75-180
 **iv) Oximes**	100-140

(continued)

Blocking Group	Deblocking Temperature Range (°C)
 **v) Amides**	100-157

[0045] B is a Blocking group, preferably selected from aromatic heterocycles, sterically hindered secondary amines, substituted phenols, oximes and amides. Preferably the Blocking group B comprises at least one nitro group, more preferably at least two nitro groups, to provide increased exothermic energy to the explosive composition.

[0046] In a preferred arrangement, R and R^1 are terminal end groups of a shell wall (monomer or polymer) precursor that forms the backbone ie the shell wall polymer of the microcapsule wall. R^2- R^6 may be selected from halo, nitro, lower chain C_{1-6} alkyl, and aryl. In a preferred arrangement the substituted phenol comprises at least two nitro groups. R^2, R^3 and R^9 to R^{13} may be selected from, nitro, lower chain C_{1-6} alkyl, C_{1-6} alkenyl, branched chain C_{1-8} alkyl, alkenyl, preferably isopropyl or tert-butyl.

[0047] B may be

I. NHR^2R^3, wherein R^2 and R^3 are alkyl, alkenyl, branched chain alkyl; aryl, phenyl or together form a heterocycle
II. $R^{11}NC(O)R^{12}$, wherein R^{11} and R^{12} are alkyl, alkenyl, branched chain alkyl; aryl, phenyl or together form a lactam.
III. OR^{15}, $O\text{-}N{=}CR^9R^{10}$

wherein R^{15} is aryl, phenyl, benzyl, preferably, at least two nitro group on the ring;
wherein R^9 and R^{10} are independently selected from alkyl, alkenyl, branched chain alkyl, aryl, phenyl, preferably provided that at least one of R^9 or R^{10} is a branched chain alkyl or aryl, or phenyl.

[0048] During the formation of the microcapsule wall polymer the R^1- BH and R-NCO may react to form a blocked isocyanate group, such that reaction forms a resonant acoustic stimulus labile linkage, and thereby forms part of the wall polymer of the microcapsule. Whereupon the complete formation of a microcapsule wall, it may be capable of encapsulating a cross linking reagent.

[0049] The microcapsule may comprise wall polymers that have both substantially no labile linkages and wall polymers that have at least one resonant acoustic stimulus labile linkage.

[0050] The delaying the onset of cross linking of the polymerisable binder ensures that extensive mixing is achieved prior to cross linking reaction, which is required to ensure homogeneous mixture. In conventional methods the cross linking reagent is free and so at the point of mixing the cross linking reaction with the polymer is already in progress. In the process defined herein the extensive mixing may be performed before the microcapsule is ruptured and the concomitant reaction of the cross linking reagent and polymerisable binder occurs.

[0051] Yet further reagents or yet further stimuli may be added to the composition, after the cross linking reagent has been released from the microcapsule, to cause the curing reaction to commence. In a highly preferred arrangement, the curing reaction will commence directly as a result of causing the microcapsule to release said cross linking reagent. The yet further stimulus may be one or more of heat, ultrasound, UV radiation, catalyst and shear force, similar to the further stimulus.

[0052] The explosive component of the polymer-bonded explosive may be in an admixture with a metal powder which may function as a fuel or which may be included to achieve a specific terminal effect. The metal powder may be selected from a wide range of metals including aluminium, magnesium, tungsten, alloys of these metals and combinations thereof. Often the fuel will be aluminium or an alloy thereof; often the fuel will be aluminium powder.

[0053] In some embodiments, the polymer-bonded explosive comprises RDX. The polymer-bonded explosive may comprise RDX as the only explosive component, or in combination with a secondary explosive component, such as HMX. Preferably, RDX comprises 50 - 100 wt% of the explosive component.

[0054] In many cases the polymerisable binder will be present in the range about 5 - 20 wt% of the polymer-bonded explosive, often about 5 - 15 wt%, or about 8 - 12 wt%. The polymer-bonded explosive may comprise about 88 wt% RDX and about 12 wt% polyurethane binder. However, the relative levels of RDX to polyurethane binder may be in the range about 75 - 95 wt% RDX and 5 - 25 wt% polyurethane binder. Polymer-bonded explosives of this composition are commercially available, for example, Rowanex 1100™.

[0055] Many defoaming agents are known and in general any defoaming agent or combination thereof which does not chemically react with the explosive may be used. However, often the defoaming agent will be a polysiloxane. In many embodiments, the polysiloxane is selected from polyalkyl siloxanes, polyalkylaryl siloxanes, polyether siloxane

co-polymers, and combinations thereof. It is often preferred that the polysiloxane be a polyalkylsiloxane; polydimethylsiloxane may typically be used. Alternatively, the defoaming agent may be a combination of silicone-free surface active polymers, or a combination of these with a polysiloxane. Such silicone-free polymers include alkoxylated alcohols, triisobutyl phosphate, and fumed silica. Commercially available products which may be used include, BYK 088, BYK A500, BYK 066N and BYK A535 each available from BYK Additives and Instruments, a subdivision of Altana; TEGO MR2132 available from Evonik; and BASF SD23 and SD40, both available from BASF. Of these, BYK A535 and TEGO MR2132 are often used as they are solventless products with good void reduction properties.

[0056] Often the defoaming agent is present in the range about 0.01 - 2 wt%, in some instances about 0.03 - 1.5 wt%, often about 0.05 - 1 wt%, in many cases about 0.25 or 0.5 - 1 wt%. At levels below this (i.e. below 0.01 wt%) there is often insufficient defoaming agent in the composition to significantly alter the properties of the polymer-bonded explosive, whereas above this level (i.e. above 2 wt%) the viscosity of the cast solution may be so low that the composition becomes inhomogeneous as a result of sedimentation and segregation processes occurring within the mixture.

[0057] The explosive composition may include a solvent, any solvent in which at least one of the components is soluble and which does not adversely affect the safety of the final product may be used, as would be understood by the person skilled in the art. However, it is preferred, for the reasons described above, that in some embodiments that solvent be absent.

[0058] Where present, the solvent may be added as a carrier for the components of the composition. The solvent will typically be removed from the explosive composition during the casting process, however some solvent residue may remain due to imperfections in the processing techniques or where it becomes uneconomical to remove the remaining solvent from the composition. Often the solvent will be selected from diisobutylketone, polypropylene glycol, isoparaffins, propylene glycol, cyclohexanone, butyl glycol, ethylhexanol, white spirit, isoparaffins, xylene, methoxypropylacetate, butylacetate, naphthenes, glycolic acid butyl ester, alkyl benzenes and combinations thereof. In some instances, the solvent is selected from diisobutylketone, polypropylene glycol, isoparaffins, propylene glycol, isoparaffins, and combinations thereof.

[0059] The composition may also contain minor amounts of other additives commonly used in explosives compositions. Examples of these include microcrystalline wax, energetic plasticisers, non-energetic plasticisers, antioxidants, catalysts, curing agents, metallic fuels, coupling agents, surfactants, dyes and combinations thereof. Energetic plasticisers may be selected from eutectic mixtures of alkylnitrobenzenes (such as dinitro- and trinitro-ethyl benzene), alkyl derivatives of linear nitramines (such as an N-alkyl nitratoethyl-nitramine, for instance butyl-NENA), and glycidyl azide oligomers.

[0060] Casting the explosive composition offers a greater flexibility of process design than can be obtained with pressing techniques. This is because the casting of different shapes can be facilitated through the simple substitution of one casting mould for another. In other words, the casting process is backwards-compatible with earlier processing apparatus. Conversely, where a change of product shape is required using pressing techniques, it is typically necessary to redesign a substantial portion of the production apparatus for compatibility with the mould, or the munition to be filled, leading to time and costs penalties. Further, casting techniques are less limited by size than pressing techniques which depend upon the transmission of pressure through the moulding powder to cause compaction. This pressure falls off rapidly with distance, making homogeneous charges with large length to diameter ratios (such as many shell fillings) more difficult to manufacture.

[0061] In addition, the casting process of the invention offers a moulded product (the cast explosive compositions described) with a reliably uniform fill regardless of the shape required by the casting. This may be partly attributed to the use of a delayed curing technique. Casting can occur in situ with the housing (such as a munition) to be filled acting as the mould; or the composition can be moulded and transferred into a housing in a separate step. Often casting will occur in situ.

[0062] Further, compositions including polymer-bonded explosives and hydroxyterminated polybutadiene binders in particular, are more elastomeric when cast than when pressed. This makes them less prone to undergoing a deflagration-to-detonation transition when exposed to accidental stimuli. Instead, such systems burn without detonating, making them safer to use than pressed systems.

[0063] Additionally, the shapes that pressing processes can be reliably applied to are more limited. For instance, it is often a problem achieving a complete fill of a conical shape using pressing techniques as air is often trapped at or towards the tip of the cone. Casting processes, being intrinsically "fluid" processes, are not limited in this way.

[0064] In some instances the explosive component is desensitized with water prior to formation of the premix, a process known as wetting or phlegmatization. However, as retention of water within the pre-cure is generally undesirable it will typically be removed from the premix prior to further processing, for instance by heating during the mixing of the explosive component and the plasticiser.

[0065] In some cases the plasticiser will be absent; however the plasticiser will typically be present in the range 0 - 10 wt% of the plasticiser and explosive premix, often in the range 0.01 - 8 wt%, on occasion 0.5 - 7 wt% or 4 - 6 wt%. The plasticiser will often be a non-energetic plasticiser, many are known in the art; however energetic plasticisers may also be used in some instances. The cast explosive composition of the invention has utility both as a main charge or a

booster charge in an explosive product. Often the composition will be the main charge. The composition of the invention may be used in any "energetic" application such as, for example, uses include mortar bombs and artillery shells as discussed above. Additionally, the inventive composition may be used to prepare explosives for gun-launch applications, explosive filings for bombs and warheads, propellants, including composite propellants, base bleed compositions, gun propellants and gas generators.

[0066] According to further aspect of the invention there is provided a process for filling a munition with a homogenous crosslinked polymer bonded explosive composition comprising the steps of:

i) forming a pre-cure castable explosive composition, said composition comprising an explosive material, a polymerisable binder, and a cross linking reagent,

ii) filling the munition,

iii) applying resonant acoustic stimulus to the munition, causing the cure process in the munition.

The reagents of the pre-cure are transferred into the munition layerwise, such that the resonant acoustic stimulus causes homogenous mixing to from an admixture and concomitantly causes the crosslinking reagent to mix with the polymerisable binder to cause the cure to start.

[0067] According to a yet further aspect of the invention there is provided a continuous filling process for filling a plurality of munitions with a homogenous crosslinked polymer bonded explosive composition comprising the steps of:

i) forming a precure castable explosive composition, by providing a continuous feed of an explosive material, a polymerisable binder, and a cross linking reagent, into a continuous resonant acoustic mixer

ii) applying a resonant acoustic stimulus to the continuous resonant acoustic mixer, to cause the cure process,

iii) filling the plurality of munitions.

[0068] Except in the examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts of material or conditions of reaction, physical properties of materials and/or use are to be understood as modified by the word "about." All amounts are by weight of the final composition, unless otherwise specified. Further, the cast explosive composition may comprise, consist essentially of, or consist of any of the possible combinations of components described above and in the claims except for where otherwise specifically indicated.

[0069] It should be appreciated that the compositions of the invention are capable of being incorporated in the form of a variety of embodiments, only a few of which have been illustrated and described above.

[0070] An embodiment of the invention will now be described by way of example only and with reference to the accompanying drawings of which:-

Figure 1 shows a prior art schematic of the fill of an HE ammunition process
Figures 2a and 2b shows a schematic of the fill of an HE ammunition using a resonant acoustic stimulus process
Figure 3 shows a continuous filling process arrangement.

[0071] Turning to fig 1 there is a general scheme 1, for filling a munition 6. The premix composition 2, is a mixture of the explosive, HTBP polymerisable binder and other processing aids, and optionally a catalyst. The premix composition 2 is agitated such as by a stirrer 3. Microcapsules comprising a cross linking reagent 4, are added to the premix to form the precure formulation. The cross linking reagent (not shown) may be a diisocyanate such as IPDI. The resultant precure admixture 5 is thoroughly mixed and is transferred to a munition 6 or mould or pot for later insertion into a munition(not shown). The munition 6 when filled with the precure 5 may then be exposed to an external stimuli, such as heat, which ruptures the microcapsules 4, causing release of the cross linking reagent. The cross linking reagent and HTPB polymerisable binder may then polymerise and form a polymer bonded explosive 7.

[0072] Turning to fig 2a and 2b there is a general scheme 11, for filling a munition 16, optional via filling funnel 19(Fig 2b). The premix formulation, is a mixture of the explosive, HTBP polymerisable binder other processing aids, optionally a catalyst and microcapsules comprising a cross linking reagent 14, are added to the premix to form the precure composition 15. The cross linking reagent (not shown) may be a diisocyanate such as IPDI. The resultant precure admixture 15 in the munition is located on a platform 13, which is in mechanical contact with a resonant acoustic stimulus source 17 to provide resonance at a frequency of 58 to 60 Hz. In order to secure the munitions 16 in place, they may be placed in a rack system 12, which may comprise further restraints 12a, 12b to secure the munition to the rack 12 and platform 13 to ensure that the acoustic, that is vibrational energy, is transferred from the source 17 to the munitions 16 and precure

composition 15.

[0073] The action of resonant acoustic energy on the precure composition 15, ensures that the composition is thoroughly mixed to a homogenous state, the continued action of resonant acoustic energy causes the microcapsules to rupture and release the cross linking reagent within said microcapsule. The further action of the resonant acoustic energy causes the released cross linking reagent to mix homogenously and concomitantly react with the HTPB polymerisable binder.

[0074] During the resonant acoustic stimulus process the application of a vacuum 18, may assist to degas the curing composition, by removing trapped gases and volatiles, to reduce the instances of voids. The mixing arrangement may require additional thermal control, such as external heating or cooling to control the temperature of the reaction.

[0075] Alternatively the composition ingredients may be dosed to a large batch mixing vessel, either volumetrically or by mass. The mixing vessel is then brought into mechanical contact with a resonant acoustic stimulus source 17 to provide a batch cure process. The resulting curing composition may then be transferred to munitions or pots, in the standard manner.

[0076] Turning to figure 3 there is provided a continuous resonant acoustic mixer system 21, comprising a mixer 28, which is primed with the components via continuous inlet feeds 24. A resonant acoustic stimulus 27 provides mixing and assists with starting the cure process. The curing admixture is then transferred via a pipe 29 to fill the munition 26. The filling may be carried out volumetrically, by mass and optionally under a vacuum.

Claims

1. A process for formulating a homogenous crosslinked polymer bonded explosive composition comprising the steps of:

   i) forming an admixture of pre-cure castable explosive composition, said composition comprising an explosive material, a polymerisable binder, a microencapsulated cross linking reagent, said microencapsulated cross linking reagent, comprising a cross linking reagent encapsulated in a microcapsule;
   wherein the microcapsule, comprises at least one shell wall polymer, wherein the microcapsule's shell wall polymer comprises at least one resonant acoustic stimulus labile linkage,
   ii) applying resonant acoustic stimulus to the admixture, causing the microcapsule to rupture and release said cross linking reagent, to cause the cure process to start.

2. A process according to claim 1, comprising the further step of iii) filling a munition with the admixture from step ii).

3. A process for filling a munition with a homogenous crosslinked polymer bonded explosive composition comprising the steps of:

   i) forming an admixture of pre-cure castable explosive composition, said composition comprising an explosive material, a polymerisable binder, a microencapsulated cross linking reagent, said microencapsulated cross linking reagent, comprising a cross linking reagent encapsulated in a microcapsule,
   wherein the microcapsule, comprises at least one shell wall polymer, wherein the microcapsule's shell wall polymer comprises at least one resonant acoustic stimulus labile linkage;
   ii) filling the munition
   iii) applying resonant acoustic stimulus to the munition, causing the microcapsule to rupture and release said cross linking reagent, to cause the cure process in the munition.

4. A process according to any one of the preceding claims wherein the polymerisable binder is selected, such that it will from with the cross linking reagent; polyurethanes, cellulosic materials such as cellulose acetate, polyesters, polybutadienes, polyethylenes, polyisobutylenes, PVA, chlorinated rubber, epoxy resins, two-pack polyurethane systems, alkyd/melanine, vinyl resins, alkyds, , butadiene-styrene block copolymers, polyNIMMO, polyGLYN, GAP, and blends, copolymers and/or combinations thereof.

5. A process according to any one of the preceding claims, wherein the explosive material is selected from RDX, HMX, FOX-7, TATND, HNS, TATB, NTO, HNIW, GUDN, picrite, aromatic nitramines such as tetryl, ethylene dinitramine, nitroglycerine, butane triol trinitrate, pentaerythritol tetranitrate, DNAN trinitrotoluene, inorganic oxidisers such as ammonium nitrate, ADN, ammonium perchlorate, energetic alkali metal salts, energetic alkaline earth metal salts, and combinations thereof.

6. A process according to claim 6 wherein the at least one shell wall polymer is selected from polyurethane, cellulosic materials, cellulose acetate, polyesters, polybutadienes, polyethylenes, polyisobutylenes, PVA, chlorinated rubber,

epoxy resins, two-pack polyurethane systems, alkyd/melanine, vinyl resins, alkyds, butadiene-styrene block copolymers, polyNIMMO, polyGLYN, GAP, and blends, copolymers and/or combinations thereof.

7. A process according to claim 6, wherein the microcapsule shell wall polymer and polymerisable binder are selected from substantially the same polymer.

8. A process according to any one of the preceding claims wherein the resonant acoustic stimulus labile linkage is selected from, acetals, blocked isocyanates, diels alder linkages.

9. A process according to claim 8 wherein the blocked isocyanates are selected from aromatic heterocycles, secondary amines, substituted phenols, oximes and amides.

10. A process according to any one of the preceding claims, wherein the step of causing the microcapsule to release said cross linking reagent, is provided by applying at least one further chemical stimulus and/or further physical stimulus.

11. A process according to any one of the preceding claims, wherein resonant acoustic stimulus system operates in the frequency range of from 50Hz to 70Hz.

12. A process according to claim 11, wherein the frequency range is of from 58Hz to 60Hz.

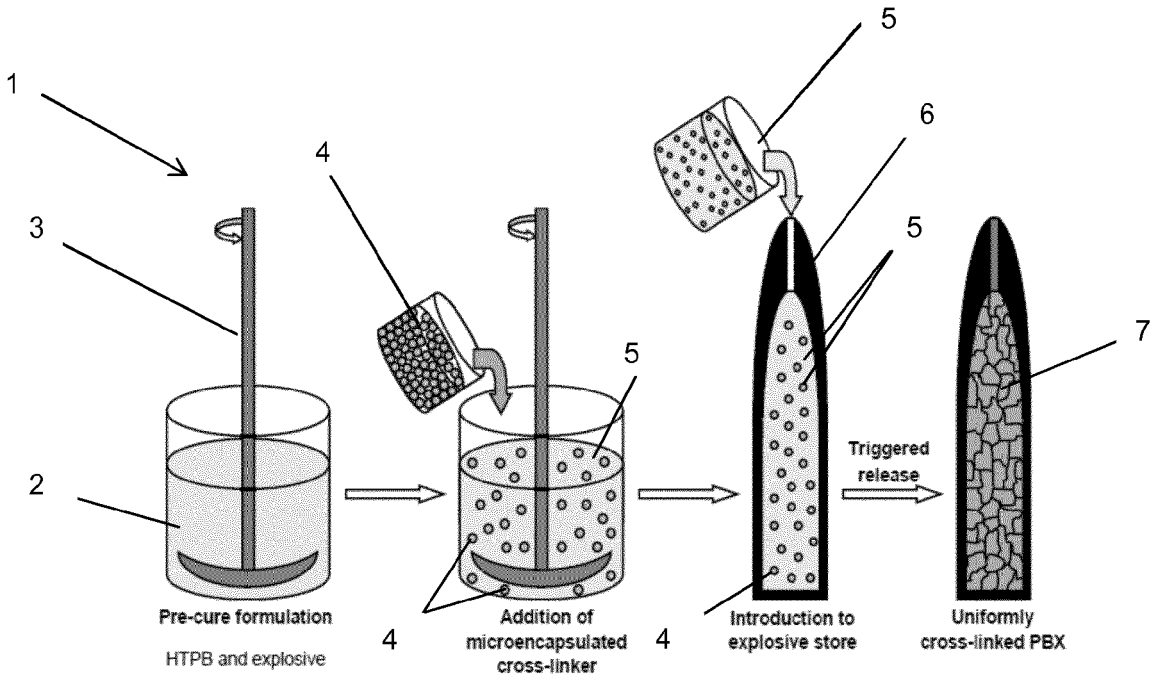
13. A process for filling a munition with a homogenous crosslinked polymer bonded explosive composition comprising the steps of:

i) forming a pre-cure castable explosive composition, said composition comprising an explosive material, a polymerisable binder, and a cross linking reagent,
ii) filling the munition,
iii) applying resonant acoustic stimulus to the munition, causing the cure process in the munition.

14. A process according to claim 13, wherein the reagents of the pre-cure are transferred into the munition layerwise, such that the resonant acoustic stimulus causes homogenous mixing to from an admixture and concomitantly causes the crosslinking reagent to mix with the polymerisable binder to cause the cure to start.

15. A continuous filling process for filling a plurality of munitions with a homogenous crosslinked polymer bonded explosive composition comprising the steps of:

i) forming a precure castable explosive composition, by providing a continuous feed of an explosive material, a polymerisable binder, and a cross linking reagent, into a continuous resonant acoustic mixer
ii) applying a resonant acoustic stimulus to the continuous resonant acoustic mixer, to cause the cure process,
iii) filling the plurality of munitions.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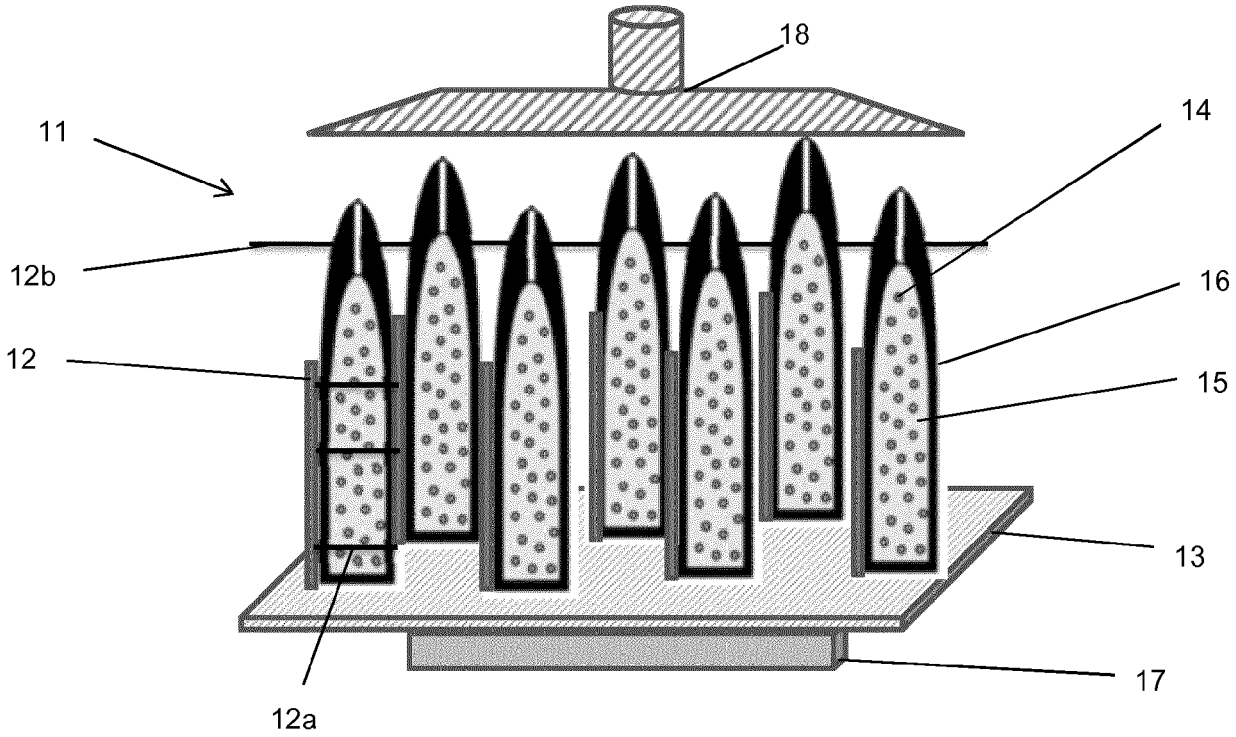
2
3
4
5
6
7
Pre-cure formulation
HTPB and explosive
Addition of
microencapsulated
cross-linker
Introduction to
explosive store
Triggered
release
Uniformly
cross-linked PBX

Fig 1


11
12
12a
12b
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14
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Fig 2a

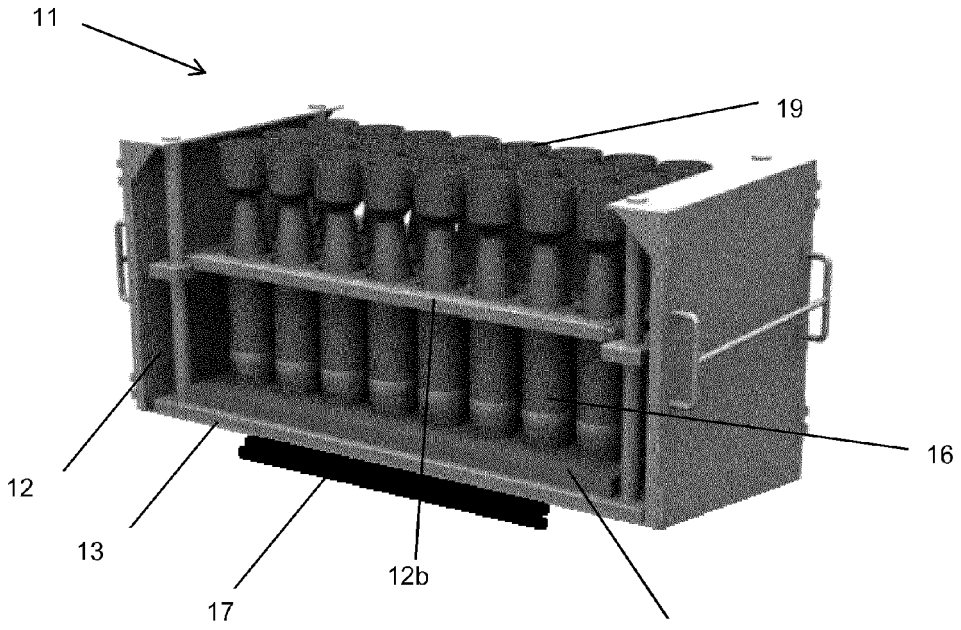

Fig 2b

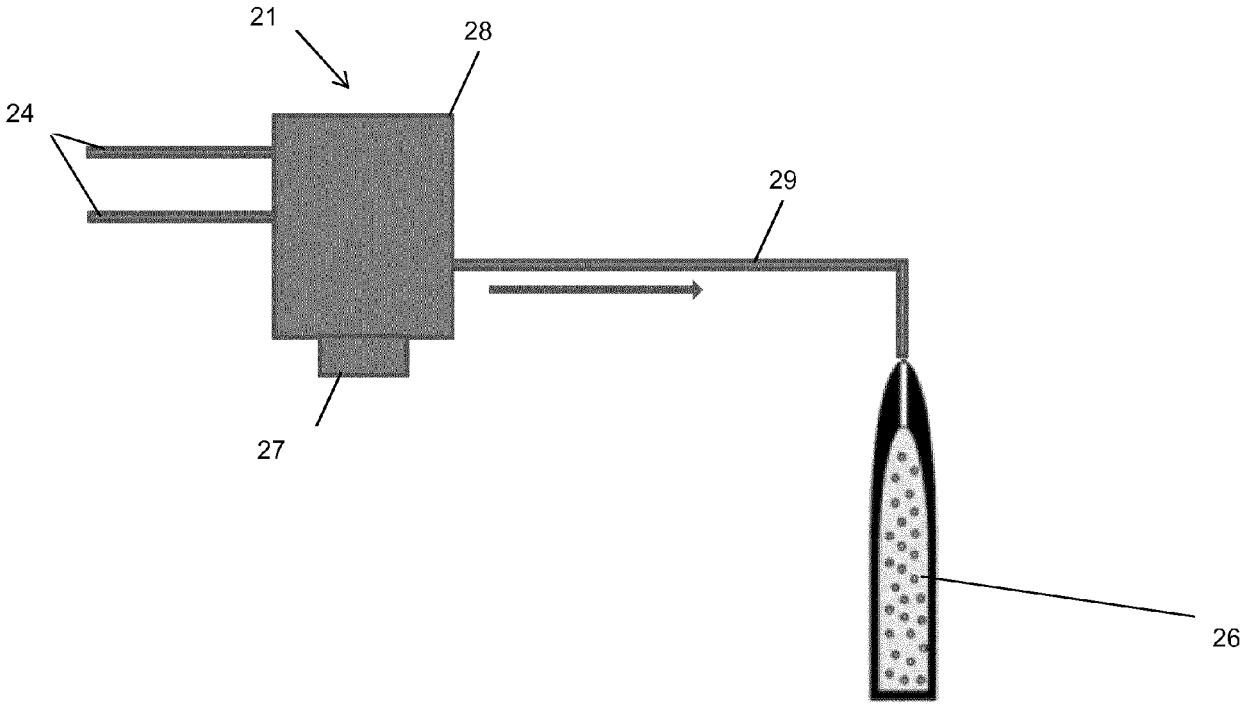

Fig 3

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EUROPEAN SEARCH REPORT

Application Number
EP 17 27 5043

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	WO 2017/006110 A1 (BAE SYSTEMS PLC [GB]) 12 January 2017 (2017-01-12)	1-13,15	INV. C06B21/00 C06B45/10
A	* page 9, line 7 - page 10, line 19; page 5, line 28 - page 6, line 7; page 7, lines 1,2; page 3, lines 4-14; page 4, lines 12-24; page 5, lines 13-18 *	14	
X	US 2010/294113 A1 (MCPHERSON MICHAEL D [US]) 25 November 2010 (2010-11-25)	13-15	
A	* paragraphs [0003], [0021], [0023], [0024]; figures 1, 2 *	1-12	
A	DE 23 27 107 A1 (ISL INST FRANCO ALLEMAND DE RE) 20 February 1975 (1975-02-20) * page 2, lines 1-2; page 4, lines 8-25 *	1-15	
A	US 3 505 428 A (KIDWELL ALFRED S ET AL) 7 April 1970 (1970-04-07) * abstract *	1-15	

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C06B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	13 October 2017	Kappen, Sascha

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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