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(54) Titre : COMPOSITION EXPLOSIVE A COULER  
(54) Title: CAST EXPLOSIVE COMPOSITION

(57) **Abrégé/Abstract:**

The invention relates to a cast explosive composition comprising a polymer-bonded explosive and a defoaming agent, and to a process for reducing the number and/or total volume of voids in a cast explosive composition comprising the steps of: combining a polymer-bonded explosive and a defoaming agent; and casting the explosive composition. The defoaming agent may be used for reducing the number and/or total volume of voids in a cast explosive composition and the cast explosive composition may be used in an explosive product.

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(57) **Abstract:** The invention relates to a cast explosive composition comprising a polymer-bonded explosive and a defoaming agent, and to a process for reducing the number and/or total volume of voids in a cast explosive composition comprising the steps of: combining a polymer-bonded explosive and a defoaming agent; and casting the explosive composition. The defoaming agent may be used for reducing the number and/or total volume of voids in a cast explosive composition and the cast explosive composition may be used in an explosive product.



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## CAST EXPLOSIVE COMPOSITION

This invention relates to cast explosive compositions, their preparation and use. In particular, the invention relates to polymer-bonded explosive compositions.

5 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.

10 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  
15 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.  
20 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  
25 where necessary.

US 6,893,516 describes an explosive mixture in which the crystalline explosive is coated with polysiloxanes to produce a granular product. The application of this coating to each crystal smoothes the surface of the crystals eliminating fine pores which could otherwise trigger unwanted reaction of the  
30 explosive. As such, the polysiloxane coating reduces the sensitivity of the

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granular explosive, improving safety in handling and during any subsequent shaping steps.

Conventional casting techniques often result in a solidified composition which retains air bubbles introduced during mixing of the material and by the placing of the composition into the mould. Typically such placing of the composition into the mould will be by pouring of the composition. These voids can reduce the performance of the composition as less explosive is present per unit volume. In addition, porosity or voids, where present in sufficient quantity, can affect the shock sensitivity of the composition, making the composition less stable to impact or ignition from a shock wave.

The invention seeks to provide a cast explosive composition in which the stability of the composition is improved, this may be through the reduction of the number and/or total volume of voids, or through other means, such as a reduction in the number of volatile components present. 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.

In one aspect of the invention there is provided a cast explosive composition comprising a polymer-bonded explosive and a defoaming agent. Another aspect relates to a cast explosive composition, comprising a polymer-bonded explosive and 0.1-2 wt% of a defoaming agent which is silicone-free, and wherein the polymer-bonded explosive comprises an explosive and a polymer binder.

The presence of the defoaming agent may reduce or substantially eliminate the voids which would often remain in the composition. Accordingly, where used herein the term "defoaming agent" is intended to mean an additive with surface active properties which acts to eliminate voids from within the polymeric binder of the cast explosive composition. Any additive which does not perform this function is not regarded as constituting a defoaming agent within the meaning of the invention. In

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the art, such additives are also known as “anti-foaming agents”, “deaerating agents” and “air release agents”.

The voids are typically found within the body of the binder component of the polymer-bonded explosive, rather than at the interface between the binder and the explosive component. Removal of these voids is particularly desirable where the intended use of the explosive will result in exposure to high g-forces, such as would be the case in an artillery shell, mortar bomb or missile. It is believed that under such conditions, adiabatic compression of the voids occurs making the region around the void more prone to premature ignition. Another application where the removal of voids is of particular importance is where the intended use of the explosive will result in rapid deceleration on impact with a target but where penetration of the target is required before the munition is detonated. This would be the case with bombs and missiles. Where voids are present, adiabatic compression of these may result in ignition on impact, before penetration of the target has occurred. In addition, the defoaming agent reduces the viscosity of the composition, allowing the casting process to be carried out more rapidly than in the absence of this additive. Further, compositions containing the defoaming agent have been seen in some instances to have a higher density in terms of %TMD achieved than when this additive is absent. This increase in density has also been linked to an improved stability and reduction in sensitivity of the explosive. In many cases, the reduction of voids will correlate with an increase in density; however as the compositions of the invention are complex, an increase in density can only be taken as an indication that the number of voids has been reduced. In many instances other methods, such as X-radiography are used to directly visualise the voids and to determine the effect of the defoaming agent.

In an additional aspect of the invention there is provided a process for reducing the number and/or total volume of voids in a cast explosive composition comprising the steps of:

combining a polymer-bonded explosive and a defoaming agent;

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and

casting the explosive composition.

Another aspect relates to a process for reducing the number or total volume of voids in a cast explosive composition, comprising the steps of: combining a polymer-  
5 bonded explosive and 0.1-2 wt% of a defoaming agent which is silicone-free; and casting the explosive composition, and wherein the polymer-bonded explosive comprises an explosive and a polymer binder.

Another aspect of the invention relates to the use of a cast explosive composition as described herein in an explosive product, and a further aspect of the  
10 invention relates to an explosive product comprising a cast explosive composition as described herein.

Another aspect relates to use of 0.1-2 wt% of a defoaming agent which is silicone-free for reducing the number or total volume of voids in a cast explosive composition also comprising a polymer-bonded explosive, and wherein the  
15 polymer-bonded explosive comprises an explosive and a polymer binder.

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Polymer-bonded explosives include a polymeric binder which forms a matrix bonding explosive particles within. The 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 binder will be 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, self-crosslinking acrylates, thermoplastic elastomers such as butadiene-styrene block copolymers, and blends, copolymers and/or combinations thereof. 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 binder component be entirely selected from the list of binders above either alone or in combination. In some embodiments the binder will comprise at least partly polyurethane, often the binder will comprise 50 - 100 wt% polyurethane, in some instances, 80 - 100 wt%. In some embodiments the binder will consist of polyurethane. Polyurethanes derived from MDI (methylene diphenyl diisocyanate) and TDI (toluene diisocyanate) and IPDI (isophorone diisocyanate) may be used. 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 binder comprises polyurethane, the polyurethane binder includes a hydroxyterminated polybutadiene.

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<sub>2</sub> group. Heteroalicyclic nitramines bear a ring containing N-NO<sub>2</sub> 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.

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The explosive component may additionally or alternatively be selected from TATND (tetranitro-tetraminodecalin), HNS (hexanitrostilbene), TATB (triaminotrinitrobenzene), NTO (3-nitro-1,2,4-triazol-5-one), HNIW (2,4,6,8,10,12-hexanitrohexaazaisowurtzitane), GUDN (guanyldylurea dinitride),  
5 FOX-7 (1,1-diamino-2, 2-dinitroethene), and combinations thereof.

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  
10 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.

15 The explosive component of the polymer-bonded explosive may be in 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  
20 aluminium or an alloy thereof; often the fuel will be aluminium powder.

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.

25 In many cases the 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%  
30 polyurethane binder. Polymer-bonded explosives of this composition are commercially available, for example, Rowanex 1100™.

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 alkoxyated 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.

The defoaming agent may be added to the composition in a solvent carrier. However, it is generally preferred that solvents be absent. It has been found that the use of defoaming agents which are not carried in a solvent, or even the use of entirely solventless systems, is advantageous as there are fewer (or substantially no) volatile components present during processing of the composition, reducing the safety precautions and/or plant modifications needed. Further, the exclusion of solvents eliminates the risk of residual volatiles separating (for instance by evaporation or leaking) from the composition during storage resulting in unpredictable modifications of the properties of the compositions such as the creation of voids as a result of volatile evaporation.

Often the defoaming agent is present in the range about 0.01 – 2 wt%, e.g. 0.1 – 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

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composition becomes inhomogeneous as a result of sedimentation and segregation processes occurring within the mixture.

Without being bound by theory, it is believed that the defoaming agent not only acts to reduce viscosity, facilitating the casting process and the egress  
5 of voids from the composition during casting, but that the defoaming agents are surface active at the void-composition interfaces, causing the void bubbles to coalesce and hence be expelled from the composition as a result of the greater buoyancy of the larger bubbles produced. This results in compositions with fewer visible voids, which are more stable than known explosive compositions.

10 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.

15 Where present, the solvent may be added as a carrier for the defoaming agent or another component 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  
20 from the composition. Accordingly, in some embodiments the polymer-bonded explosive and the defoaming agent are combined in the presence of a solvent. Often the solvent will be selected from diisobutylketone, polypropylene glycol, isoparaffins, propylene glycol, cyclohexanone, butyl glycol, ethylhexanol, white spirit, isoparaffins, xylene, methoxypropylacetate, butylacetate, naphthenes,  
25 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.

Although melt casting processes are compatible with the invention, typically the inventive composition will be cast using "cast and curing"  
30 techniques. Accordingly, where the components of the cast explosive composition are not inherently curable (for instance, where all polymer

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components are thermoplastic polymers) a curative may optionally be present. In many embodiments the casting technique used is vacuum casting as the resulting product is generally of greater density and no visible voids compared with the equivalent air-cast product. In general, the curing step will take place  
5 after the casting step has occurred.

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, anti-oxidants, catalysts, curing agents, metallic fuels, coupling agents, surfactants,  
10 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 nitrateethyl-nitramine, for instance butyl-NENA), and glycidyl azide digomers.

Casting the explosive composition offers a greater flexibility of process  
15 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  
20 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  
25 distance, making homogeneous charges with large length to diameter ratios (such as many shell fillings) more difficult to manufacture.

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  
30 the use of a casting technique, and partly to the presence of the defoaming agent. The defoaming agent substantially reduces the number of voids within the binder and hence the cast explosive composition. In some instances, the

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voids are substantially eliminated. 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.

5 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  
10 pressed systems.

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"  
15 processes, are not limited in this way.

The process of the invention may be a continuous or batch process as appropriate. Many known casting processes will be compatible for use with the invention as modification of these processes to allow for the addition of the defoaming agent to the polymer-bonded explosive and to allow the defoaming  
20 agent to perform its defoaming function during casting, is within the capabilities of the person skilled in the art. Where a continuous process is used this may make use of static mixing technology such as the technology described in EP 1485669.

The process may utilise a premix or precure as a starting material,  
25 although these are not essential. A premix will typically be a mixture of an explosive component and a binder component, usually a plasticiser. 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 premix is generally undesirable it will typically be  
30 removed from the premix prior to further processing, for instance by heating during the mixing of the explosive component and the plasticiser.

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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. A precure will typically be a combination of the premix and the other components of the composition with the exception of the catalyst and the curing agent. In some instances the defoaming agent will also be absent from the precure.

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 where the presence of voids causes safety or functional problems. Such 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 fillings for bombs and warheads, propellants, including composite propellants, base bleed compositions, gun propellants and gas generators.

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. The process for reducing the voids in the composition may comprise, consist essentially of, or consist of the steps specified above and in the claims.

The following non-limiting examples illustrate the invention.

### Examples

Example 1

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A series of commercially available defoaming agents were cast and cured with Rowanex 1100 (88 wt% RDX and 12 wt% polyurethane agent). Curing occurred over 5 days at 65° C. 105mm and 155mm shells prepared using the resulting composition were found to have no detectable voids, and no adverse effect on the chemical or mechanical properties of the polymer-bonded explosive were observed. Table 1 below illustrates the effect of binder type and level on the viscosity and density of the composition.

TABLE 1

1. Defoaming Agent*	Dosage (wt%)	Viscosity (cps) <sup>#</sup>	Density - Vacuum Cast (g/cm <sup>3</sup> )	Density - Air Cast (g/cm <sup>3</sup> )	% TMD <sup>s</sup> (air cast)
No Additive	-	0.12	1.608	1.608	99.3
Solution of foam-destroying polymers and polysiloxanes in isoparaffin solvent (BYK 088)	1.0	0.035	1.608	1.602	99.6
Solution of silicone-free foam-destroying polymers in Alkylbenzene/ methoxypropylacetate 12/1 (BYK A500)	1.0	0.033	1.612	1.606	99.9
Solution of foam-destroying polysiloxanes in diisobutylketone (BYK 066N)	0.1	0.12	1.614	1.619	99.6
Solution of foam-destroying polysiloxanes in diisobutylketone (BYK 066N)	0.5	0.063	1.618	1.608	99.6
Solution of foam-destroying polysiloxanes in diisobutylketone (BYK 066N)	1.0	0.04	1.620	1.605	99.8
Solvent free mixture of foam-destroying polymers silicone free (BYK A535)	0.1	0.076	1.6	1.6	98.9
Solvent free mixture of foam-destroying polymers silicone free (BYK A535)	0.5	0.07	1.612	1.608	99.6
Solvent free mixture of foam-destroying polymers silicone free (BYK A535)	1.0	0.034	1.59	1.597	99.3

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Concentrate based on organosiloxanes plus fumed silica (TEGO MR2132)	0.1	0.12	1.605	1.622	100
Concentrate based on organosiloxanes plus fumed silica (TEGO MR2132)	0.5	0.073	1.613	1.609	99.7
Concentrate based on organosiloxanes plus fumed silica (TEGO MR2132)	1.0	0.047	1.594	1.561	97.1
Solvent free, silicone free alkoxyated alcohol (BASF SD23)	0.1	0.133	1.611	1.612	99.6
Solvent free, silicone free alkoxyated alcohol (BASF SD23)	0.5	0.09	1.597	1.597	98.9
Solvent free, silicone free alkoxyated alcohol (BASF SD23)	1.0	0.28	1.623	1.623	100
Solvent free, silicone free triisobutyl phosphate (BASF SD40)	0.1	0.08	1.609	1.610	99.5
Solvent free, silicone free triisobutyl phosphate (BASF SD40)	0.5	0.06	1.598	1.603	99.3
Solvent free, silicone free triisobutyl phosphate (BASF SD40)	1.0	0.07	1.596	1.598	99.4
Dibutylketone only	1.0	--	1.599	1.598	99.4
Dibutylketone only	0.5	--	1.597	1.602	99.2

\* defoaming agents were procured from BYK Additives and Instruments, a subdivision of Altana; Evonik or BASF

# Viscosity determined at 60°C

§ TMD is the Theoretical Maximum Density of the composition calculated to allow for the intrinsic density lowering effect arising when additives are added. The TMD is the sum of the relative volume of each component as determined from their relative mass within the composition and known density. As a result, the TMD gives a true indication of the density modification arising as a result of a change in the number of voids.

10 As can be seen, the presence of each of the defoaming agents at levels above 0.1 wt% reduces the viscosity of the composition making it easier to cast. Further, as the level of defoaming agent is increased to 1.0 wt%, the viscosity of the composition is further reduced.

15 The presence of defoaming agent also increases the density, providing an indicator that the number of voids has been reduced. Calculation of the TMD provides a further indicator, as an increase in the TMD relative to that

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obtained where no additive is present shows that the number of voids in the sample has been reduced relative to the additive free composition.

It is clear that it is the defoaming agent having a density increasing effect as the addition of dibutylketone only (i.e. solvent only), reduces the density of the composition whether prepared by a vacuum or an air casting technique.

The data above shows that vacuum casting generally produces compositions of a higher relative density than air casting techniques where defoaming agents are present. Further, vacuum casting techniques generally have a more marked effect upon the density of compositions containing defoaming agents when compared to additive free or solvent only compositions.

However, even where air casting techniques are used, it is clear that the defoaming agents are acting to reduce the number of voids in the compositions tested as each defoaming agent provides a composition which is either of higher density, or has a higher TMD, than the control compositions including either no additive, or solvent only.

### Example 2

The compatibility of the defoaming agents with the Rowanex 1100 was also tested, and the results set out in Table 2 below.

TABLE 2

1. Defoaming Agent	Compatibility
BYK 066N*	Pass
Solution of foam-destroying polysiloxanes in propylene glycol (BYK 088A)*	Pass
BYK 088	Pass
BYK A500*	Pass
BYK A535*	Pass
TEGO MR2132#	Pass
BASF SD23 <sup>§</sup>	Pass
BASF SD40 <sup>§</sup>	Pass

\* Procured from BYK Additives and Instruments, a subdivision of Altana

# Procured from Evonik

§ Procured from BASF

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Compatibility was measured following STANAG 4147 Test 1: Procedure B, at a temperature of 100°C for 40 hours. All of the defoaming agents tested were found to meet the requirements of this test, and hence to be compatible with the Rowanex 1100 PBX product, as illustrated by the results in the table above which indicate that each of the materials tested evolved less than 1 ml/g of gas for a 5g sample. No adverse reaction was observed with any of the defoaming agents, although a particularly good compatibility was observed between Rowanex 1100 and BYK A535. Indeed, the use of BYK A535, a solventless defoaming agent, has been found to provide a particularly stable product with acceptable activity in terms of void removal.

### Example 3

The sensitivity of the Rowanex 1100 and defoaming agent mixtures was tested for sensitivity to mechanical impact (Rotter Impact) to determine the relative hazard associated with using the mixture as opposed to the pure PBX product. The results are set out in Table 3.

TABLE 3

1. Additive	Concentration (wt%)	F of I
None	-	100
BYK 088	1	130
BYK A500	1	130
BYK 066N	1	130
BYK A535	0.5	102
TEGO MR2132	1	109
BASF SD23	1	112
BASF SD40	1	121

The test determines the 50% drop height for the test sample. This examines the whole probability of ignition versus stimulus-level relationship. Seven test heights equally spaced on a logarithmic scale are chosen and caps are tested to see if ignitions take place. Results are expressed in terms of Figures of Insensitiveness (F of I) relative to standard RDX. All tests are carried out on samples of ground up material. The Rotter Impact Test method was used to determine the F of I using an LSM Rotter machine.

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The F of I value for all of the Rowanex 1100/defoaming agent samples was found to be greater than or equal to the F of I value for Rowanex 1100 alone. This indicated that the presence of the defoaming agent has no adverse effect on the sensitivity of the PBX to mechanical impact and that as a result the combination products are no more hazardous, and in some cases less hazardous, to use than Rowanex 1100 alone. Without being bound by theory, this may be due to the marginal increase in binder, and resultant reduction in nitramine content because of the presence of the defoaming agent. It is further indicated that the Rowanex 1100/defoaming agent samples are likely to be no more sensitive to ignition than untreated Rowanex 1100.

#### Example 4

A series of compositions including RDX were prepared, three of these compositions included defoaming agents.

TABLE 4: Examples of Polymer-bonded Explosive (PBX) Compositions containing Defoaming Agents

Abbreviation	Full name	Function	PBX (wt%)	PBX with 0.1% BYK-A500 Defoamer (wt %)	PBX with 0.5% BYK-A535 Defoamer (wt%)	PBX with 1% BYK-066N Defoamer (wt%)
DOA	Dioctyl Adipate	Plasticiser	7.00	6.99	6.96	6.93
HTPB	Hydroxyterminated Polybutadiene	Pre-polymer	4.28	4.28	4.26	4.24
Lecithin		Surfactant	0.30	0.30	0.30	0.30
AO2246	2,2'-methylenebis-(4-methyl-6-tertiary-butylphenol)	Anti-oxidant	0.10	0.10	0.10	0.10
IPDI	Isophorone Diisocyanate	Curing Agent	0.42	0.42	0.42	0.42
DBTDL	dibutyltin dilaurate	Catalyst	0.05	0.05	0.05	0.05
<b>Additive</b>			0.00	0.10	0.50	1.00
<b>RDX*</b>	<b>Hexogen</b>	<b>Explosive Filler</b>	QS	QS	QS	QS

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\* May be present as pure RDX or combined with a plasticiser, for instance in the ratio 94:6 RDX:plasticiser.

The compositions were prepared using cast and curing processes as described in Example 1 and no voids were detected. No adverse effect on chemical and mechanical properties was observed relative to the defoaming agent free RDX composition.

#### Example 5

The following example illustrates a method of preparing PBX compositions of the invention, such as the compositions of Example 4, using a premix. The techniques used would be well known to the person skilled in the art.

A water-jacketed, vertical mixer fitted with a rotating stirrer blade was used for the preparation of the composition. All mixing was carried out under vacuum at a pressure of less than 10 mm Hg. The compositions of this example were prepared on a 5 Kg scale using the relative proportions of components set out in Example 4 above.

The premix was prepared from RDX desensitised with water. The water was then driven off using techniques common in the art. The desensitised RDX (94 wt%) was then mixed with DOA plasticiser (6 wt%) to form the premix.

The mixer was preheated to  $60 \pm 2^\circ\text{C}$  and the following ingredients weighed into the mixer in sequential order in relative amounts as described in Example 2 above:

1. HTPB
2. DOA
3. Lecithin
4. AO 2246
5. Premix (first quarter portion, i.e. 25 wt% of total premix to be added)

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The composition was mixed for 15 minutes. The second, third and final quarter portions of premix were then added with 10 minutes of mixing between each addition and after the final addition. The mixer blades and bowl were scraped down to ensure that any unmixed material was transferred to the mixing zone of the bowl and the composition mixed for a further 60 minutes.

Defoaming agent was then added and the composition mixed until the maximum reduction in viscosity upon addition of the defoaming agent to the composition was observed. In this case mixing was for 25 minutes and viscosity reduction was measured using a torque meter fixed to the mixer, when the torque required to complete the mixing stabilised at a lower level than before the addition of the defoaming agent, the maximum reduction in viscosity is regarded as having been observed.

The DBTL was added and the composition mixed for 15 minutes, then the IPDI added and the composition mixed for a further 15 minutes. After mixing the viscosity of the composition was recorded using a Brookfield viscometer (60°C).

The composition was cast and any excess mixture removed from the shell housings. The shells were placed onto a vibrating table and allowed to vibrate for 5 minutes. The charges were cured for 5 days at  $65 \pm 2^\circ\text{C}$ .

#### Example 6

The following example illustrates a method of preparing PBX compositions of the invention, such as the compositions of Example 4, from a precure. The techniques used would be well known to the person skilled in the art.

Mixing conditions were as for Example 5. The precure was prepared from the premix described in Example 5 above. To this premix was added all of the components of the composition of Example 5 except for the defoaming agent, catalyst and curing agent.

The mixer was preheated to  $60 \pm 2^\circ\text{C}$  and the components of the precure added and heated for 15 minutes. The precure was then mixed for 30 minutes

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and the mixer blades and bowl scraped to ensure that any unmixed material was transferred to the mixing zone of the bowl. Defoaming agent was added and the composition mixed until the viscosity reducing effect of the defoaming agent is observed, this was measured as described in Example 5 and in this  
5 example required stirring for 25 minutes. The DBTL was added and the composition mixed for 15 minutes, then the IPDI added and the composition mixed for a further 15 minutes. The mixer blades and bowl were scraped to ensure that any unmixed material was transferred to the mixing zone of the bowl. After mixing the viscosity of the composition was recorded using a  
10 Brookfield viscometer (60°C).

The composition was cast and any excess mixture removed from the shell housings. The charges were cured for 5 days at  $65 \pm 2^\circ\text{C}$ .

15 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.

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CLAIMS:

1. A cast explosive composition, comprising a polymer-bonded explosive and 0.1-2 wt% of a defoaming agent which is silicone-free, and wherein the polymer-bonded explosive comprises an explosive and a polymer binder.
- 5 2. A cast explosive composition according to claim 1, wherein the polymer binder is selected from the group consisting of a polyurethane, a cellulosic material, a polyester, a polybutadiene, a polyethylene, a polyisobutylene, a PVA (polyvinyl alcohol), a chlorinated rubber, an epoxy resin, a two-pack polyurethane system, an alkyd/melanine, a vinyl resin, an alkyd, a self-crosslinking acrylate, a butadiene-styrene  
10 block copolymer, a polyNIMMO (poly(3-nitratomethyl-3-methyloxetane)), a polyGLYN (poly glycidyl nitrate), a GAP (glycidyl azide polymer), a blend, a copolymer and a combination thereof.
3. A cast explosive composition according to claim 2, wherein the cellulosic material is a cellulose acetate.
- 15 4. A cast explosive composition according to any one of claims 1 to 3, wherein the polymer-bonded explosive is selected from the group consisting of RDX, HMX, FOX-7, TATND, HNS, TATB, NTO, HNIW, GUDN, picrite, an aromatic nitramine, ammonium nitrate, ADN, ammonium perchlorate, an energetic alkali metal salt, an energetic alkaline earth metal salt and a combination thereof.
- 20 5. A cast explosive composition according to claim 4, wherein the aromatic nitramine is selected from the group consisting of tetryl, ethylene dinitramine, nitroglycerine, butane triol trinitrate, pentaerythritol tetranitrate and DNAN trinitrotoluene.
6. A cast explosive composition according to claim 1, wherein the polymer-bonded explosive comprises in the range about 75-95 wt% RDX and the polymer binder  
25 is in the range about 5-25 wt% and is a polyurethane binder.
7. A cast explosive composition according to any one of claims 1 to 6, additionally comprising a metal powder selected from the group consisting of aluminium,

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magnesium, tungsten, an alloy and a combination thereof in admixture with the polymer-bonded explosive.

8. A cast explosive composition according to any one of claims 1 to 7, further comprising a polysiloxane.

5 9. A cast explosive composition according to claim 8, wherein the polysiloxane is selected from the group consisting of a polyalkyl siloxane, a polyalkylaryl siloxane, a polyether siloxane co-polymer and a combination thereof.

10. A cast explosive composition according to any one of claims 1 to 9, wherein the defoaming agent is present in the range 0.25-1 wt%.

10 11. A process for reducing the number or total volume of voids in a cast explosive composition, comprising the steps of:

combining a polymer-bonded explosive and 0.1-2 wt% of a defoaming agent which is silicone-free; and

casting the explosive composition,

15 and wherein the polymer-bonded explosive comprises an explosive and a polymer binder.

12. A process according to claim 11, wherein the polymer binder is selected from the group consisting of a polyurethane, a cellulosic material, a polyester, a polybutadiene, a polyethylene, a polyisobutylene, a PVA (polyvinyl alcohol), a chlorinated  
20 rubber, an epoxy resin, a two-pack polyurethane system, an alkyd/melanine, a vinyl resin, an alkyd, a self-crosslinking acrylate, a butadiene-styrene block copolymer, a polyNIMMO (poly(3-nitratomethyl-3-methyloxetane)), a polyGLYN (poly glycidyl nitrate), a GAP (glycidyl azide polymer), a blend, a copolymer and a combination thereof.

13. A process according to claim 12, wherein the cellulosic material is a  
25 cellulose acetate.

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14. A process according to any one of claims 11 to 13, wherein the cast explosive composition is cured.
15. A process according to any one of claims 11 to 14, wherein the polymer-bonded explosive and the defoaming agent are combined in the presence of a solvent.
- 5 16. A process according to any one of claims 11 to 15, wherein the casting comprises vacuum casting.
17. A use of a cast explosive composition according to any one of claims 1 to 10, in an explosive product.
18. An explosive product comprising a cast explosive composition according to  
10 any one of claims 1 to 10.
19. A use of 0.1-2 wt% of a defoaming agent which is silicone-free for reducing the number or total volume of voids in a cast explosive composition also comprising a polymer-bonded explosive, and wherein the polymer-bonded explosive comprises an explosive and a polymer binder.
- 15 20. A use according to claim 19, wherein the polymer binder is selected from the group consisting of a polyurethane, a cellulosic material, a polyester, a polybutadiene, a polyethylene, a polyisobutylene, a PVA (polyvinyl alcohol), a chlorinated rubber, an epoxy resin, a two-pack polyurethane system, an alkyd/melanine, a vinyl resin, an alkyd, a self-crosslinking acrylate, a butadiene-styrene block copolymer, a  
20 polyNIMMO (poly(3-nitratomethyl-3-methyloxetane)), a polyGLYN (poly glycidyl nitrate), a GAP (glycidyl azide polymer), a blend, a copolymer and a combination thereof.
21. A use according to claim 20, wherein the cellulosic material is a cellulose acetate.