

MALLEABLE SOLID EXPLOSIVE AND METHOD FOR OBTAINING IT

The present invention relates to a novel malleable solid explosive, which constitutes an alternative, or even an improvement, to the plastic explosives known to date (see below). The invention also
5 relates to a process for obtaining said novel malleable solid explosive.

The technical field of the invention is that of malleable (pasty) solid (blocks of) explosives, commonly known as plastic explosives, primed with a detonator, for military and civil use. They are generally used in the
10 form of cakes of a few hundred grams. The malleability of these explosive cakes makes it possible to fully adapt their forms to the contours of the objects or structures to be destroyed.

The first plastic explosive known, under the name "gelignite", was invented by Alfred Nobel in 1875. It consisted of nitrocellulose
15 dissolved in nitroglycerine and mixed with wood paste and potassium nitrite.

Plastic explosives composed of an explosive charge and a binder such as wax or mineral oil, which have the drawback of having degraded malleability properties under cold conditions, have also being described in
20 the past. Patent application DE 20 27 209 described, in 1971, a malleable explosive containing, in order to improve its cold plasticity, from 8% to 15% by weight of silicone oil as binder (said explosive also advantageously contains zinc oxystearate as additive). However, as the rheological qualities of these explosives remained insufficient, it appeared
25 essential to condition said explosives, especially when they are used or stored as elements of a few hundred grams, in packages, in order to avoid their deformation by gravity. Thus, patent application DE 30 46 562 proposes explosives of this type incorporated into metal or plastic sheets.

Nowadays, the most common plastic explosives contain an
30 explosive charge (hexogen (RDX) and/or pentrite, for example), a rubber

polymeric binder (which is most often synthetic such as a butadiene-styrene rubber or a polyisobutylene), a plasticizer (such as bis(2-ethylhexyl) adipate or sebacate, di-n-octyl phthalate or tri-n-butyl citrate), and additives (such as dyes, antioxidants and detection markers).

- 5 The plasticizer (generally present in weight contents of from 2 to 5%) has the role of giving the plastic explosives their malleability and better mechanical strength not necessitating their conditioning in a structure (see the teaching of the prior art recalled above, relating to plasticizer-free malleable explosives). The most well known plastic explosives having this
- 10 type of formulation are C-4 plastic and Semtex[®], which are familiar to those skilled in the art. These plastic explosives thus contain, in their composition, with reference to their plastic nature, a rubber polymeric binder (solid) combined with a plasticizer. These two inert components do not participate in the desired explosive effect. Moreover, the controlled
- 15 dosing of the binder (polymer) and of the plasticizer, which are generally introduced in small amounts (a few percent) into the energetic charge of the plastic explosive, complicates the process for manufacturing the plastic explosive.

- In such a context, the inventor has sought a novel type of
- 20 "plastic" explosive, more precisely a novel malleable solid explosive, which is more advantageous in terms of composition (free of plasticizer), performance (with a "less dilute" energetic charge) and manufacturing process (easier).

- Without any connection with the technical problem identified
- 25 above, the manufacture of composite solid explosives was described more particularly in patent application EP-A-1 333 015. The manufacture of these explosives (non-malleable) comprises the casting of a pasty explosive composition in molds, followed by crosslinking of said pasty composition in said molds. Said pasty composition is obtained by mixing
- 30 two preconstituted components:

- a pasty component A, comprising the explosive charge (and optionally other pulverulent ingredients such as aluminum) and a crosslinkable liquid polymer, such as hydroxytelechelic polybutadiene; and
- 5 - a liquid component B, comprising the agent for crosslinking said crosslinkable liquid polymer,

(a plasticizer being distributed indiscriminately between components A and B).

Said pasty component A (obtained by simple mixing of its constituents in a
10 blender) does not exist in the form of blocks, and is never molded. It is formulated only for the purpose of mixing it with the crosslinking agent and of subsequently crosslinking it, leading to the composite solid explosive.

According to its first subject, the present invention thus relates
15 to a novel malleable solid explosive, which constitutes an alternative, or even an improvement, to the plastic explosives known to date (see above). Said explosive is solid inasmuch as it does not flow by gravity (at room temperature and above: in fact, up to the temperature at which the explosive charge it contains is no longer stable). Said explosive is
20 malleable in the sense that it can be modeled by hand (manually) at temperatures of from -40°C to +70°C. These "definitions" will not surprise a person skilled in the art; said malleable solid explosive of the invention has properties of the type of the plastic explosives of the prior art (but without plasticizer in its composition, see below).

25 The malleable solid explosive of the invention is characterized in that it is in the form of a block (solid) consisting, for at least 98% of its weight, of a pulverulent explosive charge and of a liquid chosen from polyol polymers of the group of polyisobutylene polyols, polybutadiene polyols, polyether polyols, polyester polyols and polysiloxane polyols,
30 whose number-average molecular mass is between 500 and 10 000, and

mixtures thereof. In a novel manner, said malleable solid explosive of the invention combines physical presentation (state) and composition characteristics.

5 The malleable solid explosive of the invention is thus in the form of a block, i.e. in the form of a compact mass. It is in fact a block, obtained by molding or by cutting a paste (see the process for obtaining it described below). The malleable solid explosive of the invention may thus be obtained by molding a pasty component A according to patent application EP-A-1 333 015. The invention currently claimed offers a novel
10 outlet for this component A, proposes an entirely novel use thereof (in the context of the invention, said component is not crosslinked but used "in its native form" after a simple forming operation). It is noted, however, that the field of the invention is not in any way limited to said components A according to patent application EP-A-1 333 015.

15 It is now proposed to develop the composition characteristics of the malleable solid explosive of the invention.

The pulverulent explosive charge (whose particle size(s), which are not novel per se, are conventionally generally between 2 and 500 μm) of the block contains one or more explosives (as a mixture). Said
20 explosive(s) present advantageously have different particle sizes (granulometric fractions). It is thus possible to have high charge contents. Advantageously, the pulverulent explosive charge of the block represents at least 85% by weight relative to the total weight of the block.

The liquid present also consists of a liquid (chosen from the
25 polyol polymers mentioned above) or a mixture of liquids (chosen from the polyol polymers mentioned above). It may or may not be a solvent of the pulverulent explosive charge. In the case where said liquid is a solvent for said charge, it is understood that said charge is present in concentrations above the saturation concentration, insofar as a solid block
30 is under consideration.

The malleable solid explosive block consists essentially (for at least 98% of its weight) of said charge and said liquid. In addition to said charge and said liquid, it is liable to contain only additives (see below). It may quite entirely consist solely (100%) of said charge and said liquid. No plasticizer is present in its composition.

A person skilled in the art has now grasped the novel type of malleable solid explosive proposed by the invention, based on a liquid and a pulverulent solid (explosive charge). It is conceived that the combined liquid(s) and solid(s) be appropriately combined to obtain the desired aim: a malleable solid block (see the "definitions" given above for the two terms: "solid" and "malleable"). It is conceived that the main parameters under consideration, for producing a block having adequate rheological properties (adequate consistency), are:

- the particle size of the solid charge; it has been seen above that it is convenient to use several granulometric fractions as a mixture;
- the viscosity of the liquid or of the mixture of liquids;
- the solid(s)/liquid(s) (S/L) mass ratio.

It is moreover noted that chemical interactions are entirely liable to develop between said solid(s) and liquid(s) (see below), and that in any case, said liquid(s) act as binder for the pulverulent charge.

With reference to the above three parameters, it is possible, in an entirely non limiting manner, to state as follows. In order to obtain a solid, the (S/L) weight ratio is in principle high. It has been seen above that the pulverulent explosive charge of the block advantageously represents at least 85% by weight relative to the total weight of the block. Moreover, a liquid with a dynamic viscosity of between 0.1 and 1 Pa.s in the temperature range: -40°C to +70°C and an explosive charge with a particle size of between 1 and 150 µm are advantageously combined. Most advantageously, a solid explosive charge having several granulometric fractions between 1 and 150 µm is chosen.

In any case, in other technical fields (agrifood and pharmaceutical, in particular), the combination of a pulverulent charge and of a liquid are fully controlled so as to obtain a malleable solid. The teaching in these fields, relating to the above parameters and to the process described below, is entirely transposable to the field of the invention.

The explosive charge of the solid explosive blocks of the invention is not novel *per se*. It may consist especially of octogen (HMX), hexogen (RDX), pentaerythrityl tetranitrate (pentrite or PETN), hexanitrohexaazaisowurtzitane (CL20), triaminotrinitrobenzene (TATB), 5-nitro-2,2,4-triazol-3-one (ONTA), hexanitrostilbene (HNS), 1,1-diamino-2,2-dinitroethane (DADNE or Fox-7) or a mixture thereof. It is advantageously chosen from octogen, hexogen, pentrite and CL20. Hexogen is the preferred explosive (energetic) charge of the blocks of the invention.

The liquid is thus chosen from the polyol polymers below: polyisobutylene polyols, polybutadiene polyols, polyether polyols, polyester polyols and polysiloxane polyols, with a number-average molecular mass of between 500 and 10 000, and mixtures thereof. Said liquid is advantageously chosen from said polybutadiene polyols and mixtures thereof. Said liquid most advantageously consists of a hydroxytelechelic polybutadiene of this type. In fact, the hydroxytelechelic polybutadienes usually used in crosslinked form as binder for solid propergols for self-propulsion are entirely suitable for use as liquid for the malleable solid explosives of the invention. A person skilled in the art knows this type of polymer (see especially the teaching of patent application EP-A-1 333 015).

It has been seen above that said charge and said liquid constitute from 98% to 100% (by weight) of the malleable solid explosive of the invention, of the malleable solid explosive blocks of the invention.

Said explosive blocks are in fact liable to contain additives, especially antioxidants, anti-age-curing agents, chemical detection markers, to not more than 2% of their total weight.

5 Additives that may be contained in said explosive blocks are especially:

- at least one antioxidant (of the polyol polymer liquid type), for instance di-tert-butyl-para-cresolmethane, 2,2-methylenebis(4-methyl-6-tert-butyl)phenol, and mixtures thereof;
- at least one anti-age-curing agent, especially for preventing hot curing,
10 for instance a silicone oil, tetraethylenepentamineacrylonitrile (TEPAN), soybean lecithin, and mixtures thereof;
- at least one chemical detection marker, for instance EGDN (ethylene glycol dinitrate), DMDNB (2,3-dimethyl-2,3-dinitrobutane), p-MNT (para-mononitrotoluene) or o-MNT (ortho-mononitrotoluene). The
15 presence of a chemical marker is in fact obligatory in order to comply with the Montréal convention of March 1 1991 relating to the "marking of plastic explosives and sheet explosives for the purposes of detecting them".

20 According to an advantageous variant, the malleable solid explosive block of the invention contains, as weight percentages:

- from 0% to 2% of at least one additive, and
- for at least 98% (of its weight):
 - + from 85% to 95% and most advantageously from 87% to 90% of a pulverulent explosive charge (a single charge or a mixture of
25 charges of different nature and/or particle size), and
 - from 3% to 13% and most advantageously from 8% to 12% of a polyol polymer liquid of the type mentioned above (a single liquid or a mixture of at least two liquids).

The blocks of the invention generally have a mass of between 100 g and 5 kg. Said malleable solid explosive blocks may be considered as cakes (in the sense of the plastic explosive cakes of the prior art).

5 The blocks of the invention have rheological qualities and performance that are higher than those of the malleable explosive blocks incorporating a plasticizer. They can be stored and used as cakes of high mass (for example several kilograms) without any precaution with reference to their mechanical strength, unlike the plasticizer-free malleable explosives of the prior art.

10 Without wishing to be bound by any theory, it is thought that the explosive charge and the polyol polymer liquid forming the malleable explosive of the invention interact to give said explosive particularly advantageous rheological properties. The presence of hydroxyl (OH) functions in the chemical formula of the polyol polymers (hydroxyl
15 functions not present in the chemical formulae of the polymeric binders of the prior art) is most certainly the origin of this particular interaction.

According to its second subject, the present invention relates to a process for obtaining a malleable solid explosive as described above (first subject of said invention). Said process comprises:

- 20 - the production of a paste by blending a mixture consisting, to a least 98% of its weight, of a pulverulent explosive charge and a liquid (as mentioned above),
- the molding of said paste in one (or more) molds and the removal of said molded paste from the mold(s) to produce one
25 (or more) blocks of said malleable solid explosive, or cutting of said paste to obtain blocks of said malleable solid explosive.

It is understood that this is a process by analogy recommended for the first time in a context of mixtures: pulverulent explosive charge + polyol polymer liquid as mentioned above.

The blending of pulverulent explosive charge + polyol polymer liquid, to obtain the paste, may be performed at room temperature or at elevated temperature. The blending temperature is obviously compatible with the safety standards, with regard to the exact nature of the explosive charge. In this spirit, it is generally less than 80°C.

The process for obtaining the novel explosive of the invention may be performed in continuous or batch mode.

Three implementation variants of said process are given in detail below, for purely illustrative purposes. According to a first variant: the constituents of the blocks of the invention are mixed together at elevated temperature (typically 60°C) in a blender; the mixture obtained (the mass of which may range, for example, from 100 kg to 5 tons) is then discharged in the blender and introduced into a funnel terminated with an endless screw; said mixture is entrained by the endless screw so as to be deposited in molds (whose volume may be variable, typically between 100 and 700 cm³ depending on the targeted applications, generally 350 cm³); said mixture contained in each molds is then removed from the molds to obtain a malleable explosive block. According to a second variant, the mixture is obtained by continuous hot blending and then directly extruded in molds (whose volume may be variable, typically between 100 and 700 cm³ according to the targeted applications, generally 350 cm³). According to a third variant, the mixture is obtained by continuous hot blending and is then extruded directly, the extruded rod being chopped so as to obtain blocks of determined mass directly.

The mass per unit volume (density) of the explosive block obtained may vary as a function of the amount of air trapped in the explosive charge during the production process. Said mass per unit volume (density) is advantageously between 1300 and 1700 kg/m³.

In its product and process aspects, the invention is now illustrated, in an entirely nonlimiting manner, by the example below for the

preparation of a malleable solid explosive according to the invention (from its constituent ingredients).

Table 1 below shows the composition of said malleable solid explosive according to the invention.

5 The liquid is a hydroxytelechelic polybutadiene (HTPB). It is the HTPB R45HTLO sold by the company Sartomer ($M_n \approx 3000$). It is incorporated to about 10% by weight.

 The pulverulent explosive charge (which is incorporated to 88% by weight) consists of RDX. It more specifically consists of two RDX
10 charges of different particle size, referenced as charge 1 and charge 2 in Table 1. The particle size of these two charges 1 and 2 is given by three values read on the cumulative curve of the volume percentage of particles as a function of the diameter (equivalent spherical diameter) of the particles, which is cumulative according to increasing diameters:

15 D_{10} : diameter for which the cumulative volume percentage is equal to 10%;

D_{50} : diameter for which the cumulative volume percentage is equal to 50%;

20 D_{90} : diameter for which the cumulative volume percentage is equal to 90%.

 The weight composition of the malleable solid explosive block moreover contains additives (an antioxidant, an anti-age-curing agent and a chemical marker), to less than 2% of its total weight.

Table 1

Composition of the malleable solid explosive block			
Constituents		Weight percentage (%)	Particle size
Liquid	Hydroxytelechelic polybutadiene	10.4	/
Explosive charge	Charge 1: RDX	67	d ₁₀ =40 µm, d ₅₀ =100 µm, d ₉₀ =220 µm.
	Charge 2: RDX	21	d ₁₀ =1 µm, d ₅₀ =4 µm, d ₉₀ =10 µm.
Antioxidant	2,2-Methylenebis(4-methyl-6-tert-butyl)phenol	0.4%	/
Chemical marker	2,3-Dimethyl-2,3-dinitrobutane	1	/
Anti-age-curing agent	Soybean lecithin	0.2	/

The constituents of the malleable solid explosive block of the invention are blended at elevated temperature (60°C +/- 10°C), each blending operation using about 200 kg of material. The paste obtained is then emptied out and introduced into a funnel equipped with an endless screw in order to fill the molds. The volume of the molds is about 50 cm³. The malleable explosive solid block generated in each mold is then stripped from the mold to obtain a malleable explosive cake of about 0.5 kg.

The mass per unit volume (density) of the explosive cakes obtained via this process may vary as a function of the amount of air

trapped in the paste during the process. Said mass per unit volume (density) is between 1480 and 1520 kg/m³.

CLAIMS

1. A malleable solid explosive, characterized in that it is in the form of a block consisting, for at least 98% of its weight, of a pulverulent explosive charge and of a liquid chosen from polyol polymers of the group
5 of polyisobutylene polyols, polybutadiene polyols, polyether polyols, polyester polyols and polysiloxane polyols, whose number-average molecular mass is between 500 and 10 000, and mixtures thereof.

2. The malleable solid explosive as claimed in claim 1, characterized in that said pulverulent explosive charge represents at least
10 85% by weight relative to the total weight of said block.

3. The malleable solid explosive as claimed in claim 1 or 2, characterized in that said explosive charge is chosen from octogen, hexogen, pentrite, CL20, TATB, ONTA, HNS, DADNE and mixtures thereof, and advantageously from octogen, hexogen, pentrite and CL20.

15 4. The malleable solid explosive as claimed in any one of claims 1 to 3, characterized in that said liquid is chosen from said polybutadiene polyols and mixtures thereof; in that said liquid advantageously consists of a hydroxytelechelic polybutadiene.

5. The malleable solid explosive as claimed in any one of
20 claims 1 to 4, characterized in that said block contains up to 2% by weight of at least one additive.

6. The malleable solid explosive as claimed in claim 5, characterized in that said at least one additive is chosen from: antioxidants, anti-age-curing agents and chemical detection markers.

7. The malleable solid explosive as claimed in any one of claims 1 to 6, characterized in that said block contains:

- from 0 to 2% by weight of at least one additive, and
- for at least 98% of its weight :
 - 5 + from 85% to 95% and advantageously from 87% to 90% by weight of said explosive charge,
 - + from 3% to 13% and advantageously from 8% to 12% by weight of said liquid.

8. The malleable solid explosive as claimed in any one of
10 claims 1 to 7, characterized in that said block or cake has a mass of between 100 g and 5 kg.

9. A process for obtaining a malleable solid explosive as claimed in any one of claims 1 to 8, characterized in that it comprises:

- the production of a paste by blending a mixture consisting, for
15 at least 98% of its weight, of a pulverulent explosive charge and of a liquid chosen from polyol polymers of the group of polyisobutylene polyols, polybutadiene polyols, polyether polyols, polyester polyols and polysiloxane polyols, the number-average molecular mass of which is between 500 and 10 000,
20 and mixtures thereof,
- the molding of said paste in one (or more) molds and the removal from said molded paste from the mold(s) to obtain one (or more) blocks of said malleable solid explosive or the cutting of said paste to obtain blocks of said malleable solid explosive.

25 10. The process as claimed in claim 9, characterized in that said blending is performed at room temperature or at elevated temperature, at a temperature of less than or equal to 80°C.

11. The process as claimed in claim 9 or 10, characterized in that it is performed in continuous or batch mode.