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US-B1- 6 405 627
US-B1- 6 960 267

The invention concerns detonator-sensitive assembled booster charges for use in blasting engineering.

5 Insensitive, non-toxic and inexpensive explosives, mostly based on ammonium nitrate, are preferentially used in civil blasting applications. In salt mining or tunnel driving, for example, so-called pumping explosives are used in addition to the long familiar ANFO. Pump explosives are differentiated into emulsion explosives and suspension explosives (slurries, explosive slurries).

10 ANFO (Ammonium Nitrate Fuel, trade name e. g. ANDEX) is a mixture of porous ammonium nitrate and mineral oil or diesel oil (fuel oil), which is used in the mining industry as a safe-to-handle explosive.

In addition, if not sufficient for safe ignition, these explosives require so-called primary
15 explosives in conjunction with detonator-sensitive assembled initiation charges (boosters, amplifier charges or primers). Primary explosives can be found in commercial detonators. Primary explosives are characterized by high sensitivity to friction, shock, impact and heat. Mercury fulminate, for example, can already be detonated by heating to 160°C (detonating cord) or by a 2 kg drop hammer falling from a height of 4 cm. Initial detonation with blasting
20 caps was invented in 1862 by Alfred Nobel. Important primary explosives are mercury fulminate, lead azide, silver azide, silver acetylide, silver fulminate, diazodinitrophenol, lead picrate (trinitrophenol lead), lead styphnate (lead trinitroresorcinate), tetracene, nickel hydrazine nitrate (NHN), hexamethylene triperoxide diamine (HMTD), acetone peroxide (DADP, TATP or APEX), 3-nitrobenzenediazonium perchlorate, mercury azides, tetraamine
25 copper (II) chlorate (TACC) and copper acetylide.

Pressed cylindrical explosive devices made of tetryl, trinitrotoluene, phlegmatized (reduction of sensitivity) hexogen, pentaerythritol tetranitrate (PETN), picric acid and other explosives are usually used as detonator-sensitive assembled booster charges, also referred to as initial
30 gain detonator or IG detonator. Common to all these substances is a greater sensitivity to the initial pulse than that of the explosive of the main charge (e. g. ANFO, cast TNT, powdery explosives). Primer cartridges of gelatinized explosives are often used in rock blasting as an additional amplification charge to initiate the main charge of powdery explosives or emulsion explosives. The weight and the shape of the IG detonator are calculated so that, at
35 detonation, a pulse is produced that ensures the triggering of the detonation of the main charge and the desired detonation behavior. The initiation of the IG detonator is triggered by a blasting cap, an electric detonator or a NE-igniter (non-electric igniter).

The problem with the IG detonators used to date is that they either consist of long term no longer available military explosives (pressed TNT, cast Composition B, etc), or that classic primer cartridges made of gelatinous explosives (dynamite successors on the basis of blasting oil) are used, which becomes problematic in the long term. Besides the increased health hazard from nitric acid ester, the complicated and hazardous production and the associated high cost are a significant issue.

US 3,902,933 A discloses an initial explosive charge for detonation of nitromethane. The initial explosive charge is formed by a polyurethane foam containing dispersed microspheres. The microspheres can be hollow glass microspheres, resin beads, ceramic beads, etc.

Further disclosed, in US 4,334,476 A, is an initial explosive charge for granular or liquid explosives, with an interior channel to hold the ignition device, whereby the interior channel exhibits a small wall thickness so as to improve the detonation. This ensures the separation of the liquid explosive and the ignition device.

The document US 5 970 841 A discloses a device for detonation of explosives by a two-component explosive product including a storage for this explosive, which is being flexible and comparted. Nitromethane and amines as well as hollow glass microsphere are disclosed as possible explosives. Furthermore it could learned that the explosive mixture is mixed on site and that the components are filled within the pouch by a sleeve.

The document US 3 338 165 A discloses a detonation cord filled with a stabilized sensitized explosive mixture of nitromethane and the cavity-forming means. The cavity-forming means are preferably resin balloon, with a particle diameter from about 2 to about 360 microns and which are added to the nitromethane in an amount 0,1 to about 20%. The explosive mixture is intended for use in ignition devices.

The document US 6 405 627 B1 discloses a kit for manufacturing of an explosive mixture for detonation of land mine. The kit comprises a first container with a nitroparaffin, e.g. nitromethane, and a second container with sensitizing means, which for example comprises a mixture of fumed silica and hollow glass microsphere.

Finally, US 3,797,392 A discloses microspheres, used for the sensitization of liquid explosives. These microspheres, such as hollow glass spheres, ceramic microspheres or

silicon carbide, are dispersed in the liquid explosive right away and subsequently ignited. The use of open-pored polyurethane foams is described as well.

Therefore, the task of the invention is to specify an IG detonator that can be used safely, is
5 inexpensive and safe to manufacture, and can be handled with no risk to health.

The task is solved with a detonator-sensitive booster charge according to Claim 1. Advantageous embodiments are specified in the dependent claims.

10 According to the invention, a detonator-sensitive assembled booster charge comprising a mixture including nitromethane and a cavity-forming means, in which the cavity-forming means is configured as a hollow glass microsphere, as well as a slot for an ignition device, is suggested.

15 Surprisingly, it was found that nitroalkanes are well-suited for use in detonator-sensitive booster charges.

Nitroalkanes can be activated chemically, e. g. by addition of amine, and/or mechanically via the creation of small hollow spaces or gas-filled cavities (foaming), i.e. they become
20 detonator sensitive and behave like volatile explosives. In order to maintain a uniform distribution of the cavity formers, the addition of a thixotropic agent is indicated. Such mixtures are disclosed in US 3,713,915.

According to the invention the nitroalkane is nitromethane.

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Nitromethane mixtures, which are produced with commercially available hollow glass microspheres (glass microballoons, GMB) and which detonate at more than 6000 m/s and are detonator-sensitive, are also known (Presles et al. Shock Waves, April 1995, Volume 4, Issue 6, p. 325-329).

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In one embodiment of the invention, the detonator-sensitive booster charge is made of a liquid-impermeable material. This prevents leaking of the nitroalkane.

In a further embodiment of the invention, the detonator-sensitive booster charge exhibits a
35 concave curvature arranged on the opposite side of the slot for the ignition device. In the sense of the present invention, a concave curvature is a conical or hemispherical curvature on the direction of the center of the booster charge. With the concave curvature, the effect of

a hollow charge is achieved, which results in an increased detonation velocity. The curvature causes the energy released by the detonation to be focused in this direction. For this reason, the booster charge is inserted with the concave curvature in the direction of the main charge. The advantageous design with concave curvature significantly increases the effectiveness of the inventive booster charge.

In a further embodiment of the invention, the concave curvature exhibits a metallic coating. The metallic coating can be made of aluminum and applied to the surface of the concave curvature by spraying, steaming or as a metallic film. The metallic coating of the concave curvature affects an intensifying initial pulse in a specified direction.

The concave curvature with a metallic coating is of particular importance for achieving a high chemical implementation rate, in which the implementation process comes very close to the theoretical value. This significantly reduces the level of harmful substances in the borehole column charge for the commercial explosives to be activated.

In another embodiment of the invention, the ignition device is a blasting cap, a detonating cord or a non-electric detonator.

In a further embodiment of the invention, the detonator-sensitive booster charge exhibits a suitable wall thickness. This ensures a secure ignition transfer from the cap or the cord to the nitroalkane mixture. The wall thickness is dependent on the material of the wall as well as the mixture used.

According to the invention the cavity-forming means is configured as a hollow glass microsphere.

In a further embodiment of the invention, the cavity-forming means is configured as a hollow glass microsphere with a grain size of 20-200 μm , preferably 40-150 μm , particularly preferred 80-120 μm .

In a further embodiment of the invention, the cavity-forming means is configured as a hollow glass microsphere with a grain size of substantially 100 μm .

According to the invention, the mixture includes Aerosil. In this context Aerosil is a fumed silica.

In a further embodiment of the invention, the mixture exhibits 1.5—10 weight %, preferably 3-8 weight %, particularly preferred 5-7 weight % Aerosil, 0.2-10 weight %, preferably 0.5-5 weight %, particularly preferred 0.8-2 weight % hollow glass microspheres and 85-98,3 weight %, preferably 89-95, particularly preferred 91-93 weight % nitromethane.

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In a further embodiment of the invention, the mixture exhibits 6.5 weight % Aerosil, 1 weight % hollow glass microspheres with a grain size of substantially 100 μm and 92.5 weight % nitromethane.

10 In a further embodiment, the mixture also comprises at least one oxygen-containing compound selected from the nitrates group to increase the oxygen balance. In one design of the embodiment, the oxygen-containing compound is ammonium nitrate.

The use of the inventive detonator-sensitive booster charge is also the subject matter of the
15 invention.

The inventive detonator-sensitive booster charges are used to initiate non-detonator-sensitive commercial explosives, preferentially in boreholes on the surface and below ground, to initiate larger amplifier charges and for direct use for special blasting (avalanches, ice, etc.). In particular, the inventive detonator-sensitive booster charges are used for the
20 initiation of explosives in mining applications and tunnel construction.

In doing so the inventive detonator-sensitive booster charges exhibit the following advantages:

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Detonation velocities of ca. 6000 m/s are achieved with the inventive detonator-sensitive booster charges, allowing the detonation of non-detonator-sensitive explosives. Moreover, no nitroaromatics, which are suspected to be carcinogenic, and no nitroesters, which are physiologically problematic due to possible vasodilation, are formed when the detonator-sensitive booster charges are used. Health problems among users can thus be avoided. In
30 addition, the inventively preferred nitroalkane nitromethane is an inexpensive product that, due to the gas-phase nitration of propane, is available for the long term - even when recycled military explosives become scarce.

35 Nitromethane is also not a classic explosive, which makes transport and storage inexpensive, and is of storage class 3 (flammable liquids). In addition, nitromethane has low toxicity: LD50 oral rat: 940 mg/kg, WHC 2.

It is also advantageous that, in the event of damage, the inventive detonator-sensitive booster charges "deactivate" themselves by complete volatilization of the nitromethane into the air.

5

The inventive detonator-sensitive booster charges are designed to be absolutely waterproof and temperature-resistant. There is no exudation of fluids. Thus, because there are no chemical reactions between the mixture components, the inventive detonator-sensitive booster charges in a mixture with Aerosil and GMBs have a practically unlimited shelf life.

10

Moreover, the manufacturing of the inventive detonator-sensitive booster charges invention does not require dangerous melting processes. In addition, no long waiting period is necessary after mixing of the components, which is why manufacturing can be easily and safely (away from people) automated.

15

It is also important that the components in the mixture are not explosive materials, necessitating only minor storage and transportation costs.

Preferred embodiments of the invention result from combinations of the claims or individual features thereof.

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In the following, the invention will be described in detail with reference to several design examples. The design examples are intended to describe the invention without limiting it.

25 In one design example of the invention, pure ammonium nitrate and ANFO (in each case with 13 g of the inventive composition in a cylindrical booster charge) with the following composition were brought to a detonative reaction: 6.5% Aerosil, 1% GMBs ca 100 μm , 92.5% nitromethane.

30 In the process, detonation velocities of ca. 4500 m/s were measured, which indicates adequate suitability of the mixture for the initiation of non-detonator-sensitive commercial explosives to initiate larger amplifier charges and for direct use for special blasting (avalanches, ice, etc.).

Patentkrav

- 5 1. Sprængkapselfølsom konfektioneret initieringsladning til sprængtekniske anvendelser omfattende en blanding, der omfatter nitromethan og et hulrumsdannende middel, hvor det hulrumsdannende middel er udformet som hul mikrogaskugle, og aerosil samt en optagelse til en tændanordning, hvor initieringsladningen er udformet vandfast og temperaturbestandigt.
- 10 2. Sprængkapselfølsom initieringsladning ifølge krav 1, **kendetegnet ved, at** initieringsladningen er udformet af et væskeuigennemtrængeligt materiale.
3. Sprængkapselfølsom initieringsladning ifølge et af kravene 1 eller 2, **kendetegnet ved, at** initieringsladningen har en konkav krumning, der er anbragt på den modsatte side af optagelsen til tændanordningen.
- 15 4. Sprængkapselfølsom initieringsladning ifølge et af de foregående krav, **kendetegnet ved, at** den konkave krumning har en metallisk coating.
- 20 5. Sprængkapselfølsom initieringsladning ifølge et af de foregående krav, **kendetegnet ved, at** tændanordningen er en sprængkapsel, sprængsnor eller en ikke-elektrisk tændsats.
- 25 6. Sprængkapselfølsom initieringsladning ifølge krav 8, **kendetegnet ved, at** det hulrumsdannende middel er udformet som hul mikrogaskugle med en kornstørrelse på 20-200 µm, fortrinsvis 40-150 µm, særligt foretrukket 80-120 µm.
- 30 7. Sprængkapselfølsom initieringsladning ifølge et af de foregående krav, **kendetegnet ved, at** blandingen omfatter 1,5-10 vægtprocent, fortrinsvis 3-8 vægtprocent, særligt foretrukket 5-7 vægtprocent aerosil, 0,2-10 vægtprocent, fortrinsvis 0,5-5 vægtprocent, særligt foretrukket 0,8-2 vægtprocent hul mikrogaskugle og 85-98,3 vægtprocent, fortrinsvis 89-95, særligt foretrukket 91-93 vægtprocent nitromethan.
- 35 8. Sprængkapselfølsom initieringsladning ifølge et af de foregående krav, **kendetegnet ved, at** blandingen omfatter 6,5 vægtprocent aerosil, 1 vægt-

procent hul mikroglasskugle med en kornstørrelse på i det væsentlige 100 µm samt 92,5 vægtprocent nitromethan.

5 **9.** Sprængkapselølsom initieringsladning ifølge et af de foregående krav, endvidere omfattende en oxygenholdig forbindelse, der er valgt fra gruppen af nitrater.

10 **10.** Anvendelse af en sprængkapselølsom initieringsladning ifølge et af kravene 1 til 9 til initiering af ikke-kapselølsomme industrielle sprængstoffer, fortrinsvis i borehuller over og under jordniveau, til initiering af større forstærkerladninger og til direkte anvendelse til specialsprængninger.

15 **11.** Anvendelse ifølge krav 10 til initiering af sprængstoffer ved bjerganvendelse og tunnelbygning.