Pyrotechnic millisecond delay charge for industrial detonators with delay time of explosion of 25 to 1,000 ms from initiation, the way of manufacture of the delay charge, and electric and non-electric detonator

Pyrotechnic delay charge that contains FeSiZr as combustible and Bi₂O₃ as oxidizer in proportion 50 ± 15 wt. % FeSiZr and 50 ± 15 wt. % Bi₂O₃. FeSiZr is an alloy of dominant elements Si, Zr, Fe and Ti with content of trace impurities originating from aluminosilicates. The limit representation of dominant elements in FeSiZr is as follows: Si at least 30 wt. %, Zr at least 10 wt. %, Fe at the most 25 wt. %, Ti at least 1 wt. %. The controller of combustion speed is the additive TiO₂ in the amount of up to 5 wt. % of the total weight.

The way of manufacture of the pyrotechnic millisecond delay charge in which FeSiZr with limit representation of dominant elements Si at least 30 wt. %, Zr at least 10 wt. %, Fe at the most 25 wt. % and Ti at least 1 wt. %, are prepared in the physical process of grinding to the particle size in the range of 1-10 μm, Bi₂O₃ to the particle size in the range of 1-10 μm, whereupon these two components in proportion 50 ± 10 wt. % FeSiZr and 50 ± 10 wt. % Bi₂O₃ are mechanically homogenized nad pelletized with pressure of 255 MPa, and after that are crushed to grading of 0.2 - 0.8 mm grain size. Finally, the charge is pressed into the delay tube with pressure of 280 MPa with column height of 5 up to 40 mm.

Industrial non-electric detonator has an enclosure in shape of a shell (1) with inserted detonation tube. In the enclosure there is created a space at least for the primary explosive and for the delay charge. The shell (1) closed at the bottom side has in its bottom part created a space (11) for the secondary explosive, which is from above closed with delay tube (12), in the cylindrical box of which there is placed primary explosive (13) and delay charge (14) above it. Over the delay charge (12) in shell (1) is inserted a sleeve (15) with amplifying charge (16) closed with cover (17), and inserted from the upper part into shell (1) there is the detonation tube (19), fitted with insulation (18) against the enclosure of the shell (1).

Industrial electric detonator has in shell (2) the fuse-head (25) inserted, with in-lead wires (26) fitted with insulation (27) against enclosure of the shell (2).
The invention relates to pyrotechnic millisecond delay charge for industrial detonators with explosion delay time of 25 to 1,000 ms from initiation. The charge is intended to be compacted into the delay tube, for detonators initiated by fusehead, by a blasting machine generated pulse, and also for detonators initiated by detonation tube non-electrically - by detonating wave, or by a blasting machine generated spark. It relates to electric detonators in a series connection or a series-parallel connection and to non-electric detonators as well, where the firing circuit is created by connecting of detonation tubes of non-electric detonators, especially in underground destruction of rocks, mining in stone quarries, underground mining of rocks and driving of tunnels.

The nature of the invention

The specified objective is reached by a pyrotechnic millisecond delay charge for both electric and non-electric industrial detonators with delay time of explosion of 25 to 1,000 ms from initiation, the subject-matter of which is the proportion according to the invention. It contains ferrosiliconzirconium (hereinafter referred to as FeSiZr) as combustible matter and bismuth ochre (hereinafter referred to as Bi2O3) as oxidizer. These are in proportion of 50 ± 15 wt. % FeSiZr and 50 ± 15 wt. % Bi2O3. FeSiZr is an alloy of dominant elements Si, Zr, Fe and Ti, containing also trace impurities originating from aluminosilicates, which are input substances in manufacture of alloys. The limit representation of dominant elements in FeSiZr according to the invention is as follows: Si at least 30 wt. %, Zr at least 10 wt. %, Fe at the most 25 wt. %, Ti at least 1 wt. %.

The technical field

At present, to reach the delay of detonators in the range of up to 1,000 milliseconds, pyrotechnic delay charges containing combustible matter and oxidizer are used. It is altogether Si, B, Zr, Ti metallic powders and Fe+Si+Cr, Si+Se+Fe, Zr+B, Zr+Ni alloys and others that are used as combustibles. Lead monoxide-dioxide and lead dioxides are mostly used as oxidizers. However, such charges contain heavy metals, which get into the environment after the detonator has been used. Therefore, there has been general endeavour aiming at excluding of heavy metals. There are known designs, e.g. according to SE patents 446180 and 457380, where oxidizers are carried out on a non-toxic tin base. Nevertheless, these designs are more demanding in terms of manufacture and have a negative impact on the possibility of time setting up. Also the design by the US patent 5654520 is known, where bismuth ochre is used as oxidizer and elementary silicon is used as combustible. A disadvantage of the solution according to this patent is the necessity of adding a big amount of various additives to achieve the function needed.

Survey of figures in the drawings

Both the electric and non-electric detonator is described in examples of execution by means of attached drawings where Figure 1 shows a non-electric detonator and Figure 2 shows an electric detonator.

Description

Technical field

[0001] The invention relates to pyrotechnic millisecond delay charge for industrial detonators with explosion delay time of 25 to 1,000 ms from initiation. The charge is intended to be compacted into the delay tube, for detonators initiated by fusehead, by a blasting machine generated pulse, and also for detonators initiated by detonation tube non-electrically - by detonating wave, or by a blasting machine generated spark. It relates to electric detonators in a series connection or a series-parallel connection and to non-electric detonators as well, where the firing circuit is created by connecting of detonation tubes of non-electric detonators, especially in underground destruction of rocks, mining in stone quarries, underground mining of rocks and driving of tunnels.

[0002] The invention also relates to the way of manufacture of the said charge.

[0003] The invention also relates to electric detonator on its own and is also meant as an independent invention of non-electric detonator, to be used together with the pyrotechnic delay charge.

The contemporary state of art

[0004] At present, to reach the delay of detonators in the range of up to 1,000 milliseconds, pyrotechnic delay charges containing combustible matter and oxidizer are used. It is altogether Si, B, Zr, Ti metallic powders and Fe+Si+Cr, Si+Se+Fe, Zr+B, Zr+Ni alloys and others that are used as combustibles. Lead monoxide-dioxide and lead dioxides are mostly used as oxidizers. However, such charges contain heavy metals, which get into the environment after the detonator has been used. Therefore, there has been general endeavour aiming at excluding of heavy metals. There are known designs, e.g. according to SE patents 446180 and 457380, where oxidizers are carried out on a non-toxic tin base. Nevertheless, these designs are more demanding in terms of manufacture and have a negative impact on the possibility of time setting up. Also the design by the US patent 5654520 is known, where bismuth ochre is used as oxidizer and elementary silicon is used as combustible. A disadvantage of the solution according to this patent is the necessity of adding a big amount of various additives to achieve the function needed.

[0005] The objective of the invention is to develop such a charge and weight ratios of combustible and oxidizer, which would not be intensive in terms of manufacture and costs, with minimum need of complete additives to achieve time variability and delay exactness. However, the solution should above all meet the condition of absence of heavy metals.

[0006] Again, the objective of the invention is to develop such a way of manufacture of the created delay charge that the resulting parameters agree with the defined ob-jective, and minimum manufacture costs are kept.

[0007] The objective of the invention is also to create electric and non-electric detonator, in which the created composition can be employed.

[0008] Both the electric and non-electric detonator is described in examples of execution by means of attached drawings where Figure 1 shows a non-electric detonator and Figure 2 shows an electric detonator.

The contemporary state of art

[0009] The specified objective is reached by a pyrotechnic millisecond delay charge for both electric and non-electric industrial detonators with delay time of explosion of 25 to 1,000 ms from initiation, the subject-matter of which is the proportion according to the invention. It contains ferrosiliconzirconium (hereinafter referred to as FeSiZr) as combustible matter and bismuth ochre (hereinafter referred to as Bi2O3) as oxidizer. These are in proportion of 50 ± 15 wt. % FeSiZr and 50 ± 15 wt. % Bi2O3. FeSiZr is an alloy of dominant elements Si, Zr, Fe and Ti, containing also trace impurities originating from aluminosilicates, which are input substances in manufacture of alloys. The limit representation of dominant elements in FeSiZr according to the invention is as follows: Si at least 30 wt. %, Zr at least 10 wt. %, Fe at the most 25 wt. %, Ti at least 1 wt. %.

[0010] The pyrotechnic charge can contain the additive, titanic oxide (hereinafter referred to as TiO2) in the amount of up to 5 wt. % as combustion speed controller.

[0011] In the pyrotechnic millisecond delay charge, the purity of the substance Bi2O3 is at least 90%.

[0012] In one of the advantageous executions of the pyrotechnic millisecond charge, the FeSiZr alloy consists of Si 52.1 wt. %, Zr 27.4 wt. %, Fe 12.7 wt. %, Ti 5.8 wt. % and impurities 2 wt. %, with Bi2O3 of purity 99.8 wt. %, in proportion of 52.8 wt % Bi2O3 and 47.2 wt. % FeSiZr.

[0013] In another execution, depending on the required qualities, the FeSiZr alloy consists of Si 52.1 wt. %, Zr 27.4 wt. %, Fe 12.7 wt. %, Ti 5.8 wt. %, impurities 2 wt. %, with Bi2O3 of purity 99.8 wt. %, in proportion 60.0 wt % Bi2O3 and 40.0 wt. % FeSiZr.

[0014] In another advantageous execution, which proves the variability of final qualities, the FeSiZr alloy consists of Si 63.5 wt. %, Zr 21.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi2O3 of purity 99.8 wt. %, in proportion 60.0 wt % Bi2O3 and 40.0 wt. % FeSiZr.

[0015] In another advantageous execution, the FeSiZr alloy consists of Si 63.5 wt. %, Zr 21.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi2O3 of purity 99.8 wt. %, in proportion 50.0 wt % Bi2O3 and 50.0 wt. % FeSiZr, eventually the FeSiZr alloy consists of Si 63.5 wt. %, Zr 21.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi2O3 of purity 99.8 wt. %, in proportion
55.0 wt % Bi₂O₃ and 45.0 wt % FeSiZr.

[0016] In an execution with TiO₂ additive, the FeSiZr alloy can consist of Si 63.5 wt. %, Zr 21.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi₂O₃ of purity 99.8 wt. % and with TiO₂ of purity 98 wt. %, in proportion 53.9 wt % Bi₂O₃, 44.1 wt % FeSiZr and 2.0 wt % TiO₂.

[0017] In another advantageous execution with TiO₂ additive, the FeSiZr alloy consists of Si 63.5 wt. %, Zr 21.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi₂O₃ of purity 99.8 wt. % and with TiO₂ of purity 98 wt. %, in proportion 52.3 wt % Bi₂O₃, 42.7 wt % FeSiZr and 5.0 wt % TiO₂.

[0018] The subject matter of the invention is also the way of manufacture of the pyrotechnic millisecond delay charge for electric and non-electric industrial detonators with delay time of explosion of 25 up to 1,000 ms from initiation. The principle of the way of manufacture consists in that ferrosilliconzirconium (hereinafter referred to as FeSiZr) with limit representation of the dominant elements Si at least 30 wt. %, Zr at least 10 wt. %, Fe at the most 25 wt. % and Ti at least 1 wt. %, is prepared, usually by physical grinding, to the particle size in the range from 1-10 μm, bismuth ochre (hereinafter referred to as Bi₂O₃) of purity at least 95% is also prepared to the particle size in the range of 1-10 μm. Then these two components in proportion 50 ± 10 wt. % FeSiZr and 50 ± 15 wt. % Bi₂O₃ are mechanically homogenized and pelletized with pressure of 255 MPa. Next, they are crushed to grading of 0.2 - 0.8 mm grain size.

[0019] Afterwards, the charge is pressed into the delay tube of the detonator under pressure of 280 MPa with the column height of 20 mm.

[0020] The principle of the way of manufacture according to the invention is also that up to 5 wt. % TiO₂ of purity at least 95%, prepared to particle size in the range of 1-10 μm, is added to FeSiZr and Bi₂O₃ before homogenization.

[0021] The subject matter of the non-electric industrial detonator with enclosure in the shape of a shell with inserted detonation tube is the fact that in the enclosure there is created a space at least for primary explosive and for delay charge, and the shell, which is closed at the bottom, has a space in the bottom part that has been created for secondary explosive, which space is closed with the delay tube from above. In its cylindrical box there is arranged primary explosive, and delay charge is above it. Above the delay tube, in the shell there is inserted a sleeve with amplifying composition, closed with a cover. A detonation tube, fitted with insulation against the enclosure, is inserted into the shell from the upper side.

[0022] The subject matter of the electric industrial detonator is that in the shell it has a fusehead inserted, with lead-in wires, which are fitted with insulation against the shell enclosure, the other technical features are the same as those of their non-electric detonator described above.

[0023] The main advantage, and at present a particularly appreciated enhanced effect, is the absence of heavy metals, seeing that the presence of heavy metals even in consumables, e.g. in mineral salt, apparently due to the way of mining, is a great issue in those parts of the world that are actively used for industry. The pyrotechnic charge is free of lead oxides or chromates, and free of barium. The benefit of this solution is that while the above mentioned main advantage is preserved, simplicity of manufacture and versatility of use for various intervals of required delay, even at high accuracy, are provided. The variability of delay is achieved due to the proportion of the basic components and it is not necessary to add any other additives. As far as the field of application is concerned, this solution appears to be very simple and practical and not demanding for technology or investment in terms of production.

Examples of execution of the invention

General information common for all examples of execution

[0024] Ferrosilliconzirconium (hereinafter referred to as FeSiZr) acts as combustible in the delay charge. Here is the definition thereof for the purposes of description of the invention:

An alloy of dominant elements Si, Zr, Fe, Ti with content of trace impurities originating from aluminosilicates, which are input substances in manufacture of alloys. The limit representation of dominant elements in FeSiZr for the purposes of the invention is as follows:

\[ \text{Si at least 30 wt. %} \]
\[ \text{Zr at least 10 wt. %} \]
\[ \text{Fe at the most 25 wt. %} \]
\[ \text{Ti at least 1 wt. %} \]

[0025] The FeSiZr alloy is prepared in the physical process of grinding to the particle size in the range of 1-10 μm.

[0026] Bismuth ochre (hereinafter referred to as Bi₂O₃) acts as oxidizer in the delay charge. Here is the definition thereof for the purposes of description of the invention:

A substance of purity at least 90%, prepared, usually by physical grinding, to the particle size in the range of 1-10 μm.

[0027] Titanium dioxide (hereinafter referred to as TiO₂) acts as additive in the delay charge, it does not participate actively in the process of combustion, it influences the combustion speed in the desired way.

[0028] A substance of purity at least 95%, prepared, usually by physical grinding, to the particle size in the range of 1-10 μm.
Example 1

[0029] In this example of execution, FeSiZr alloy with the following composition was used:

- Si 52.1 wt. %
- Zr 27.4 wt. %
- Fe 12.7 wt. %
- Ti 5.8 wt. %
- Impurities 2 wt. %

[0030] Further, Bi$_2$O$_3$ of purity 99.8 wt % was used.

[0031] FeSiZr and Bi$_2$O$_3$ were used in proportion 52.8 wt % Bi$_2$O$_3$ and 47.2 wt % FeSiZr.

[0032] The FeSiZr alloy was prepared to particle size 1.86 μm and Bi$_2$O$_3$ was prepared to particle size 1.98 μm.

[0033] The mixture was mechanically homogenized and pelletized with pressure of 255 MPa. Next, it was crushed to grading of grain size of 0.2 - 0.8 mm.

[0034] The composition so prepared is pressed into the delay tube of the non-electric detonator by means of pressure of 280 MPa with column height of 20 mm.

[0035] The average delay time of detonator explosion with this composition of delay charge is 267.4 ms and standard deviation 3.3 ms.

Example 2

[0036] In this example of execution, FeSiZr alloy with the following composition was used:

- Si 52.1 wt. %
- Zr 27.4 wt. %
- Fe 12.7 wt. %
- Ti 5.8 wt. %
- Impurities 2 wt. %

[0037] Further, Bi$_2$O$_3$ of purity 99.8 wt % was used.

[0038] FeSiZr and Bi$_2$O$_3$ were used in proportion 60.0 wt % Bi$_2$O$_3$ and 40.0 wt % FeSiZr.

[0039] The FeSiZr alloy was prepared to particle size 1.86 μm and Bi$_2$O$_3$ was prepared to particle size 1.98 μm.

[0040] The mixture was mechanically homogenized and pelletized with pressure of 255 MPa. Next, it was crushed to grading of grain size of 0.2 - 0.8 mm.

[0041] The composition so prepared is pressed into the delay tube of the non-electric detonator by means of pressure of 280 MPa with column height of 20 mm.

[0042] The average delay time of detonator explosion with this composition of delay charge is 235.8 ms and standard deviation 3.4 ms.

Example 3

[0043] In this example of execution, FeSiZr alloy with the following composition was used:

- Si 63.5 wt. %
- Zr 21.3 wt. %
- Fe 11.7 wt. %
- Ti 1.1 wt. %
- Impurities 2.4 wt. %

[0044] Further, Bi$_2$O$_3$ of purity 99.8 wt % was used.

[0045] FeSiZr and Bi$_2$O$_3$ were used in proportion 60.0 wt % Bi$_2$O$_3$ and 40.0 wt % FeSiZr.

[0046] The FeSiZr alloy was prepared to particle size 2.09 μm and Bi$_2$O$_3$ was prepared to particle size 1.98 μm.

[0047] The mixture was mechanically homogenized and pelletized with pressure of 255 MPa. Next, it was crushed to grading of grain size of 0.2 - 0.8 mm.

[0048] The composition so prepared is pressed into the delay tube of the non-electric detonator with pressure of 280 MPa with height of the column of 20 mm.

[0049] The average delay time of detonator explosion with this composition of delay charge is 247.5 ms and standard deviation 2.8 ms.

Example 4

[0050] In this example of execution, FeSiZr alloy with the following composition was used:

- Si 63.5 wt. %
- Zr 21.3 wt. %
- Fe 11.7 wt. %
- Ti 1.1 wt. %
- Impurities 2.4 wt. %

[0051] Further, Bi$_2$O$_3$ of purity 99.8 wt % was used.

[0052] FeSiZr and Bi$_2$O$_3$ were used in proportion 50.0 wt % Bi$_2$O$_3$ and 50.0 wt % FeSiZr. The FeSiZr alloy was prepared to particle size 2.09 μm and Bi$_2$O$_3$ was prepared to particle size 1.98 μm.

[0053] The mixture was mechanically homogenized and pelletized with pressure of 255 MPa. Next, it was crushed to grading of grain size of 0.2 - 0.8 mm.

[0054] The composition so prepared is pressed into the delay tube of the non-electric detonator with pressure of 280 MPa with height of the column of 20 mm. The average delay time of detonator explosion with this composition of delay charge is 372.4 ms and standard deviation 3.4 ms.

Example 5

[0055] In this example of execution, FeSiZr alloy with the following composition was used:

- Si 63.5 wt. %
- Zr 21.3 wt. %
- Fe 11.7 wt. %
- Ti 1.1 wt. %

Further, Bi₂O₃ of purity 99.8 wt % and TiO₂ of purity 98 wt. % were used.

[0071] The FeSiZr alloy, Bi₂O₃ and TiO₂ were used in proportion 52.3 wt % Bi₂O₃, 42.7 wt. % FeSiZr and 5.0 wt % TiO₂.

[0072] The FeSiZr alloy was prepared to particle size 4.88 µm and Bi₂O₃ was prepared to particle size 1.98 µm and TiO₂ was prepared to particle size 0.45 µm.

[0073] The mixture was mechanically homogenized and pelletized with pressure of 255 MPa. Next, it was crushed to grading of grain size of 0.2 - 0.8 mm.

[0074] The composition so prepared is pressed into the delay tube of the non-electric detonator with pressure of 280 MPa with height of the column of 20 mm.

[0075] The average delay time of detonator explosion with this composition of delay charge is 640.4 ms and standard deviation 6.5 ms.

Example 8

This example of execution describes an industrial non-electric detonator, in which the pyrotechnic delay charge according to the above given examples of execution is used. The detonator has an enclosure in the shape of a shell with inserted detonation tube 17. In the bottom part of the enclosure there has been created a space for secondary explosive 11.

An industrial non-electric detonator with pyrotechnic delay charge that has an enclosure in the shape of a shell with inserted detonation tube 17. In the shell 1, which is closed at the bottom, space 11 for secondary explosive has been created in its bottom part, which is closed from above with the delay tube 12. In the cylindrical box of which primary explosive 13 is arranged and delay charge 14 over it. Over the delay tube 12 in the shell 1, the sleeve 15 with amplifying composition 16 is inserted, which is closed with cover 17. From above, detonation tube 19, fitted with insulation 18 against the enclosure of the shell 1, is inserted into shell 1.

Example 9

This example of execution describes an industrial electric detonator, in which the pyrotechnic delay charge 24 according to the above given examples of execution is used. The industrial electric detonator with pyrotechnic delay charge 24 has an enclosure in the shape of shell 2 with inserted fusehead 25 and it is fitted with in-lead wires 26. In the lower part of the enclosure there has been created space 21 for secondary explosive, which is closed with the delay tube 22 from above. In the cylindrical box of the delay tube 22 there is placed primary explosive 23 and delay charge 24 is placed over it. Over the delay tube 22, in the shell 2 there is inserted the fusehead 25 with in-lead wires 26. These are fitted with insulation 27 against the enclosure of shell 2.
The function of both detonator types is apparent from their design and does not differ from that of commonly used detonators.

**Industrial applicability**

The pyrotechnic delay charge according to the invention, the way of manufacture thereof and also industrial detonators with the delay charge can be employed in industrial applications. The charge can be employed especially in detonators in aboveground excavation of rocks and mining in stone quarries, in underground mining or driving of tunnels, in destructions and other similar specialized works.

**Claims**

1. Pyrotechnic millisecond delay charge for electric and non-electric industrial detonators with delay time of explosion of 25 to 1,000 ms from initiation, characterized in that it contains ferrosiliconzirconium (hereinafter referred to as FeSiZr) as combustible matter and bismuth ochre (hereinafter referred to as Bi\(_2\)O\(_3\)) as oxidizer in proportion 50 ± 15 wt. % FeSiZr and 50 ± 15 wt. % Bi\(_2\)O\(_3\), where FeSiZr is a an alloy of dominant elements Si, Zr, Fe and Ti with content of trace impurities originating from from aluminosilicates, which are input substances in manufacture of alloys, where the limit representation of dominant elements in FeSiZr is as follows: Si at least 30 wt. %, Zr at least 10 wt. %, Fe at the most 25 wt. %.

2. Pyrotechnic millisecond delay charge according to claim 1, characterized in that the combustible matter FeSiZr contains Ti at least 1 wt. %.

3. Pyrotechnic millisecond delay charge according to claim 1, characterized in that it contains the additive titanic oxide (hereinafter referred to as TiO\(_2\)) in the amount of up to 5 wt. % out of the total weight and in purity of the substance at least 95 wt. %. as combustion speed controller.

4. Pyrotechnic millisecond delay charge according to claim 1, characterized in that Bi\(_2\)O\(_3\) is a substance of at least 90% purity.

5. Pyrotechnic millisecond delay charge according to claim 1, characterized in that the FeSiZr alloy consists of Si 52.1 wt. %, Zr 27.4 wt. %, Fe 12.7 wt. %, Ti 5.8 wt. % and impurities 2 wt. %, with Bi\(_2\)O\(_3\) of purity 99.8 wt. %, in proportion 52.8 wt. % Bi\(_2\)O\(_3\) and 47.2 wt. % FeSiZr.

6. Pyrotechnic millisecond delay charge according to claim 1, characterized in that the FeSiZr contains Si 52.1 wt. %, Zr 27.4 wt. %, Fe 12.7 wt. %, Ti 5.8 wt. %, impurities 2 wt. %, with Bi\(_2\)O\(_3\) of purity 99.8 wt. %, in proportion 60.0 wt % Bi\(_2\)O\(_3\) and 40.0 wt. % FeSiZr.

7. Pyrotechnic millisecond delay charge according to claim 1, characterized in that the FeSiZr alloys contains Si 63.5 wt. %, Zr 21.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi\(_2\)O\(_3\) of purity 99.8 wt. %, in proportion 60.0 wt % Bi\(_2\)O\(_3\) and 40.0 wt. % FeSiZr.

8. Pyrotechnic millisecond delay charge according to claim 1, characterized in that the FeSiZr alloy contains Si 63.5 wt. %, Zr 21.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi\(_2\)O\(_3\) of purity 99.8 wt. %, in proportion 50.0 wt % Bi\(_2\)O\(_3\) nd 50.0 wt. % FeSiZr.

9. Pyrotechnic millisecond delay charge according to claim 1, characterized in that the FeSiZr alloy contains Si 63.5 wt. %, Zr 21.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi\(_2\)O\(_3\) of purity 99.8 wt. %, in proportion 55.0 wt % Bi\(_2\)O\(_3\) and 45.0 wt. % FeSiZr.

10. Pyrotechnic millisecond delay charge according to claim 2, characterized in that the FeSiZr alloy contains Si 63.5 wt. %, Zr 21.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi\(_2\)O\(_3\) of purity 99.8 wt. % and with TiO\(_2\) of purity 98 wt. %, in proportion 53.9 wt % Bi\(_2\)O\(_3\), 44.1 wt % FeSiZr and 2.0 wt % TiO\(_2\).

11. Pyrotechnic millisecond delay charge according to claim 2, characterized in that the FeSiZr alloy contains Si 63.5 wt. %, Zr 23.3 wt. %, Fe 11.7 wt. %, Ti 1.1 wt. %, impurities 2.4 wt. %, with Bi\(_2\)O\(_3\) of purity 99.8 wt % and with TiO\(_2\) of purity 98 wt. %, in proportion 52.3 wt % Bi\(_2\)O\(_3\), 42.7 wt % FeSiZr and 5.0 wt % TiO\(_2\).

12. The way of manufacture of pyrotechnic millisecond delay charge for electric and non-electric industrial detonators with delay time of explosion of 25 to 1,000 ms from initiation, characterized in that ferrosiliconzirconium (hereinafter referred to as FeSiZr) with the limit representation of dominant elements Si at least 30 wt. %, Zr at least 10 wt. %, Fe at the most 25 wt. %.
13. The way of manufacture of pyrotechnic millisecond delay charge according to claim 12, **characterized in that** FeSiZr is used containing at least 1 wt.% Ti or Ti is added to FeSiZr.

14. The way of manufacture of pyrotechnic millisecond delay charge according to claim 12, **characterized in that** the charge is pressed into the delay tube of the detonator with pressure of 280 MPa with column height of 5 to 40 mm.

15. The way of manufacture of pyrotechnic millisecond delay charge according to claim 10, **characterized in that** up to 5 wt. % TiO$_2$ of purity at least 95%, prepared to particle size in the range of 1-10 μm, is added to FeSiZr and Bi$_2$O$_3$ before homogenization.

16. Industrial non-electric detonator with pyrotechnic delay charge, which has an enclosure in the shape of a shell with inserted detonation tube, and in the enclosure there is created a space at least for primary explosive and for the delay charge, **characterized in that** the shell (1) closed at the bottom side has in its bottom part a space (11) created for secondary explosive, which is from above closed with the delay tube (12), in the cylindrical box of which there is placed primary explosive (13) and the delay charge (14) over it, where over the delay tube (12) in the shell (1) is inserted a sleeve (15) with amplifying charge (16) closed with cover (17), and there is inserted from above into shell (1) the detonation tube (19), fitted with insulation (18) against the enclosure of the shell (1).

17. Industrial electric detonator with pyrotechnic delay charge, which has an enclosure in the shape of a shell with inserted fusehead and is fitted with in-lead wires, and in the enclosure there is created a space at least for primary explosive and for the delay charge, **characterized in that** the shell (2) closed at the bottom side has in its bottom part a space (21) created for secondary explosive, which is from above closed with the delay tube (22), in the cylindrical box of which there is placed primary explosive (23) and the delay charge (24) over it, where over the delay tube (22) in the shell (2) there is inserted fusehead (25) with in-lead wires (26) fitted with insulation (27) against the enclosure of the shell (2).
REFERENCES CITED IN THE DESCRIPTION

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