

A method to produce pyrotechnical igniting mixtures
(PCT/DE99/01160 - original version)

The invention relates to a method for producing pyrotechnical igniting mixtures on the basis of metal powders or metal hydrides, potassium perchlorate and binding agents.

Pyrotechnical mixtures are mixtures of solid matter in mostly the powdery state whose components consist mainly of reducing agents and oxidizing agents. When a sufficient quantity of energy is supplied, e.g. in form of an igniting flame, an oxidation-reduction process is initiated: the pyrotechnical mixture will burn away more or less intensely depending on make-up and arrangement.

Pyrotechnical mixtures have numerous uses and are used, for example, as igniting heads of matchsticks, in flare and signal ammunition, in smoke and cloud bodies, in gas generators, e.g. for safety airbags and in numerous other arrangements in fireworks bodies.

Pyrotechnical mixtures are usually produced by dry mixing of the individual components. If this is performed by hand, the comminuted components are pressed through screens and mixed thoroughly. In the case of mixing by machines, the components of the pyrotechnical mixture are filled in the unmixed state into the receptacle, with optional prior comminution, and mixed in the same by stirrers, rotational movements of the mixing receptacle or devices that apply shearing forces. Suitable mixing devices are asymmetric moved mixers, tetrahedral mixers, planetary mixers or mixing apparatuses derived from or combined with the same.

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Pyrotechnical mixtures are often used as granulate, because they can be better poured and apportioned in this form. Granulation is performed by adding a suitable solvent to the dry mixture and mixing in special receptacles. In this process the solvent can already be contained in the binding agent in dissolved form, or the binding agent component which is swellable with the solvent or is soluble in the same is already located in powder form in the pyrotechnical mixture, so that on adding the solvent adhesive forces are able to form which finally lead to the granulate form. Special granulate mixers are provided for the formation of the granulate form. The solvent is removed again by subsequent drying, so that a pourable material is obtained that can be apportioned.

When the components of the pyrotechnical mixture are very fine or the energy stored in the same is very high, measures must be taken in order to keep the hazards manageable during production. The mechanical and thermal sensitivity of these mixtures is often so strong, that handling the same without suitable safety measures is not advisable.

Numerous safety regulations take into account the hazardousness during production. Accordingly, pyrotechnical mixtures are listed according to groups of hazardousness in the accident prevention regulations as issued by the social insurance institutions against occupational accidents. The regulations demand graded safety precautions in the production of the mixtures. The two most hazardous groups may no longer be mixed by hand. They are mixed automatically behind protective walls or in a separated room which is closed off from the control room by a resisting wall. This type of production is usually called

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"working under security". This applies primarily for dry powdery components.

If measures are taken during the mixing which reduce the ignitability and the mechanical or thermal sensitivity of the mixtures, reductions in the grading can be made for the above breakdown into groups. One such measure is mixing the components not in the dry state, but together with a liquid.

This method is used particularly during the mixture of pyrotechnical igniting mixtures. By adding solvents such as water, pyrotechnical igniting mixtures can be produced with considerably fewer hazards than in the dry state. The energy stored in the igniting mixtures is still so high, however, that the effects of an ignition caused by an accident prevent the processing by hand even in the wet state. Moreover, the mass of the mixture quantity must be kept low (usually under 100 grams), so that any ignition even during production remains securely manageable.

A further difficulty in this method is the dimensioning of the quantity of the liquid. On the one hand it must be large enough to clearly reduce the hazard of an ignition while mixing the pyrotechnical mixture. On the other hand, any increase in the quantity of liquid also increases the subsequent duration of drying. Moreover, the danger of cracking and shrinkage cavitation increases during drying. Cracks and shrinkage endanger the secure function of the igniting mixture during its ignition.

Since the liquid is simultaneously dosed in the subsequent dosing for the application during the production of the mixture, but is not involved in the actual conversion of

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the igniting mixture, the liquid content of the mixture must be precisely definable and must also be kept constant during the dosing. Only in such cases will the igniting mixtures have the same properties during the subsequent drying.

It is further known that liquid paste-like mixtures for pyrotechnical igniting mixtures with components of different density, solubility or electric environment, e.g. the formation of dipoles or charging in the same or opposite direction, are relatively difficult to handle. In the mixtures the various solid components have different sedimentation speeds, so that after a short dwell time the liquid and the solids separate and make the reproducible dosing of the mixture more difficult.

The invention is based on the object of providing a method to produce pyrotechnical igniting mixtures of the kind mentioned above with which the employed components can be mixed homogeneously and the hazard of an ignition can simultaneously be reduced considerably and a reproducible dosing is enabled.

This object is achieved in accordance with the invention by the features of claim 1.

Accordingly, a homogeneous suspension is produced from the individual components for the pyrotechnical igniting mixture with the help of a suitable liquid dispersing agent, with said suspension being produced with the help of ultrasonic sound. The mixture is dosed immediately thereafter in this consistency, e.g. in igniters or on igniting elements.

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The grain sizes of the employed solids, i.e. metal powder or metal hydrides and the potassium perchlorate, are smaller than 50 μm , preferably smaller than 20 μm .

In accordance with the invention, a suitable quantity of dispersing agent achieves both an optimal mixture of the components as well as a suitable viscosity of the suspension for the subsequent dosing. The energy required for the homogenous distribution of the components in the suspension is introduced into the mixture by cavitation. The cavitation is produced by ultrasonic sound with frequencies preferably higher than 16 kHz. During the implosion of the gas bubbles produced by the cavitation temperatures of approx. 5500°C and pressures up to 500 bar can be reached. As a result of the speed of the disintegration of the gas bubbles in a time interval of less than 1 μs and by the small magnitude of the gas bubbles which are usually smaller than 150 μm , the cooling speed during the implosion is so high that the heating of the suspension remains negligible. The chemical effects of ultrasonic sound have already been described by K. S. Suslick in the publication "Spektrum der Wissenschaft", Edition 4, pages 60ff, 1989, where essentially aspects of the sono-chemistry of liquids and solid surfaces as well as of suspended particles were examined.

It is a further feature of the invention that the components are mixed directly in the receptacle from which the dosing is made immediately after the production of the dispersion. This is easily possible by using respectively shaped sonotrodes. The mixtures are produced in cartridges which are thereafter inserted into a dosing apparatus. The liquid mixtures are then dosed with slight pressure or by

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vacuum into prepared igniter housings or on igniter elements.

In order to prevent sedimentations or coagulation effects in the course of the dosing process, the cartridges which contain the igniting mixture can be subjected to mechanical oscillations or sound waves.

Filling and re-filling processes after the mixing are avoided by performing the mixing directly in the dosing receptacle. Such processes could lead to incrustations or desiccated material on the walls, which should be avoided under all circumstances due to the explosive character of the mixture.

A further application of the invention by avoiding the hazards which may occur during the mixing of larger quantities is the dosing in a relatively small mixing space of components of the igniting mixture which are mixed preliminarily in suspension and which are not explosive or marginally explosive and the subsequent filling or dosing therefrom into an igniter shell. The mixing space can be provided in this process with a sonotrode connection or a mechanical sonotrode contact.

In this way, only as much of this actually hazardous mixture is produced as is required for an igniter. The production can be controlled mechanically in a more economic manner at a cycle speed which is high enough for series production. If a composition of the igniting mixture is chosen of potassium perchlorate, zirconium powder, a binding agent and a solvent, two suspension-like pre-mixes can be produced which are not or only marginally explosive, namely as the one component the potassium perchlorate

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dispersed in the solvent and as the second component the zirconium powder dispersed in the solvent, with the binding agent already being dissolved in the solvent.

In summary, the method in accordance with the invention to produce pyrotechnical igniting mixtures on the basis of metal powders, metal hydrides, potassium perchlorate and binding agents therefore consists of the following method steps:

1. Weighing and filling the components or pre-mixes which are not or only marginally explosive into a mixing or dosing cartridge or metering cartridge;
2. production of the mixture in the cartridge or a small mixing space by application of ultrasonic sound;
3. dosing of the pyrotechnical igniting mixture, unless the mixing has been performed anyway in the receptacle used for the application of the pyrotechnical igniting mixture.

Thereafter the igniting mixtures are relieved of the remaining dispersing agents, which is performed by drying for example, and then supplied to further processing.

A composition of the igniting mixture as illustrated by way of an example is as follows:

55 % zirconium powder
43 % potassium perchlorate
2 % binding agent;

all percentage figures are given in percent by weight.

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The ratio of solids to dispersing agent is variable and is usually in the range of 70 to 80 % solids.

Titanium or zirconium, or their hydrides respectively, are preferably used as metal. The binding agent is preferably chosen from the group of the fluorinated polymeric aliphatic compounds.

The dispersing agent preferably acts as a solvent for the binding agent and preferably comes from the family of aliphatic ketones. Acetone or methyl ethyl ketone have proven to be suitable for this purpose.

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Claims

1. A method for producing pyrotechnical igniting mixtures on the basis of metal powders or metal hydride powders, potassium perchlorate and binding agents, characterized in that the powdery components of the metal powders, the metal hydrides of potassium perchlorate and the binding agents are mixed with a liquid dispersing agent as a suspension under the application of ultrasonic sound and are dosed in this consistency after the production.
2. A method to produce pyrotechnical igniting mixtures on the basis of metal powders or metal hydride powders, potassium perchlorate and binding agents, characterized in that the powdery components made of metal, metal hydride, potassium perchlorate and the binding agent are mixed with a liquid dispersing agent in a suspension by using ultrasonic sound directly in a housing receiving the pyrotechnical igniting mixture.
3. A method as claimed in claim 1 or 2, characterized in that the employed powdery components of metal, metal hydride and potassium perchlorate have a grain size of $< 50 \mu\text{m}$, preferably $< 20 \mu\text{m}$.
4. A method as claimed in one of the preceding claims, characterized in that titanium or zirconium, or their hydrides, are used as metal.
5. A method as claimed in one of the preceding claims, characterized in that the binding agent is chosen from the family of the fluorinated polymeric aliphatic

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compounds.

6. A method as claimed in one of the preceding claims, characterized in that the dispersing agent acts as a solvent for the binding agent.
7. A method as claimed in one of the preceding claims, characterized in that the dispersing agent is chosen from the family of the aliphatic ketones.
8. A method as claimed in claim 7, characterized in that acetone or methyl ethyl ketone is used as a binding agent.
9. A method as claimed in one of the preceding claims, characterized in that for the purpose of producing the finished mixture of the igniting mixtures suspensions of pre-mixes which are not or only marginally explosive are produced from the individual components of the igniting mixture, which thereafter are mixed in small quantities into the pyrotechnical igniting mixture.
10. A method as claimed in claim 9, characterized in that the mixing for the pyrotechnical igniting mixture is performed directly in a housing for receiving the same.
11. A method as claimed in one of the preceding claims, characterized in that the mixture is made to oscillate during the dosing.
12. A method as claimed in claim 11, characterized in that sound waves are introduced into the mixture.

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Abstract

Pyrotechnical igniting mixtures are made on the basis of metal powders or metal hydride powders, potassium perchlorate and binding agents. In order to obtain a homogenous mixture it is proposed to mix the powdery components with a liquid dispersing agent in a suspension with the help of ultrasonic sound and to perform dosing in this consistency. The mixture into a suspension can also be performed directly in a housing provided for receiving the pyrotechnical igniting mixture.

A method to produce pyrotechnical igniting mixtures

(PCT/DE99/01160 - amended version as annexed to the international preliminary examination report)

The invention relates to a method for producing pyrotechnical igniting mixtures on the basis of metal powders or metal hydrides, potassium perchlorate and binding agents.

Pyrotechnical igniting mixtures are mixtures of solid matter in mostly the powdery state whose components consist mainly of reducing agents and oxidizing agents. When a sufficient quantity of energy is supplied, e.g. in form of an igniting flame, an oxidation-reduction process is initiated: the pyrotechnical mixture will burn away more or less intensely depending on make-up and arrangement.

Pyrotechnical igniting mixtures have numerous uses and are used, for example, as igniting heads of matchsticks, in flare and signal ammunition, in smoke and cloud bodies, in gas generators, e.g. for safety airbags, and in numerous other arrangements in fireworks bodies.

Pyrotechnical igniting mixtures are usually produced by dry mixing of the individual components. If this is performed by hand, the comminuted components are pressed through screens and mixed thoroughly. In the case of mixing by machines, the components of the pyrotechnical mixture are filled in the unmixed state into the receptacle, with optional prior comminution, and mixed in the same by stirrers, rotational movements of the mixing receptacle or devices that apply shearing forces. Suitable mixing devices are asymmetric moved mixers, tetrahedral mixers, planetary mixers or mixing apparatuses derived from or combined with the same.

Pyrotechnical igniting mixtures are often used as granulate, because they can be better poured and apportioned in this form. Granulation is performed by adding a suitable solvent to the dry igniting mixture and mixing in special receptacles. In this process the solvent can already be contained in the binding agent in dissolved form, or the binding agent component which is swellable with the solvent or is soluble in the same is already located in powder form in the pyrotechnical mixture, so that on adding the solvent adhesive forces are able to form which finally lead to the granulate form. Special granulate mixers are provided for the formation of the granulate form. The solvent is removed again by subsequent drying, so that a pourable material is obtained that can be apportioned.

When the components of the pyrotechnical igniting mixture are very fine or the energy stored in the same is very high, measures must be taken in order to keep the hazards manageable during production. The mechanical and thermal sensitivity of these igniting mixtures is often so strong, that handling the same without suitable safety measures is not advisable.

Numerous safety regulations take into account the hazardousness during production. Accordingly, pyrotechnical mixtures are listed according to groups of hazardousness in the accident prevention regulations as issued by the social insurance institutions against occupational accidents. The regulations demand graded safety precautions in the production of the mixtures. The two most hazardous groups may

no longer be mixed by hand. They are mixed automatically behind protective walls or in a separated room which is closed off from the control room by a resisting wall. This type of production is usually called "working under security". This applies primarily for dry powdery components.

If measures are taken during the mixing which reduce the ignitability and the mechanical or thermal sensitivity of the mixtures, reductions in the grading can be made for the above breakdown into groups. One such measure is mixing the components not in the dry state, but together with a liquid.

This method is used particularly during the mixture of pyrotechnical igniting mixtures. By adding solvents such as water, pyrotechnical igniting mixtures can be produced with considerably fewer hazards than in the dry state. The energy stored in the igniting mixtures is still so high, however, that the effects of an ignition caused by an accident prevent the processing by hand even in the wet state. Moreover, the mass of the mixture quantity must be kept low (usually under 100 grams), so that any ignition even during production remains securely manageable.

A further difficulty in this method is the dimensioning of the quantity of the liquid. On the one hand it must be large enough to clearly reduce the hazard of an ignition while mixing the pyrotechnical mixture. On the other hand, any increase in the quantity of liquid also increases the subsequent duration of drying. Moreover, the danger of cracking and shrinkage cavitation increases during drying. Cracks and shrinkage endanger the secure function of the igniting mixture during its ignition.

Since the liquid is simultaneously dosed in the subsequent dosing for the igniter during the production of the mixture, but is not involved in the actual conversion of the igniting mixture, the liquid content of the mixture must be precisely definable and must also be kept constant during the dosing. Only in such cases will the igniting mixtures have the same properties during the subsequent drying.

It is further known that liquid paste-like mixtures for pyrotechnical igniting mixtures with components of different density, solubility or electric environment, e.g. the formation of dipoles or charging in the same or opposite direction, are relatively difficult to handle. In the mixtures the various solid components have different sedimentation speeds, so that after a short dwell time the liquid and the solids separate and make the reproducible dosing of the mixture more difficult, which again impairs the quality of the igniter.

The invention is based on the object of providing a method to produce pyrotechnical igniting mixtures of the kind mentioned above with which the employed components can be mixed homogeneously, the hazard of an ignition can simultaneously be reduced considerably and a reproducible dosing is enabled.

This object is achieved in accordance with the invention by the features of claim 1.

Accordingly, several homogeneous suspensions are produced from the individual components for the pyrotechnical igniting mixture with the help of suitable liquid dispersing agents, with said suspensions not being explosive or only marginally so. Said suspensions are mixed in small quantities with the

help of ultrasonic sound. The mixture is dosed in this consistency immediately thereafter for the igniter in the respectively desired quantity, e.g. in igniters or on igniting elements, whereupon the dispersing agents are removed from the dosed quantity.

The application of ultrasonic sound on liquid mixtures made of several components is known per se; in DE-A1-27 12 603 for example, a method and an apparatus for the modification of the characteristics of a liquid have been described, with the said several components of the liquid being homogenized with the help of ultrasonic sound while flowing through a pipe. It is also known from Soviet patent applications 2050963 and 2056926 to use ultrasonic dispersing mixers in order to thoroughly mix different components, particularly in the foodstuff area. The homogenization or mixing is performed in all these mixing methods in a continuous manner. A respective dosing or drying of the dosed mixture is not provided. Moreover, these methods do not consider any safety measures which need to be considered in the mixture of pyrotechnical igniting mixtures.

In accordance with the invention the suspensions which are not explosive, or only marginally so, are mixed in small quantities in batches and dosed immediately after said mixing, e.g. in the housing of an airbag igniter. In this way, an absolutely homogenous distribution of the components is achieved which is maintained even during the removal of the dispersing agent from the liquid mixture, so that the formation of cracks and shrinkages are avoided and the igniting properties of the igniter are reproducible.

The grain sizes of the employed solids, i.e. metal powder or metal hydrides and the potassium perchlorate, are preferably smaller than 50 μm , or smaller than 20 μm .

In accordance with the invention, a suitable quantity of dispersing agent achieves both an optimal mixture of the components as well as a suitable viscosity of the suspension for the subsequent dosing. The energy required for the homogenous distribution of the components in the suspension is introduced into the mixture by cavitation. The cavitation is produced by ultrasonic sound with frequencies preferably higher than 16 kHz. During the implosion of the gas bubbles produced by the cavitation temperatures of approx. 5500°C and pressures up to 500 bar can be reached. As a result of the speed of the disintegration of the gas bubbles in a time interval of less than 1 μs and by the small magnitude of the gas bubbles which are usually smaller than 150 μm , the cooling speed during the implosion is so high that the heating of the suspension remains negligible. The chemical effects of ultrasonic sound have already been described by K. S. Suslick in the publication "Spektrum der Wissenschaft", Edition 4, pages 60ff, 1989, where essentially aspects of the sono-chemistry of liquids and solid surfaces as well as of suspended particles were examined.

It is a further feature of the invention that the components are mixed directly in the receptacle from which the dosing is made immediately after the production of the dispersion. This is easily possible by using respectively shaped sonotrodes. The mixtures are produced in cartridges which are thereafter inserted into a dosing apparatus. The liquid mixtures are then dosed with slight pressure or by vacuum into prepared igniter housings or on igniter elements.

In order to prevent sedimentations or coagulation effects in the course of the dosing process, the cartridges which contain the igniting mixture can be subjected to mechanical oscillations or sound waves.

Filling and re-filling processes after the mixing are avoided by performing the mixing directly in the dosing receptacle. Such processes could lead to incrustations or desiccated material on the walls, which should be avoided under all circumstances due to the explosive character of the mixture.

The avoidance of the hazards which may occur during the mixing of larger quantities is the mixing as provided for by the invention in a relatively small mixing space of components of the igniting mixture which are mixed preliminarily in suspension and which are not explosive or marginally explosive and the subsequent filling or dosing therefrom into an igniter shell. The mixing space can be provided in this process with a sonotrode connection or a mechanical sonotrode contact.

In accordance with the invention, preferably only as much of this actually hazardous mixture is produced as is required for a single or a few igniters. The production can then be controlled mechanically in a more economic manner at a cycle speed which is high enough for series production. If a composition of the igniting mixture is chosen of potassium perchlorate, zirconium powder, a binding agent and a solvent, two suspension-like pre-mixes can be produced which are not or only marginally explosive, namely as the one component the potassium perchlorate dispersed in the solvent and as the second component the zirconium powder dispersed in the

solvent, with the binding agent already being dissolved in the solvent.

In summary, the method in accordance with the invention to produce pyrotechnical igniters with an igniting mixture on the basis of metal powders, metal hydrides, potassium perchlorate and binding agents therefore consists of the following method steps:

1. Weighing and filling the components or pre-mixes which are not or only marginally explosive into a mixing or dosing cartridge or metering cartridge;
2. production of the mixture in the cartridge or a small mixing space by application of ultrasonic sound;
3. dosing of the pyrotechnical igniting mixture, unless the mixing has been performed anyway in the receptacle used for the application of the pyrotechnical igniting mixture.

Thereafter the igniting mixtures are relieved of the remaining dispersing agents, which is performed by drying for example, and then supplied to further processing.

A composition of the igniting mixture as illustrated by way of an example is as follows:

- 55 % zirconium powder
- 43 % potassium perchlorate
- 2 % binding agent;

all percentage figures are given in percent by weight.

The ratio of solids to dispersing agent is variable and is usually in the range of 70 to 80 % solids.

Titanium or zirconium, or their hydrides respectively, are preferably used as metal. The binding agent is preferably chosen from the group of the fluorinated polymeric aliphatic compounds.

The dispersing agent preferably acts as a solvent for the binding agent and preferably comes from the family of aliphatic ketones. Acetone or methyl ethyl ketone have proven to be suitable for this purpose.



(New) claims

1. A method for producing pyrotechnical igniting mixtures on the basis of metal powders or metal hydride powders, potassium perchlorate and binding agents, characterized in that suspensions are produced from the individual components of the pyrotechnical igniting mixture with the help of liquid dispersing agents, with said suspensions, which are not explosive or only marginally so, being mixed by using ultrasonic sound, that immediately after the mixing the mixture is dosed in this consistency in the desired quantity, and thereafter the dispersing agent is removed from the dosed quantity.
2. A method as claimed in claim 1, characterized in that the suspensions are mixed by using ultrasonic sound in the desired quantity directly in a housing for receiving the pyrotechnical igniting mixture.
3. A method as claimed in claim 1 or 2, characterized in that the employed powdery components of metal, metal hydride and potassium perchlorate have a grain size of < 50 μm , preferably < 20 μm .
4. A method as claimed in one of the preceding claims, characterized in that titanium or zirconium, or their hydrides, are used as metal.



5. A method as claimed in one of the preceding claims, characterized in that the binding agent is chosen from the family of the fluorinated polymeric aliphatic compounds.
6. A method as claimed in one of the preceding claims, characterized in that the dispersing agent acts as a solvent for the binding agent.
7. A method as claimed in one of the preceding claims, characterized in that the dispersing agent is chosen from the family of the aliphatic ketones.
8. A method as claimed in claim 7, characterized in that acetone or methyl ethyl ketone is used as a dispersing agent.
9. A method as claimed in one of the preceding claims, characterized in that the mixture is made to oscillate during the dosing.
10. A method as claimed in claim 9, characterized in that sound waves are introduced into the mixture.