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(54) **Titre :** PROCEDE RELATIF A L'ELABORATION D'UN EXPLOSIF A EMULSION SENSIBLE
(54) **Title:** A METHOD FOR PREPARING A SENSITISED EMULSION EXPLOSIVE

(57) **Abrégé/Abstract:**

This invention relates to a method for rapid chemical gassing of an emulsion explosive without having toxic nitrogen oxides in the finished emulsion explosive product, when nitrite is used as the gassing component. Urea acts as a gassing accelerator and urea are added in the water lubrication solution or in both the water lubrication solution and in the gassing component. To achieve rapid gassing of an emulsion explosive, the emulsion is prepared at a pH in the range of 0-3, by using an organic acid having at least 3 carbon atoms.

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(54) Title: A METHOD FOR PREPARING A SENSITISED EMULSION EXPLOSIVE

(57) Abstract: This invention relates to a method for rapid chemical gassing of an emulsion explosive without having toxic nitrogen oxides in the finished emulsion explosive product, when nitrite is used as the gassing component. Urea acts as a gassing accelerator and urea are added in the water lubrication solution or in both the water lubrication solution and in the gassing component. To achieve rapid gassing of an emulsion explosive, the emulsion is prepared at a pH in the range of 0-3, by using an organic acid having at least 3 carbon atoms.

A method for preparing a sensitised emulsion explosive.

Description:

The present invention relates to a method for preparing a sensitised water-in-oil emulsion explosive. (Hereafter referred to as “emulsion explosive”). More particularly, the invention relates to a method of reducing the formation of toxic nitrogen oxides (NOx) in the finished emulsion explosive product that is sensitised quickly, or gassed with nitrite at low pH values.

Background of the invention:

Emulsion explosives are well known in the art. They are fluid when formed (and can be designed to remain fluid at temperatures of use) and are used in both packaged and bulk forms. They can be used as straight emulsions or be mixed with ammonium nitrate prills and/or ANFO to form a heavy ANFO product, having higher energy and, depending on the ratios of components, better water resistance than ANFO. Such emulsions can be reduced in density by the addition of voids in the form of hollow microspheres, other solid air entraining agents or gas bubbles, which materially sensitise the emulsion to detonation. A uniform, stable dispersion of air entraining agent or gas bubbles is important to detonation properties of the emulsion. Gas bubbles, if present, normally are produced by the reaction of chemical gassing agents.

When blast-holes are loaded with a chemically gassed or sensitised emulsion explosive, it is important to have the correct part of the blast-hole unloaded to prevent fly-rocks and possible damage to man and properties. If the gassing process is slow, it is difficult to know when to stop the loading process and how much the emulsion will expand upwards in the blast-hole, in order to have the correct unloading part of the blast hole.

On the other hand if the gassing process is quick, and of the same order as, or lower than the time it takes to load a blast-hole, it is easy to find the correct loading-height, and the stemming of the blast-hole can be accomplished at once. Also in tunnel blasting, is it important to have a gassing and expansion process that is as quick as possible, especially when loading upright blast-holes.

A common sensitising agent is nitrite, which generates nitrogen bubbles in the emulsion when nitrite reacts with ammonium, preferably in the presence of an accelerator.

The reaction between these components may be illustrated as follows:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2\,H_2O$$

However, when an emulsion explosive gases rapidly, using nitrite as the gassing component and at low pH, there will often be formation of some toxic nitrogen oxide beside the nitrogen gas as the main gas-product.

Gassed emulsion explosives can under certain conditions fall or slide out of a blasthole and thereby loose some of the sensitising gas. In bench loading, some sensitised emulsion may collapse and loose gas, especially when stemming is applied to a blast-hole with a low-density emulsion explosive. Under poor ventilation conditions, people can be exposed to dangerous NO_2 levels, when working close to a sensitised emulsion explosive loosing its sensitising gas, both in the field and at laboratory work. NO_2 is very toxic gas and has a threshold limit in Europe as low as 2 ppm.

The present invention provides a new method for quickly sensitising an emulsion explosive where the toxic NOx-gas will be reduced or eliminated during the gassing process.

Prior art technology:

A process and apparatus for the manufacture of emulsion explosive components is disclosed in US Patent No. 6,165,297. This patent also refers to different accelerators, e.g. in claim 12, where thiourea, thiocyanate, iodide, cyanate, acetate and combinations thereof are mentioned.

In accordance therewith the present invention provides a method for preparing a sensitised emulsion explosive in a blast hole or a package, wherein

a) a fuel phase and
b) an oxidizer solution containing ammonium species and oxidizer salt, and having a pH in the range 0-3,

are emulsified to form an emulsion, which is subjected to gassing by mixing it with

c) a gassing solution containing inorganic nitrite,

in the presence of urea as gassing accelerator,

and wherein the emulsion explosive is delivered to a blast hole or a package by means of a loading tube or hose, allowing the gassing to take place at the end of said tube or hose.

The pH should be adjusted to a value in the range of 0-3, preferably by means of an organic acid having at least 3 carbon atoms, such as citric and/or tartaric acid. A preferred pH is in the range of 0,4-2,0 in particular about 1.

This means that the oxidizer solution of the emulsion normally should contain the organic acid such as citric acid in a concentration of from 0,2 to 5 % preferably from 1,5 to 3%.

When urea is used as a gassing accelerator there is practically no generation of nitrous gasses (NO_x), or any other toxic gases that might be produced using other gassing accelerators.

Urea has been used or suggested for use in water-bearing blasting agents of the emulsion or water-gel type and in ANFO blasting agents. For example, U.S. Pat. No. 5,159,153 discloses the use of urea in the oxidizer salt solution phase of an emulsion blasting-agent for purposes of stabilizing the blasting agent against thermal degradation in the presence of reactive sulfide and pyrite ores. U.S. Pat. No. 4,338,146 discloses the use of urea as an additive in a cap-sensitive emulsion explosive in an amount of less than 5% by weight. U.S. Pat. No. 4,500,369 discloses the use of urea in an emulsion blasting-agent to lower its crystallization temperature. U.S. Pat. No. 3,708,356 discloses the use of urea to stabilize ANFO against reaction with pyrite ores.

U.S. Pat. No. 5,608,185 discloses a method of reducing the formation of toxic nitrogen oxides (NO.sub.x) in after-blast fumes by using an emulsion blasting agent that has an appreciable amount of urea in its discontinuous oxidizer salt solution phase. Thus, the urea in said patent is used for reducing the amount of nitrogen oxides formed in after-blast fumes, while according to the present invention the urea is used together with the gassing agent in connection with the sensitising of the emulsion explosive, to avoid the formation of NOx in the sensitised emulsion before it is detonated.

USP 5,972,137 relates to the gassing of an emulsion explosive, but the purpose is not to reduce the amount of NOx in the sensitised emulsion, but to use an organic solvent for the gassing agent in order to minimize the total amount of water in the explosive composition, and thereby increasing the energy of the explosive. A relative high pH is used, and the gassing agent is a combined hose lubricant and gassing agent. The gassing accelerator is added to the fuel phase and will extract over to the oxidizer solution as the emulsion is formed. Rapid gassing using a low oxidizer pH is not possible with this patent as urea (gassing accelerator) will decompose under these conditions.

In USP 3,711,678 a gassing technique is also described, but in this case the gassing takes place at very early stage, namely at the stage where the initial emulsion is formed. The process of this patent cannot be used for rapid gassing, as the emulsion has to be formed at an elevated temperature of about 60°C, and under these conditions trying to use a low pH will cause the emulsion to gas within seconds, as shown in the present invention, see example 14 below. Rapid gassing of an emulsion can only be done by using an end of hose mixing device, otherwise the emulsion will loose its sensitising gas in the emulsion pump and in the loading hose.

The sensitised emulsion explosive prepared according to the present invention is delivered to a blast hole or a package (cartridge) by means of a loading tube or hose, which may suitably be lubricated by lubricating water to reduce the friction of the emulsion explosive through the tube or house. Suitably, urea may be added to said lubricating water. It is also possible to add further desired substances to the lubricating water, and examples of such other substances are organic acids to reduce the pH value to the necessary level and also energy and flame reducing agents.

In the gassing solution the concentration of urea should preferably be from 10 to 45%, in particular from 20 to 30% by weight. In the lubricating water the concentration of urea should preferably be from 5 to 50%, preferably from 20 to 40% by weight.

In the state of the art, such as USP 6,165,297 mentioned above, urea is added in small quantities in the gas forming composition. In the referred USP 6,165,297 it is necessary to mix two different gassing ingredients just prior to the gassing process, as the gassing ingredients in said patent otherwise will self gas. USP 6,165297 (see col.12; line 8-31) describes the gassing process in Example 3 as follows: "An aqueous solution sodium nitrite (SNI) and urea was stored in one container of the apparatus of the current invention, while an aqueous solution of the ammonium nitrate (AN) and urea was stored in a separate container. The SNI solution and AN/urea solution were pumped from their containers through separate conduits into a small tank and were mixed together using a rapidly turning propeller. The premix so formed was then injected into the water-in oil emulsion just prior to the water-in-oil emulsion passing through a series of static mixing elements, which evenly distributed the components suitable for gas formation throughout the water-in-oil emulsion. The water-in-oil emulsion incorporating the components passed through the remaining length of stainless steel conduit into a flexible loading hose, the other end of which was loaded in a blasthole.

The blasthole was filled with the combinations of water-in-oil emulsions and mixed components. The mixed components started to react after about 30 seconds and it took about 30 minutes for the gassing reaction to be completed. The density of the gassed water-in-oil emulsion was 1,00 g/cc compared with 1,38 g/cc for the ungassed water-in-oil emulsion. The blasthole was detonated successfully. USP 6,165,297 describes a gassing process very different from that of the present invention. Although USP 6,165,297 and the present invention both comprises the use of urea, these two patents are very different:

- USP 6,165,297 gasses slowly (typical 30 min. to reach a density of 1,05 g/cc), and is not concerned about the NOx that might be formed in the gassing process itself.
- The goal with the present invention is rapid gassing, and at the same time to eliminate or minimize the NOx formed in the gassing process. This is achieved by using an organic acid in the oxidizer solution, where citric acid and/or tartaric acid are the preferred organic acid.

- USP 6,165,297 mixes two gassing ingredients just prior to injection to the emulsion. This premix is self-gassing, and the water-in-oil emulsion itself has a relatively high pH of 4,2 (See col.10, line 45), and the ammonium species in the oxidizer solution do not (or very slowly) react directly with the nitrite in the gassing solution.
- In the present method, a urea solution is used as a loading hose lubricant, and is mixed with the emulsion in a spray nozzle at the end of the loading hose. The pH of the water-on-oil emulsion is very low (less than 3). The gassing component can alternatively be added as a string in the centre of the emulsion (See WO99/14554) or be blended with a static mixer or in a mechanical mixer just before the emulsion enters the loading hose.

USP 5,608,185 uses urea as a component in the discontinuous oxidizer salt phase to reduce the formation of nitrogen oxide in the after-blast fumes. This patent is also very different from the present invention for the following reasons:

- USP 5,608,185 uses urea to reduce after-blast fumes.
- The present invention uses urea to eliminate pre-detonation nitrogen oxides that can generate during rapid gassing.
- USP 5,608,185 uses from 5 to 30% urea. Preferably the urea is dissolved in oxidizer salt solution.
- The present invention uses urea as an additive to the water lubrication solution, which is necessary to use, in order to pump the emulsion through a long and thin loading hose. At the end of the loading hose (or conduit) the emulsion and the lubrication solution are mixed in a mixing nozzle.
- According to the present invention the goal is to sensitise the emulsion rapidly, and therefore gas rapidly. In order to gas rapidly the emulsion should have a low pH in the oxidizer solution, and in this case is it impossible to have urea as a component in the oxidizer solution, as urea will decompose slowly in acid solution. Under these conditions urea will decompose to carbon dioxide and ammonia, which raises the pH and slows down the gassing rate.

USP 5,159,153 also describes the use of urea in water-in-oil emulsion explosives, but said patent is also very different from the present invention for the following reasons:

- In USP 5,159,153 urea is added with the purpose of stabilizing the emulsion against thermal degradation with reactive sulfide/pyrite ores. So the purpose with this patent is completely different than in USP 5,08,185 and the current patent application where the purpose is to reduce after blast fumes and to eliminate NOx during the gassing-process (or sensitivitation) of the emulsion respectively.
- In USP 5,159,153 urea is added from 5–20% preferably dissolved in the oxidizer phase, but may also be added as a powdered or solid phase.
- In the present method, urea is dissolved in the water-lubrication solution, and mixed with the emulsion at the end of the conduit, where urea acts as a gassing accelerator and minimizes or reduces the NOx normally formed during a rapid gassing process, or alternatively urea is used in the gassing solution or in both the gassing solution and the water lubrication solution.

Several patents describe the use of gassing accelerators to accelerate the rate of gas generation by the chemical gassing agent. USP 4,960,475; USP 5,017,251; USP 5,076,867; USP 5,346,564 and USP 6,165,297 all mention the use of gassing accelerators, but none of them mentions urea as a gassing accelerator.

USP 6,165,297 is mentioning gassing accelerators such as thiocyanate salts, iodides, sulphanic acid and its salts or thiourea. (Se column 3, line 11-12) In these patents it most common to add the gassing accelerator to the oxidizer solution of the water-in-oil emulsion, or add the gassing accelerator in the gassing solution.

In the present method urea is used as a gassing accelerator, and is added to the water lubrication solution or to the gassing solution. Alternatively urea can be added both to the water lubrication solution and to the chemical gassing solution.

USP 4,273,147 and USP 4,259,977 describe a method of reducing the pumping pressure in conduits using a lubricant fluid that moves in an annular stream around the emulsion. The lubricating fluid comprises a solution of ammonium nitrate, or an aqueous salt solution wherein the salt of the said lubricating fluid corresponds to the major salt present in the explosive emulsion. The main purpose with these two patents is to lower the pumping pressure of an emulsion in a conduit, and to prevent the conduit to plug up during interruption of the pumping.

In the present invention lubricating fluid does not contain a salt present in explosive emulsion, and the main presence of urea in the lubricating fluid is not to lower the pumping pressure, but to eliminate or reduce the amount of NOx created during the gassing process with nitrite.

Conclusion:

The purpose with this patent is to be able to chemically gas an emulsion explosive rapidly both at low and high temperatures without creating NOx during the gassing process. To accomplish this it is necessary to have an emulsion with a low pH and to use a gassing accelerator. It has surprisingly been found that by lowering the pH by using an organic acid such as citric acid practically eliminates the production of NOx during the gassing process, when urea is used as a gassing accelerator.

According to one aspect of the present invention, there is provided a method for preparing a sensitised emulsion explosive in a blast hole or a package, wherein (a) a fuel phase and an oxidizer solution, comprising ammonium species and oxidizer salt, are emulsified to form an emulsion, and (b) said emulsion is subjected to gassing by mixing it with a gassing solution comprising inorganic nitrite in the presence of urea as gassing accelerator, and wherein: the emulsion is delivered to the blast hole or the package by means of a loading tube or hose, allowing the gassing to take place at the end of said tube or hose, the oxidizer solution has a pH value in the range 0-3 and comprises one or more organic acid(s) having at least three carbon atoms, and urea is present in the gassing solution and/or is present in a lubrication fluid added to the loading tube or hose.

The invention comprises the addition of urea as a gassing accelerator in the gassing solution, and/or using urea as a gassing accelerator in the lubrication fluid. It is also surprisingly found that by lowering the pH of the oxidizer solution in the emulsion by using citric acid (CA), completely eliminate NOx during the gassing process. As can be seen from the given examples an increased amount of CA gives a decreasing pH, but also reduced NOx as the amount of CA is increased. CA is found to be particularly advantageous and at a level of 2% CA, where the NOx from the gassing process is completely eliminated. The gassing rate is also increased as the amount of CA is increased. Also tartaric acid (TA) was found to have a positive effect on the reduction of NOx in the gassed emulsion.

On the other and hand, if CA is replaced by acetic acid (HAc), this also gives increased gassing rate, but it is also gives more NOx. And as the amount HAc is increased, more NOx are produced, so HAc does not have the same advantageous effect as CA and TA.

It was also surprisingly found that the gassing rate at these low pH emulsions also increased by replacing some ammonium nitrate (AN) in a straight AN emulsion (see example 16), by other inorganic nitrates like sodium nitrate (see examples 6-8 and 10-15) and calcium nitrate. (Se example 17). The NOx produced during the gassing process was still kept at a very low level.

To illustrate that urea acts as a gassing accelerator as claimed in this current invention, the gassing rate using different gassing accelerators in the gassing composition were tested. The NOx level in the finished sensitised emulsion explosives were also measured.

All different gassing compositions had the same level of 15% sodium nitrite and were tested at a 1% level in the given standard emulsion.

The percentage values recited herein for the components of the oxidizer solution represent percentages by weight.

EXAMPLE 1 (not according to the invention)

A standard water-in-oil emulsion of the following composition was prepared for use in the following examples:

Oxidiser solution:

94 wt % comprising:

Ammonium nitrate	72,5 wt %
Sodium nitrate	9,8 wt %
Water	15,7 wt %
Citric acid	2,0 wt %

pH of the oxidiser was measured to 0,98

Fuel Phase :

6 wt % comprising:

A hydrocarbon oil and emulsifier mix.

The emulsifier was of a polymeric type.

The emulsion was prepared by slowly adding a stream of oxidiser solution to the fuel phase, with rapid stirring to form a homogeneous water-in-oil emulsion. Both phases kept at an elevated temperature of 80 °C during the preparation of the emulsion. The resulting standard emulsion was left for a day to cool down to room temperature.

The following components in aqueous solution were combined to provide the following gas forming composition:

Sodium nitrite	15,0 %
Water	85,0 %

1,0 % of this gas forming composition was added to the water-in-oil emulsion. The blend was mixed for 40 seconds, and transferred to a 160 cc plastic cup. The emulsion was filled to the top of the cup, and levelled off using a stiff, plane blade. As the emulsion in the cup gassed, the emulsion expanded beyond the top of the cup, and was scraped off to en even level. The levelled off cup was weighted every minute and the weight of the emulsion explosive was recorded. The density of gassing emulsion explosive was found by dividing its weight by the cup volume of 160 cc. When the emulsion explosive had reached its final density, the cup with the sensitised emulsion explosive was transferred to self-made glove-box. The glove-box contained a volume of 100 litres, and was equipped with a small 12-volt fan for mixing the air in the box, and a Multi-gas monitor (pm-7400) from Metrosonics Inc. The box had a removable Plexiglas* top, and the mounted gloves enabled one to use a spatula to stir out the sensitising gas from the emulsion explosive. The fan efficiently mixed the sensitising gas with the total of 100 litres of air in the box, and the Multi-gas monitor measured the NOx concentration. For this particular blend, no accelerator was used in the gas forming composition, and the gassing rate was found to be more than 3 hours, and a concentration of 10 ppm NOx was measured in the glove-box.

EXAMPLE 2 (not according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Sodium thiocyanate	30 %
Water	55 %

*Trade-mark

1% of this gassing component was added to the standard emulsion, and mixed for 40 seconds. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc in 6 minutes, and the final cup density ended at 0,68 g/cc. When the gas was stirred out of the emulsion in the glove-box, the Multi-gas monitor from Metrosonics showed a NOx concentration of 130ppm.

EXAMPLE 3 (not according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Thiourea	5 %
Water	80 %

1% of this gassing component was added to the standard emulsion, and mixed for 40 seconds. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 55 minutes, and ended up with a final cup density of 0,75 g/cc. after 2 hours. When the gas was wiped out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics, showed a NOx level of 300ppm.

EXAMPLE 4 (not according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Potassium iodine	30 %
Water	55 %

1% of this gassing component was added to the standard emulsion, and mixed for 40 seconds. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 70 minutes, and ended up with a final cup density of 0,75 g/cc. after 2,5 hours. When the gas was wiped out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics, showed a NOx level of 22ppm.

EXAMPLE 5 (not according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Ammonium sulphate	30 %
Water	55 %

1% of this gassing component was added to the standard emulsion, and mixed for 40 seconds. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 160 minutes. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics, showed a NOx concentration of 33ppm.

EXAMPLE 6 (according to the invention)

The same emulsion and the same type and amount of gassing component as in EXAMPLE 1 were added. In addition 2% of lubricating solution, containing 50% urea and 50% water, was also added. This was done by first blending in the gassing component for 10 seconds, and then mixing in 2% of the lubricating water in 40 seconds. The gassing rate was measured. It was found that this emulsion composition gassed to density of 0,80 g/cc in 9 min., and reached a final density of 0,68 g/cc. When the sensitising gas was stirred out of the emulsion in the glove box, no NOx could be detected. This example shows that urea both acts as an accelerator and eliminates the NOx formation during the gassing process.

EXAMPLE 7 (according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Urea	42 %
Water	43 %

1% of this gassing component was added to the standard emulsion and mixed for 40 seconds. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 9 min., reaching a final cup density of 0,68 g/cc. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics could not detect any NOx .

EXAMPLE 8 (according to the invention)

The standard emulsion and the same type and amount of gassing component as in EXAMPLE 7 were added. In addition 2% of lubricating water containing 50% urea, was also added. This was done by, first blending in the gassing component for 10 seconds, and then mixing in 2% of the lubrication water for 40 seconds. The gassing rate was measured. It was found that this emulsion composition gassed to density of 0,80 g/cc in 9 min., and reached a final cup density of 0,68 g/cc. When the gas was stirred out of the emulsion in the glove box, no NOx could be detected.

EXAMPLE 9 (not according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Urea	42 %
Water	43 %

1% of this gassing component was added to an emulsion where the 2% of citric acid was replaced by 2% of Acetic acid (60%). The gassing component and this emulsion was blended for 40 seconds. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 40 min. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics detected a NOx-concentration of 45 ppm.

EXAMPLE 10 (according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Water	85 %

And the following water lubrication solution was made:

Water	60 %
Urea	40%

1% of this gassing component was added to the standard emulsion together with 2% of the water lubrication solution, and mixed for 40 seconds, at temperature of 50 ^{O}C. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 1 min., and reaching a final cup density of 0,68 g/cc. after 3 min. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics could not detect any NOx .

EXAMPLE 11 (according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Urea	42 %
Water	43 %

1% of this gassing component was added to a standard emulsion containing 0,3% citric acid in the oxidizer solution, and was mixed for 40 seconds, at room temperature. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 180 min. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics detected a NOx-concentration of 2,5 ppm.

EXAMPLE 12 (according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Urea	20 %
Water	65 %

And the following water lubrication solution was made:

Water	50 %
Urea	50%

1% of this gassing component was added to a modified standard emulsion together with 2% of the water lubrication solution, and mixed for 40 seconds, at temperature of 23 ^{O}C. The modified standard emulsion had 3% of citric acid in the oxidizer solution, instead of 2% as described in example 1. The pH-value on this oxidizer solution was 0,65. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 9 min. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics detected a NOx –concentration of 2,9 ppm.

EXAMPLE 13 (according to the invention)

The following gassing component was made for this experiment:

Sodium Nitrite	15 %
Urea	42 %
Water	43 %

And the following water lubrication solution was made:

Urea	42 %
Citric acid	14 %
Water	44 %

1% of this gassing component was added to a standard emulsion containing 0,8% citric acid in the oxidizer solution, and was mixed for 10 seconds. Then 2% of the water lubrication solution was added, and mixed for 40 seconds, at room temperature. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 15 min., with a final cup density of 0,76 g/cc. after 20 min. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics detected a NOx-concentration of 0,2 ppm .

EXAMPLE 14 (according to the invention)

The following gassing component was prepared for this experiment:

Sodium Nitrite	15 %
Urea	20 %
Water	65 %

And the following water lubrication solution was made:

Water	70 %
Urea	30%

These solutions were filled into the containers of Dyno's SME (Site Mixes Emulsion) truck. The SME-truck produced an emulsion equal to the one given in EXAMPLE 1, except that the fuel-phase contains sorbitan mono-oleate (SMO) as an emulsifier rather than a polymeric type. The emulsion is produced at a temperature of about 80 ^{O}C, pumped through an 80 meter long loading hose, into the borehole.

0,8% of the gassing component was added to centre of the emulsion as described in PCT/NO/00275, and 2% of the water lubrication solution was used for lubricating the loading hose. A mixing nozzle was mounted at the end of the loading hose. 100 kg/min was pumped through the loading hose into the boreholes, and the gassing component and the water lubrication solution were mixed with the emulsion at the end of the loading hose. This blend was loaded into 40 blastholes off a diameter of 102mm. The whole round was successfully shot. During the loading process the gassing rate was recorded in a small density cup, and it was found that this emulsion gassed completely within 10 seconds, reaching a final cup density of 0,80 g/cc. When the gas was stirred out of the emulsion in the glove-box, the Multi-gas monitor from Metrosonics could not detect any NOx .

EXAMPLE 15 (according to the invention)

The following gassing component was prepared for this experiment:

Sodium Nitrite	15 %
Urea	20 %
Water	65 %

And the following water lubrication solution was made:

Water	50 %
Urea	50%

1% of this gassing component and 2% of the water lubrication component was added to a standard emulsion where the 2% of citric acid was replaced by 2% of Tartaric Acid. The oxidizer solution had a pH of 0,55 before the emulsion was made. The gassing solution plus the water lubrication solution were added to the emulsion was blended for 40 seconds. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 6 min. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics detected a NOx-concentration of 2,1 ppm.

EXAMPLE 16 (according to the invention)

The following gassing component was prepared for this experiment:

Sodium Nitrite	15 %
Urea	20 %
Water	65 %

And the following water lubrication solution was made:

Water	50 %
Urea	50%

1% of this gassing component and 2% of the water lubrication component were added to an emulsion prepared as described in EXAMPLE 1 using an oxidizer solution of the following composition:

Ammonium nitrate	55 %
Calcium nitrate (Hydro TQ)	30 %
Water	13 %
Citric acid	2 %

and 6,5 % of the polymeric fuel phase. The pH of oxidizer solution was measured to 0,0 before the emulsion was made. The gassing solution plus the water lubrication solution were added to the emulsion, and blended for 40 seconds. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 4 min. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics detected a NOx-concentration of 0,0 ppm.

EXAMPLE 17 (according to the invention)

The following gassing component was prepared for this experiment:

Sodium Nitrite	15 %
Urea	20 %
Water	65 %

And the following water lubrication solution was made:

Water	50 %
Urea	50%

1% of this gassing component and 2% of the water lubrication component was added to an emulsion prepared as described in EXAMPLE 1 using an oxidizer solution:

Ammonium nitrate	82 %
Water	16 %
Citric acid	2 %

and 5,6 % of the polymeric fuel phase. The pH of the oxidizer solution was measured to 0,75 before the emulsion was made. The gassing solution plus the water lubrication solution were added to the emulsion, and blended for 40 seconds. The gassing rate was recorded, and it was found that this emulsion composition reached a density of 0,80 g/cc after 18 min. When the gas was stirred out of the emulsion in the glovebox, the Multi-gas monitor from Metrosonics detected a NOx-concentration of 1,7 ppm.

The examples are summarized in the following table

Example no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Oxidizer solution:																	
Ammonium nitrate	72,5	72,5	72,5	72,5	72,5	72,5	72,5	72,5	72,5	72,5	73,7	71,8	73,4	72,5	72,5	55,0	82,0
Sodium nitrate	9,8	9,8	9,8	9,8	9,8	9,8	9,8	9,8	9,8	9,8	10,0	9,7	9,9	9,8	9,8	-	-
Calsium nitrate (Hydro, TQ)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	30,0	-
Water	15,7	15,7	15,7	15,7	15,7	15,7	15,7	15,7	15,7	15,7	16,0	15,5	15,9	15,7	15,7	13,0	16,0
Citric acid	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	-	2,0	0,3	3,0	0,8	2,0	-	2,0	2,0
Tartaric acid	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2,0	-	-
Acetic acid (60%ig)	-	-	-	-	-	-	-	-	2,0	-	-	-	-	-	-	-	-
pH of oxidizer solution:	0,98	0,98	0,98	0,98	0,98	0,98	0,98	0,98	1,90	0,98	1,60	0,65	1,10	0,98	0,55	0,00	0,75
Fuel phase:																	
Mineral oil + polymeric emulsifier (% of total emulsion)	6,0	6,0	6,0	6,0	6,0	6,0	6,0	6,0	6,0	6,0	6,0	6,0	6,0	-	6,0	6,5	5,6
Mineral oil + sorbitan monooleate (% of total emulsion)	-	-	-	-	-	-	-	-	-	-	-	-	-	6,0	-	-	-
Gassing solution:																	
Sodium nitrite	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0	15,0
Sodium thiocyanate	-	30,0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Thiourea	-	-	5,0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Potasium iodine	-	-	-	30,0	-	-	-	-	-	-	-	-	-	-	-	-	-
Ammonium sulphate	-	-	-	-	30,0	-	-	-	-	-	-	-	-	-	-	-	-
Urea	-	-	-	-	-	-	42,0	42,0	42,0	-	42,0	20,0	42,0	20,0	20,0	20,0	20,0
Water	85,0	55,0	80,0	55,0	55,0	85,0	43,0	43,0	43,0	85,0	43,0	65,0	43,0	65,0	65,0	65,0	65,0
Amount in % of emulsion	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Water lubrication solution:																	
Urea	-	-	-	-	-	50,0	-	50,0	-	40,0	-	50,0	42,0	30,0	50,0	50,0	50,0
Citric acid	-	-	-	-	-	-	-	-	-	-	-	-	14,0	-	-	-	-
Water	-	-	-	-	-	50,0	-	50,0	-	60,0	-	50,0	44,0	70,0	50,0	50,0	50,0
Amount in % of emulsion	0,0	0,0	0,0	0,0	0,0	2,0	0,0	2,0	0,0	2,0	0,0	2,0	2,0	2,0	2,0	2,0	2,0
Gassing temperature (^{O}C)	23	23	23	23	23	23	23	23	23	50	23	23	23	74	23	20	20
Gassing rate [1]	210 min	6 min	55 min	70 min	160 min	9 min	9 min	9 min	41 min	1 min	180 min	9,0 min.	15 min	10 sec	6 min	4 min	18 min
NOx (ppm) in sensitized emulsion [2]	10	130	300	22	33	0,0	0,0	0,0	45	0,0	2,5	2,9	0,2	0,0	2,1	0,0	1,7
According to invention	no	no	no	no	no	yes	yes	yes	no	yes	yes	yes	yes	yes	yes	yes	yes

[1] **Gassing rate is measured as time to reach a cup density of 0,80 g/cc**

[2] **NOx is measured as the concentration when the sensitising gas is stirred out of 160 cm^3 gassed emulsion and diluted to 100 litres.**

CLAIMS:

1. A method for preparing a sensitised emulsion explosive in a blast hole or a package, wherein

(a) a fuel phase and an oxidizer solution, comprising ammonium species and oxidizer salt, are emulsified to form an emulsion, and

(b) said emulsion is subjected to gassing by mixing it with a gassing solution comprising inorganic nitrite in the presence of urea as gassing accelerator,

and wherein:

the emulsion is delivered to the blast hole or the package by means of a loading tube or hose, allowing the gassing to take place at the end of said tube or hose,

the oxidizer solution has a pH value in the range 0-3 and comprises one or more organic acid(s) having at least three carbon atoms, and

urea is present in the gassing solution and/or is present in a lubrication fluid added to the loading tube or hose.

2. The method of claim 1, wherein the pH value of the oxidizer solution is in range of 0.4 - 2.

3. The method of claim 1, wherein the pH value of the oxidizer solution is 1.

4. The method of claim 1 wherein the oxidizer solution comprises citric acid as one of the one or more organic acid(s).

5. The method of any one of claims 1 to 4, wherein the oxidizer solution comprises tartaric acid as one of the one or more organic acid(s).

6. The method of any one of claims 1 to 5, wherein the oxidizer solution contains 0.2 - 5% by weight of the one or more organic acid.

7. The method of claim 6 wherein the oxidizer solution contains 1.5 - 3% by weight of the one or more organic acid.

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