

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11)

Publication number:

**0 037 862**  
**A2**

(12)

**EUROPEAN PATENT APPLICATION**
(21) Application number: **80300973.7**(51) Int. Cl.<sup>3</sup>: **C 06 B 21/00, C 06 B 47/00**(22) Date of filing: **28.03.80**(43) Date of publication of application: **21.10.81**  
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(84) Designated Contracting States: **AT BE CH DE FR GB IT LU NL SE**(74) Representative: **Kosmin, Gerald Emmanuel et al, HASLTINE, LAKE & CO. Hazlitt House 28 Southampton Buildings Chancery Lane, London, WC2A 1AT (GB)**(54) **Manufacture of blasting explosive compositions.**

(57) Blasting explosive compositions, generally in the form of slurry explosive compositions, which contain ammonium nitrate as the sole or principal inorganic oxidising salt and a methylamine nitrate mixture as the sole or principal sensitizer, are prepared by reacting in the liquid phase ammonium nitrate and formaldehyde to form an oxidizer/sensitizer blend which can then be mixed with other appropriate constituents to form the required blasting explosive composition, the reaction of the ammonium nitrate and formaldehyde being carried out in the presence of urea in order to reduce the amount of free formic acid which is unexpectedly produced in the reaction, since the presence of formic acid in the reaction mixture is undesirable in that it affects the production of a stable gel therefrom and if converted into a formate reduces the strength of the explosive composition.

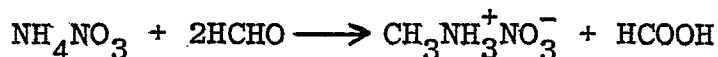
**EP 0 037 862 A2**

"MANUFACTURE OF BLASTING EXPLOSIVE  
COMPOSITIONS"

This invention relates to the manufacture of blasting explosive compositions, particularly but not exclusively slurry explosive compositions.

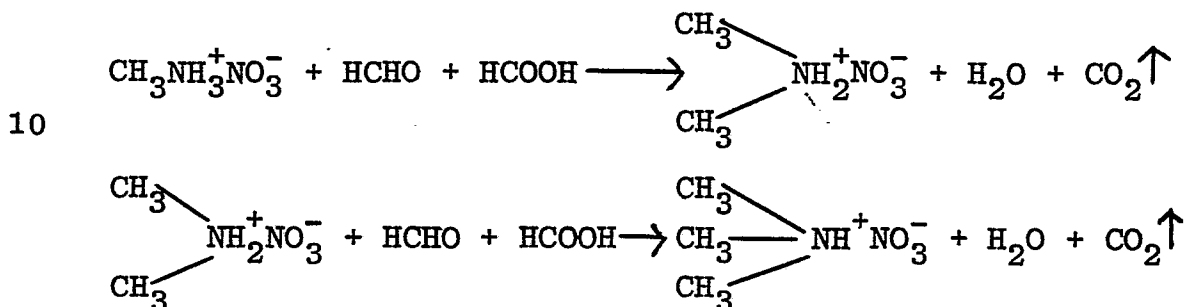
Slurry explosive compositions are extensively  
5 used in many blasting operations. Known slurry explosives include thickened compositions normally comprising at least one inorganic oxidising salt, generally ammonium nitrate, at least one sensitizer, for example monomethyl-  
amine nitrate, water, a thickening agent, and if required  
10 a fuel, for example sulfur or a carbonaceous fuel, and/or a cross-linking agent, for example potassium pyroantimonate. Slurry explosive compositions can be formulated so as to be suitable as a general purpose blasting slurry explosive or as a permitted explosive of any of the classified groups  
15 P1 to P5. Permitted explosives are explosives designed for use in gassy or dusty coal mines and which have met stringent official safety tests for safety against the risk of igniting methane and coal dust.

In the case of slurry explosive compositions  
20 containing ammonium nitrate as the sole or principal inorganic oxidising salt and monomethylamine nitrate as the sole or principal sensitizer, it is possible to form the sensitizer in situ by reacting in the liquid phase excess ammonium nitrate with formaldehyde at a temperature  
25 of around 100°C., viz.



In this connection we refer to our British Patent Specification No. 1,548,827.

It might be expected that the formic acid produced by this reaction would be involved in the formation of dimethylamine nitrate and/or trimethylamine nitrate by the following secondary reactions, viz.



In practice, however, it has been found that considerable quantities of formic acid are formed in the reaction of the ammonium nitrate and formaldehyde, the quantity of formic acid formed in fact being a measure of the completion of the reaction, and that a proportion of the formaldehyde remains unreacted even when the reaction temperature is maintained at about 100°C. for an extended period, such as 4 to 5 hours.

For the production of a stable gel it is essential to reduce to the absolute minimum the amount of the free formic acid before the reaction mixture is converted into an explosive composition. Formic acid has a boiling point of 100.9°C., but forms an azeotrope with water. Hence even prolonged distillation leaves a certain amount of formic acid in the reaction mixture. We have found that while the residual formic acid can be neutralised with either gaseous or liquid ammonia or with caustic soda, the resulting quantity of formate formed by such neutralisation of the residual formic acid acts as a diluent in the final explosive composition, which owing to the high calorific value of the formate, reduces the strength of the explosive. Furthermore, we have found that the presence of any such formate appears to have a

deleterious effect on the storage life of the explosive, resulting in exudation of amine nitrates when it is stored under warm conditions over an extended period of time.

When the reaction between ammonium nitrate and  
5 a 37% aqueous solution of formaldehyde is carried out in the ratio of 1:1, the resulting reaction mixture has been found to have the following general composition:

10	Solids	:	60 - 66% by weight
	Water	:	25 - 30% by weight
	Formic acid	:	9 - 10% by weight

For the production of a commercially desirable slurry explosive from such a reaction mixture, we have  
15 found it essential to reduce the formic acid content to at most about 1% and also the water content to at most 10%, with a consequent increase in the solids content to about 89%. By distilling the reaction mixture under a vacuum of 150-100 mm. Hg at a temperature of 100 - 110°C.  
20 it is possible to remove the bulk of the formic acid as an aqueous distillate. However, the distilland still contains about 5% of formic acid, which could be removed in the form of the methyl or ethyl ester by adding the requisite quantity of respectively methyl or ethyl alcohol  
25 and subjecting the mixture to distillation. If methyl alcohol is used, most of the formic acid is converted into methyl formate which distils over at about 35°C., while if ethyl alcohol is used, the formic acid can be recovered as ethyl formate which distils over at a  
30 temperature of 55-60°C. However, unless the methyl formate or ethyl formate produced in this manner can be of commercial use, it will be appreciated that the foregoing procedure is a relatively expensive method of removing formic acid. Furthermore, the aqueous distillate contains  
35 about 12% by weight of formic acid and the recovery of an 85% or above concentrated formic acid from such a weak solution is not commercially viable. Neutralisation with

either lime or caustic soda and the disposal of the resultant crude calcium formate or sodium formate respectively also poses problems. Thus the necessary removal of the formic acid presents both environmental and commercial  
5 problems.

It is an object of the invention to provide a reaction mixture having a formic acid content which is sufficiently low enough to avoid the foregoing disadvantages and which reaction mixture will therefore form an  
10 effective oxidizer/sensitizer blend from which various types of explosive compositions can readily be formulated.

We have found that in accordance with the invention an oxidizer/sensitizer blend suitable for use in the formulation of blasting explosive compositions, particularly  
15 slurry explosive compositions, and comprising ammonium nitrate and a mixture of monomethylamine nitrate, dimethylamine nitrate and trimethylamine nitrate can be produced by reacting ammonium nitrate and formaldehyde in the liquid phase in the presence of urea, whereby the amount  
20 of formic acid present in the resulting reaction mixture can be reduced to the desired minimum. If required, the water content of the reaction mixture can be reduced by a subsequent evaporation step.

It is believed that the urea reacts with some of  
25 the formaldehyde present in the reaction mixture to form monomethylol urea and/or dimethylol urea, which in the presence of the ammonium nitrate and the formic acid produced in the primary reaction form monomethylamine nitrate and/or dimethylamine nitrate with the evolution  
30 of carbon dioxide.

Thus by carrying out the reaction in the presence of urea not only is the content of the formic acid in the oxidizer/sensitizer blend produced substantially reduced but at the same time the methylamine nitrate content of  
35 the blend can also be increased.

The oxidizer/sensitizer blend produced in accordance with the invention can be employed in the production of various types of blasting explosive

compositions. For the production of slurry explosives, the blend can have incorporated therein in a known manner additional constituents selected from one or more additional oxidising salts, for example sodium perchlorate, sodium nitrate or solid ammonium nitrate, a thickening agent, for example guar gum, an auxiliary fuel, for example wood meal, graphite or sulfur, a cross-linking agent, for example potassium pyroantimonate, a stabilizer, for example sodium nitrite, or sodium chloride. For the production of a powder explosive, the blend can have incorporated therein, for example, solid ammonium nitrate and guar gum.

The following Examples illustrate the invention.

EXAMPLE 1

800 G. of a 37% by weight aqueous formaldehyde solution were mixed with 48 g. of urea and to the resulting mixture were added 800 g. of solid ammonium nitrate. On warming the mixture so formed to 60°C. an exothermic reaction set in and the temperature rose to 90-95°C. The reaction mixture was maintained at a temperature of 95-100°C. by applying heat when necessary for a period of 3 to 4 hours. Considerable quantities of carbon dioxide were released and at the end of the reaction period the reaction mixture had the following composition:

Solids	:	67%
Formic acid	:	1%
Water	:	32%

The reaction mixture so formed, containing unreacted ammonium nitrate and a methylamine nitrate mixture, can be evaporated in any suitable evaporation system to a water content that is desired in the final explosive. The distillate thus obtained contains only a minor quantity of formic acid, which can easily be neutralised and disposed of without causing environmental problems. The foregoing reaction mixture was distilled in vacuo

until 250 ml. of water had been collected in the receiver. 95 Ml. of a 55% solution of sodium perchlorate were added to the distilland and then a further quantity of 40 ml. of water was distilled off. Alternatively, 62 g. of solid sodium perchlorate ( $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ ) can be added. The resulting reaction mixture had the following composition:

	Solids	:	77%
	Formic acid	:	1%
10	Water	:	22%

Ammonia gas was then bubbled into this reaction mixture until the pH rose to 6 - 6.5. 580 G. of ammonium nitrate (solid), 58 g. of sodium nitrate and 19 g. of guar gum were mixed and then added to the reaction mixture which was then stirred rapidly at a speed of at least 300 rpm to hydrate the gum. 10 Ml. of a saturated solution of potassium pyroantimonate in water (4%) were added together with 58 g. of sulfur. 0.3 G. of sodium nitrite were also added as stabilizer. On vigorously mixing the resulting mixture in a double ribbon blender the density of the mixture fell to 1.05 - 1.10 g./cc. The resulting slurry explosive composition at this stage was sufficiently flowable to be packed in polythene tubes of 25 mm. diameter. After a period of 24 to 36 hours the slurry explosive composition set to a firm uniform gel. This gel could be initiated with a No. 6 commercial detonator giving a velocity of detonation of over 4000m./sec. and a Trauzl lead block value of 275-300 ml. The monomethylamine nitrate content of this slurry explosive composition was 16.5%, whilst the dimethylamine nitrate and trimethylamine nitrate content were respectively 4% and 2%. The water content was 10-12% and this explosive composition is a general purpose water gel explosive having a strength of 90% on the Blasting Gelatine scale. It can have a shelf-life of over 2 years even under warm storage conditions. It is sensitive to a No. 6 Detonator at temperatures as low as 5°C. and as high as 45°C.

7  
EXAMPLES 2 - 7

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The reaction mixture containing ammonium nitrate and a methylamine nitrate mixture produced in the manner described in Example 1 was used as an oxidizer/sensitizer blend in the production of the following explosive compositions:-

Example	Explosive Type	% Blend	AN	SPC	SN	NaCl	Guar Gum	Gra-phite	S	PPA	NaNO <sub>2</sub>
2	GPSD	57	31	5.0	3.0	-	1.0	-	3.0	.02	.03
3	P1	70	17.2	5.0	-	6.0	1.5	0.3	-	.04	.03
4	P1	70	15	-	7.0	6.5	1.5	-	-	.04	.03
5	P3	70	14.5	5.0	-	9.0	1.5	-	-	.04	.03
6	P3	70	12.5	-	7.0	9.0	1.5	-	-	.04	.03
7	P5	70	11.5	5.0	-	12.0	1.5	-	-	.04	.03

In the foregoing Table the abbreviations have the following meanings:-

GPSD = General Purpose Small Diameter  
 AN = Ammonium nitrate (solid)  
 SPC = Sodium perchlorate  
 SN = Sodium nitrate  
 PPA = Potassium pyroantimonate

The explosive composition of Example 2 can be packed in cartridges of 75 mm. and used as an effective column charge in open cast blasting.

The explosive compositions of Examples 3 to 7 respectively pass the incendivity tests prescribed for explosives for use in group 1, 2 and 3 gassy coal mines and when fired in a gallery containing 8.3% methane with or without coal dust will conform to the standards prescribed for the respective explosives, thus qualifying for use as permitted explosives in the prescribed category of gassy coal mines.

EXAMPLE 8

A powder explosive was produced by mixing the oxidizer/sensitizer blend produced in the manner described in Example 1 with additional constituents to give a mixture



comprising 25% of the above blend, 65% of solid ammonium nitrate, 10% of wood meal, and 0.5% of guar gum.

5 The resulting mixture was a powder explosive which in a 25 mm. cartridge had a velocity of detonation of 2400 m./sec. and a Trauzl lead block value of 342 ml., thus constituting a powder explosive of use for general purpose blasting.

CLAIMS:

1. A method of manufacturing a blasting explosive composition comprising ammonium nitrate as an oxidizing salt and a methylamine nitrate mixture as a sensitizer, wherein ammonium nitrate and formaldehyde are reacted in the liquid phase to form an oxidizer/sensitizer blend which is mixed with other constituents to form a required blasting explosive composition, characterized in that an oxidizer/sensitizer blend comprising ammonium nitrate and a mixture of monomethylamine nitrate, dimethylamine nitrate and trimethylamine nitrate is formed by the reaction of ammonium nitrate and formaldehyde in the liquid phase in the presence of urea in order to reduce the amount of formic acid which would otherwise be present in the reaction mixture when urea is absent therefrom.
2. A method according to Claim 1, wherein the required blasting explosive composition is a slurry explosive composition.
3. A method according to Claim 1, wherein the required blasting explosive composition is a powder explosive composition.
4. A method according to Claim 1, 2 or 3, wherein the explosive composition is a permitted explosive of group P1, P2 or P3.