



(86) Date de dépôt PCT/PCT Filing Date: 2013/02/11
(87) Date publication PCT/PCT Publication Date: 2013/08/15
(45) Date de délivrance/Issue Date: 2020/06/02
(85) Entrée phase nationale/National Entry: 2014/08/08
(86) N° demande PCT/PCT Application No.: IB 2013/051107
(87) N° publication PCT/PCT Publication No.: 2013/118103
(30) Priorité/Priority: 2012/02/10 (GB1202402.2)

(51) Cl.Int./Int.Cl. *C06B 25/36* (2006.01),
C06B 31/12 (2006.01), *C06B 31/32* (2006.01),
C06B 47/00 (2006.01)
(72) Inventeur/Inventor:
ZIMMERMANN, LEON MICHAEL, ZA
(73) Propriétaire/Owner:
MAXAM DANTEX SOUTH AFRICA (PROPRIETARY)
LIMITED, ZA
(74) Agent: BLAKE, CASSELS & GRAYDON LLP

(54) Titre : SOLUTION OXYDANTE AYANT UN BAS POINT DE CRISTALLISATION
(54) Title: OXIDIZER SOLUTION WITH LOW CRYSTALLIZATION POINT

(57) **Abrégé/Abstract:**

According to this invention there is provided an aqueous oxidizer solution containing a mixture of dissolved oxidizing salts, for use in the preparation of explosives formulations, which a crystallization point as low as below 0°C. The solution has a water content of 25% by mass or less and contains ammonium nitrate and calcium nitrate wherein the ratio of the the molar concentration of ammonium nitrate to calcium nitrate is preferably approximately 1. When the water content of the solution is 24% by mass or less, the solution further contains monomethylammonium nitrate. This solution can be used for manufacturing watergel explosives, or emulsion explosives or ANE's (ammonium nitrate emulsion suspension or gel explosives). It can be easily transported underground in deep level mines through relatively small diameter pipelines, using existing access ways and shafts, to the working places at which point it can then be converted into a watergel or emulsion explosive or an ANE.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 August 2013 (15.08.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/118103 A3

(51) International Patent Classification:

C06B 25/36 (2006.01) *C06B 31/12* (2006.01)
C06B 47/00 (2006.01) *C06B 31/32* (2006.01)

(21) International Application Number:

PCT/IB2013/051107

(22) International Filing Date:

11 February 2013 (11.02.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1202402.2 10 February 2012 (10.02.2012) GB

(71) Applicant: **MAXAM DANTEX SOUTH AFRICA (PROPRIETARY) LIMITED** [ZA/ZA]; Rand Leases Mine, Main Reef Road, 1710 Florida (ZA).

(72) Inventor: **ZIMMERMANN, Leon Michael**; C313 Summerfield Park, 32 Maudehurst Street, 2194 Jukskei Park (ZA).

(74) Agents: **SPOOR & FISHER** et al.; P O Box 454, 0001 Pretoria (ZA).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(88) Date of publication of the international search report:

7 November 2013

(54) Title: OXIDIZER SOLUTION

(57) Abstract: According to this invention there is provided an aqueous oxidizer solution containing a mixture of dissolved oxidizing salts, for use in the preparation of explosives formulations, which a crystallization point as low as below 0°C. The solution has a water content of 25% by mass or less and contains ammonium nitrate and calcium nitrate wherein the ratio of the the molar concentration of ammonium nitrate to calcium nitrate is preferably approximately 1. When the water content of the solution is 24% by mass or less, the solution further contains monomethylammonium nitrate. This solution can be used for manufacturing watergel explosives, or emulsion explosives or ANE's (ammonium nitrate emulsion suspension or gel explosives). It can be easily transported underground in deep level mines through relatively small diameter pipelines, using existing access ways and shafts, to the working places at which point it can then be converted into a watergel or emulsion explosive or an ANE.



WO 2013/118103 A3

OXIDIZER SOLUTION WITH LOW CRYSTALLIZATION POINT

BACKGROUND OF THE INVENTION

In most countries where bulk explosives are used they fall in a category defined in the United Nations Handbook on the Transportation of Dangerous Goods as ammonium nitrate emulsions suspensions or gels (abbreviated ANE) and are transported and stored as oxidizers 5.1 with U.N. number 3375. As the name implies these are either in the form of emulsions or watergels (or slurries). Because they are not classified as explosives the regulations regarding transportation and storage are considerably less stringent than they would be if they were classified as explosives. These ANE's are sensitized to become explosives as they are pumped into the blast hole either by mechanical gas entrainment or by the addition of a chemical blowing agent during the pumping process.

One of the problems with existing bulk explosives formulations (whether they are of the watergel or emulsion type) are that they are extremely viscous fluids and are difficult to pump or transport in pipelines over long distances. This is not normally a problem in surface mining where vehicle access is simply a matter of driving to the hole to be charged and lowering the charging hose down the hole and then pumping the explosive into the hole. However when using bulk products in underground applications it would be very convenient if one could place the pumping unit at a point some distance from the working face to be charged and simply run a long length of hose to the hole to be charged. This is especially true in narrow reef stoping as encountered in many gold and platinum mines.

A second problem is the problem of getting the explosive underground in the first place. Since this must be done by transporting it in containers using the same lifting equipment or access ways used for men, equipment and ore, this can seriously hamper production. Since they are non-explosive until they are pumped into the shot hole it is at least theoretically possible to pump them through a long pipeline to the point where they are needed underground. Here again the viscosity is a problem as there is a finite limit on how far a viscous fluid can be pumped

1 bearing in mind the energetic nature of the material being pumped and therefore the limitation
2 on maximum pumping pressure to which it can be exposed.

3
4 The physical nature of the ANE's is another limitation as to the distance that it can be
5 transported in a pipeline. In the case of a watergel or a slurry type ANE the product is in the
6 form of a saturated solution of oxidizer salts and soluble fuels thickened with a thickener of
7 some sort (normally guar gum) into which is mixed further quantities of oxidizer salts and
8 (possibly) insoluble fuels. When pumping such a suspension through a very long line one runs
9 the risk of the solids blocking the line entirely and stopping the pumping process entirely. If one
10 were considering dropping or pumping such a suspension through a long vertical (or inclined)
11 pipe in order to get it underground the risk of the pipeline blocking would be so great as to make
12 this a foolhardy exercise indeed. In the case of an emulsion type ANE these are made by
13 preparing a solution of oxidizer salts in water at an elevated temperature and then emulsifying
14 this solution into a fuel phase consisting of oil and emulsifier and then allowing the emulsion to
15 cool down to ambient temperature. Due to the very small size of the emulsion micelles the salts
16 are incapable of recrystallizing. It must be remembered that the fuel phase of the emulsion only
17 makes up about 6% or 7% of the product and that this is the continuous phase. The oxidizer salt
18 solution makes up in excess of 90% of the emulsion and this is the disperse phase. This means
19 that the cell walls around the oxidizer solution droplets is extremely thin and stretched and that if
20 these cell walls should fail for any reason the oxidizer solution droplets would agglomerate
21 together and once the micelles get big enough the salts will then start crystallizing out of
22 solution. When this happens the growing crystals start piercing further micelle walls and the
23 emulsion rapidly breaks down and the salts crystallize because they are so far below their
24 crystallization temperature. When this happens the entire mass solidifies and ceases to be a
25 pumpable fluid. If one is contemplating transporting the emulsion from surface to underground
26 through a long pipeline the risk of the emulsion breaking down during transportation must be
27 considered and if this happens the pipeline would block completely with severe economic and
28 production consequences.

29

1 Theft is also a major problem both of packaged explosive and of bulk explosives used in the
2 mining industry. Stolen explosives can find their way into the hands of criminals or terrorists and
3 are a major threat to the public.

4
5 It is an object of this invention to address these problems.

6
7 **SUMMARY OF THE INVENTION**

8
9 According to the present invention there is provided an aqueous oxidizer solution consisting
10 essentially of a mixture of dissolved oxidizing nitrate salts with less than 25% by mass water, for
11 use in the preparation of explosives formulations, which has a crystallization point of 10°C or
12 less, as low as 5°C or less, even as low 0°C or less, said solution containing:

13 ammonium nitrate; and

14 calcium nitrate or mixture of calcium nitrate and magnesium nitrate, preferably calcium
15 nitrate;

16 wherein the molar concentration of ammonium nitrate to calcium nitrate or mixture of
17 calcium nitrate and magnesium nitrate is between 0.5:1 and 1.5:1, more preferably between
18 0.75:1 and 1.25:1 and most preferably approximately 1; and

19 an alkylamine nitrate or monoethanolamine nitrate present in an amount of 1% to 20% by
20 mass.

21
22 By "crystallization point" is meant the temperature at which one or more of the dissolved oxidizing
23 salt/s begin to precipitate from the oxidizer solution.

24
25 When the solution comprises a mixture of calcium nitrate and magnesium nitrate, the ratio of the
26 molar concentrations of the calcium nitrate to the magnesium nitrate should not be less than
27 about 4:1 and preferably not less than about 4.5:1.

28
29 Typically, the oxidizer solution has a water content of between 10% and 25%, between 12% and
30 24%, preferably between 17% and 22%, by mass.

1 The alkylamine nitrate or monoethanolamine nitrate may be present in an amount of 1% to 20%
2 by mass, typically in an amount of 10% to 18% by mass, or from 12% to 17% by mass.

3

4 For every 1% reduction in the water content below 24%, the solution preferably contains at least
5 an additional 1.67% alkylamine nitrate or monoethanolamine nitrate in order to retain a low
6 crystallization point for the solution. Put in another way, the alkylamine nitrate or
7 monoethanolamine nitrate is preferably present in at least a quantity to satisfy the equation: $M >$
8 $5(24-W)/3$ (where W = the percentage water in the solution and M = the percentage alkylamine
9 nitrate or monoethanolamine nitrate in the solution).

10

11 The alkylamine nitrate may be methylamine nitrate (also called monomethylammonium nitrate),
12 dimethylamine nitrate or trimethylamine nitrate, preferably methylamine nitrate.

13

14 This solution can be used for the manufacture of either a watergel or an emulsion explosives or
15 an ANE. Other nitrates, such as magnesium nitrate, sodium nitrate and potassium nitrate can be
16 introduced but these must be at molar concentrations significantly lower than the calcium nitrate.

17

18 The invention also covers a method of manufacturing an explosives formulation by mixing the
19 oxidizer solution described above with a fuel.

20

21 The invention further covers an explosives formulation comprising a mixture of the oxidizer
22 solution described above with a fuel.

23

24 The fuel may be a hydrocarbon fuel such as diesel fuel, paraffin, oil etc, a water soluble alcohol
25 or polyol (e.g. monoethylene glycol, glycerol, ethanol, methanol, propanol) a water soluble
26 carbohydrate such as sugar. In general if one were making a watergel type ANE one might well
27 choose a water soluble fuel, however immiscible fuels can also be used with great success to
28 make a watergel. If one were making an emulsion type ANE then the choice would be for one of
29 the hydrocarbon fuels mentioned above or even recovered lubricating or other oil such as
30 vegetable oil.

31

DESCRIPTION OF PREFERRED EMBODIMENTS

I have invented an aqueous oxidizer solution containing a mixture of dissolved oxidizing salts with less than 25% water that does not crystallize below 10°C, and even as low as 0°C or less (as low as -7°C), and that can be used to make a watergel or an emulsion explosive or an ANE (ammonium nitrate emulsion suspension or gel) provided that it meets the following criteria:

- 1) The solution contains less than 25% water;
- 2) The solution contains ammonium nitrate (NH_4NO_3) and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) in a molar ratio of ammonium nitrate to calcium nitrate of between 0.5:1 and 1.5:1 and preferably between 0.75:1 and 1.25:1 and most preferably as close to 1:1 as possible; and
- 3) When the water content of the solution drops below 24%, for every 1% of water removed from the solution one adds at least 1.67% of monomethylammonium nitrate ($\text{CH}_3\text{NH}_3\text{NO}_3$, also known as methylamine nitrate). Put differently, the content of monomethylammonium nitrate should satisfy the equation: $M > 5(24-W)/3$ (where W = the percentage water in the solution and M = the percentage monomethylammonium nitrate in the solution).

Since the molecular mass of ammonium nitrate is 80.043 and the molecular mass of calcium nitrate is 164.086, condition 2) can be restated as (for example): The solution contains ammonium nitrate and calcium nitrate in a percentage ratio of calcium nitrate to ammonium nitrate of between 4.1:1 and 1.37:1 and preferably between 2.73:1 and 1.64:1 and ideally as close to 2.05:1 as possible.

If it is desired one can replace some of the calcium nitrate with magnesium nitrate (i.e. have a calcium nitrate/magnesium nitrate mixture), provided that the ratio of the molar concentration of ammonium nitrate to the sum of the molar concentrations of the calcium nitrate and the magnesium nitrate should be between 0.5:1 and 1.5:1 and preferably between 0.75:1 and 1.25:1 and most preferably as close to 1:1 as possible. Furthermore the ratio of the molar concentrations of the calcium nitrate to the magnesium nitrate should not be less than about 4:1 and preferably not less than about 4.5:1. Sodium nitrate and/or potassium nitrate can be

1 introduced as well but in this case, in order to obtain a sub-zero crystallization point, the
2 controlling factor is the ratio of molar concentrations of the ammonium nitrate and the calcium
3 nitrate as well as the relative water and monomethylammonium nitrate percentages and the
4 quantity of sodium or potassium nitrate that can be introduced is determined mainly by their
5 solubility in the available water.

6
7 This solution can then be used for manufacturing (among other things) watergel or emulsion
8 explosives or ANE's. It can be most advantageously easily transported underground in deep
9 level mines through relatively small diameter pipelines, using existing access ways and shafts,
10 to the working places at which point it can then be converted into a watergel or emulsion
11 explosive or an ANE.

12
13 When using the oxidizer solutions according to the present invention for making emulsion
14 explosives, it is possible to transport the oxidizer solution and the fuel/emulsifier mixture
15 separately and create the emulsion at the point of use in such a way that if the explosive is left
16 without being used for more than a few days (for example) then the emulsion would separate and
17 render it non-explosive due to the inherently unstable nature of any emulsion. This new system
18 can provide a major step forward in the fight against criminal activity and terrorism, since it
19 makes the theft of the explosives unattractive due to the extremely short shelf life of the final
20 explosive. Obviously, since the two components of the emulsion are liquids, there is no practical
21 limit to how far they can be transported in a pipeline and what is more the pipeline could be of a
22 very small diameter and therefore of very low cost which is not the case with a normal emulsion
23 type ANE.

24
25 In addition the free flowing characteristics of this product is such that pumping through a long
26 hose presents no difficulties whatsoever. In a narrow reef mining situation one could place the
27 pumping unit in a safe location and run a hose from there to the working face. Once the
28 charging up is complete the miner would wind the hose up and the next day, once the face has
29 been cleaned he would unreel the hose to the new working face and charge up once more. It
30 would probably not be necessary to move the pumping unit more than once per month making a
31 huge saving in time and manpower.

The Invention will be described in more detail with reference to the following non-limiting Examples.

In the Examples described below the solutions were made from 80% monomethylammonium nitrate solution and either solid ammonium nitrate or 88% ammonium nitrate solution as well as agricultural calcium nitrate manufactured by South African company OMNIA Fertilizer Ltd and sold under the trade name OMNICAL[™] which contains about 80% calcium nitrate and about 15% water with the balance being ammonium nitrate. The reason for using this and not chemically pure material is that the standard chemically pure calcium nitrate contains 30.5% water in the form of water of crystallization and by using the agricultural material I was able to prepare solutions containing high levels of calcium nitrate while still maintaining relatively low levels of water. The mixture was then heated to prepare a clear solution which was then cooled while stirring and the crystallization point was measured and reported as being the point at which the first crystals appeared.

The invention will now be demonstrated by means of some examples shown in Table 1 below:

Table 1:

Mix number	A1	A2	A3	A4	A5	A6	A7	A8
Ammonium nitrate (AN) (%)	6.6	12.0	16.3	20.0	23.1	25.8	28.1	30.1
Calcium nitrate (CN) (%)	54.4	49.0	44.7	41.0	37.9	35.2	32.9	30.9
Moles AN/Moles CN	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
Water (%)	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
Monomethylammonium nitrate (%)	17.0	17.0	17.0	17.0	17.0	17.0	17.0	17.0
Crystallization point (°C)	16	4	-7	-6	3	6	11	14
Mix number	B1	B2	B3	B4	B5	B6	B7	B8
Ammonium nitrate (AN) (%)	7.0	12.5	17.1	21.0	24.2	27.0	29.5	31.6
Calcium nitrate (CN) (%)	57.0	51.5	46.9	43.0	39.8	37.0	34.5	32.4

Moles AN/Moles CN	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
Water (%)	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
Monomethylammonium nitrate (%)	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Crystallization point (°C)	6	3	-4	-4	3	8	13	17
Mix number	C1	C2	C3	C4	C5	C6	C7	C8
Ammonium nitrate (AN) (%)	7.3	13.1	17.9	22.0	25.4	28.3	30.9	33.1
Calcium nitrate (CN) (%)	59.7	53.9	49.1	45.0	41.6	38.7	36.1	33.9
Moles AN/Moles CN	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
Water (%)	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
Monomethylammonium nitrate (%)	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0
Crystallization point (°C)	38.8	20.5	-6	-5	3	9	15	18

1

2 These results demonstrate that at constant quantities of water, even when the water content is
3 relatively high (22%) the crystallization point is well above 0°C when the molar ratio of
4 ammonium nitrate to calcium nitrate is outside the range 0.5:1 to 1.5:1 and is always below 0°C
5 when the molar ratio of ammonium nitrate to calcium nitrate is 1:1.

6

7 Table 2:

Mix number	G1	G2	G3	G4	G5	G6	G7	G8
Ammonium nitrate (AN) (%)	7.3	13.3	18.2	22.3	25.8	28.7	31.3	33.6
Calcium nitrate (CN) (%)	59.5	54.7	49.8	45.7	42.2	39.3	36.7	34.4
Moles AN/Moles CN	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
Water (%)	15.6	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Monomethylammonium nitrate (%)	17.6	17.0	17.0	17.0	17.0	17.0	17.0	17.0
Crystallization point (°C)	27	18	-4	-4	8	19	22	28
Mix number	H1	H2	H3	H4	H5	H6	H7	H8
Ammonium nitrate (AN) (%)	7.6	13.9	19.0	23.3	26.9	30.0	32.7	35.1
Calcium nitrate (CN) (%)	62.7	57.1	52.0	47.7	44.1	41.0	38.3	35.9

Moles AN/Moles CN	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
Water (%)	15.4	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Monomethylammonium nitrate (%)	14.3	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Crystallization point (°C)	54.5	37.5	17.6	4	10	18	25	28
Mix number	J1	J2	J3	J4	J5	J6	J7	J8
Ammonium nitrate (AN) (%)	8.0	14.5	19.8	24.3	28.0	31.3	34.1	36.5
Calcium nitrate (CN) (%)	65.8	59.5	54.2	49.7	46.0	42.7	39.9	37.5
Moles AN/Moles CN	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
Water (%)	15.1	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Monomethylammonium nitrate (%)	11.1	11.0	11.0	11.0	11.0	11.0	11.0	11.0
Crystallization point (°C)	53	48	25	17	9	17	27	32

1

2 These results show that with solutions having a low water content if the content of
3 monomethylammonium nitrate drops below a certain level the solution, while still having a
4 minimum crystallization point when the molar ratio of ammonium nitrate to calcium nitrate is in
5 the range 0.75:1 to 1.25:1, this minimum is no longer below 0°C. While a sub-zero crystallization
6 point is almost certainly not needed for handling and use underground it is certainly of great
7 benefit during transport to the mine as well as for storage both at the point of manufacture and
8 at the mine. The point is that what has been discovered is a method of minimizing the
9 crystallization point of an oxidizer solution while maintaining relatively low water levels which in
10 turn allows one to produce an explosive at the point of end use which has sufficient energy to
11 perform well when breaking rock.

12

13 Table 3:

Mix number	Z1	Z2	Z3
Ammonium nitrate (AN) (%)	26.2	25.6	24.9
Calcium nitrate (CN) (%)	53.8	52.4	51.1
Moles AN/Moles CN	1.00	1.00	1.00
Water (%)	20.0	22.0	24.0

Monomethylammonium nitrate (%)	0	0	0
Crystallization point (°C)	18	11	-3

1

2 Here the results show that when the molar ratio of ammonium nitrate to calcium nitrate is 1:1, if
3 the water content of the solution is 24% or higher no monomethylammonium nitrate is needed in
4 order to achieve a sub-zero crystallization point.

5

6 Table 4:

Mix number	G4	G4A	G4B	H4
Ammonium nitrate (AN) (%)	22.3	22.6	23.0	23.3
Calcium nitrate (CN) (%)	45.7	46.4	47.0	47.7
Moles AN/Moles CN	1.00	1.00	1.00	1.00
Water (%)	15.0	15.0	15.0	15.0
Monomethylammonium nitrate (%)	17.0	16.0	15.0	14.0
Crystallization point (°C)	-4	-4	-1	4

7

8 These results indicate that at a water content of 15% if the monomethylammonium nitrate
9 content is 15% then one can still achieve a sub-zero crystallization point provided that the molar
10 ratio of ammonium nitrate to calcium nitrate is 1:1.

11

12 Table 5 below looks at a series of results for solutions where the molar ratio of ammonium
13 nitrate (AN) to calcium nitrate (CN) was held at 1:1 while the water content was reduced in 1%
14 steps from 24% to 14% while the monomethylammonium nitrate (MMAN) content was increased
15 from 0 to 16.67% in steps of 1.67%. In every single case the crystallization point remained
16 below 0°C.

17

18 Table 5:

Mix number	K1	K2	K3	K4	K5	K6	K8	K9	K10	K11	K12
% AN	24.9	24.7	24.5	24.3	24.0	23.8	23.6	23.4	23.2	23.0	22.7
% CN	51.1	50.6	50.2	49.7	49.3	48.8	48.4	47.9	47.5	47.0	46.6

Moles AN/Moles CN	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
% Water	24.0	23.0	22.0	21.0	20.0	19.0	18.0	17.0	16.0	15.0	14.0
% MMAN	0.00	1.67	3.33	5.00	6.67	8.33	10.00	11.67	13.33	15.00	16.67
Crystallization point (°C)	-3	-3	-4	-4	-2	-5	-3	-2	-2	-1	-5

Table 6 below looks at a series of results for solutions where the molar ratio of ammonium nitrate (AN) to calcium nitrate (CN) was once more held at 1:1 while the water content was again reduced in 1% steps from 24% to 14% while the monomethylammonium nitrate (MMAN) content was increased from 0 to 20% in steps of 2%. In every single case the crystallization point remained below 0°C.

Table 6:

Mix number	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11
% AN	24.9	24.6	24.3	23.9	23.6	23.3	23.0	22.6	22.3	22.0	21.6
% CN	51.1	50.4	49.7	49.1	48.4	47.7	47.0	46.4	45.7	45.0	44.4
Moles AN/Moles CN	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
% Water	24.0	23.0	22.0	21.0	20.0	19.0	18.0	17.0	16.0	15.0	14.0
% MMAN	0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	20.0
Crystallization point (°C)	-6	-6	-5	-7	-6	-6	-5	-6	-6	-5	-4

The above two sets of results show that maintaining these constant proportions yields remarkably consistent crystallization points.

One can introduce magnesium nitrate into the solution and still maintain a sub-zero crystallization point provided that the molar ratio of calcium nitrate to magnesium nitrate does not drop below about 4.0:1 and preferably that this ratio does not drop below about 4.25:1 and most preferably that this ratio does not drop below 4.5:1 in addition the ratio of the molar

concentration of ammonium nitrate to the sum of the molar concentrations of calcium nitrate and magnesium nitrate must be as close to 1:1 as possible.

This is demonstrated in the results shown in Table 7 below where MN refers to magnesium nitrate:

Table 7:

Mix number	N1	N2	N3	N4	N5	N6	N7	N8	N9
% AN	13.5	18.3	22.4	25.8	28.8	18	22.5	25.9	22.5
% CN	45	41.0	37.6	34.7	32.2	39	35.5	32.8	32.9
% MN	9	8.2	7.5	6.9	6.4	10.5	9.6	8.8	12.1
Moles CN/Moles MN	4.5	4.5	4.5	4.5	4.5	3.4	3.4	3.4	2.46
Moles AN/(Moles CN + Moles MN)	0.50	0.75	1.00	1.25	1.50	0.73	1.00	1.25	1.00
Moles AN/Moles CN	0.61	0.92	1.22	1.53	1.83	0.95	1.30	1.62	1.40
% Water	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5
% MMAN	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Crystallization point (°C)	6	1	-2	11	20	11	7	9	11

In Table 8 below we show results for solutions made with identical quantities of water and MMAN but without the presence on magnesium nitrate.

Table 8:

Mix number	E1	E2	E3	E4	E5	E6	E7	E8
% AN	7.3	13.2	18.1	22.1	25.6	28.5	31.1	33.3
% CN	60.2	54.3	49.4	45.4	41.9	39.0	36.4	34.2
Moles AN/Moles CN	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00
% Water	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5
% MMAN	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Crystallization point (°C)	6	4	-3	-7	7	14	18	22

This demonstrates that with relatively low concentrations of magnesium nitrate, at a molar ratio of calcium nitrate to magnesium nitrate of about 4.5:1 or greater, one can still achieve a sub-zero crystallization point provided that the molar ratio of ammonium nitrate to the sum of calcium and magnesium nitrate is about 1:1. It is clear that where there is magnesium nitrate present the molar ratio is between ammonium nitrate and the sum of calcium and magnesium nitrate and not between ammonium nitrate and calcium nitrate alone.

Solutions were then prepared with varying quantities of sodium nitrate (SN) together with the same quantities of monomethylammonium nitrate and water as those used in mixes A1 to A8 in Table 1 above but now without the calcium nitrate. The results are shown in Table 9 below:

Table 9:

Mix number	SN1	SN2	SN3	SN4	SN5	SN6	SN7	SN8	SN9	SN10
% AN	61	59	57	55	53	51	49	47	45	43
% SN	0	2	4	6	8	10	12	14	16	18
Moles AN/Moles SN	-	31.3	15.1	9.7	7.0	5.4	4.3	3.6	3.0	2.5
% Water	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
% MMAN	17.0	17.0	17.0	17.0	17.0	17.0	17.0	17.0	17.0	17.0
Crystallization point (°C)	35	33	32	31	30	30	31	30	33	47

This shows clearly that while there is a slight crystallization point depressing effect with addition of sodium nitrate up to about 16% the effect is almost negligible when compared to the system containing only ammonium nitrate, monomethylammonium nitrate and water, unlike the system when calcium nitrate is used where the crystallization point depression is dramatic when the ratio of the molar concentration of ammonium nitrate to calcium nitrate is close to 1:1.

Solutions were prepared with sodium nitrate (SN) together with calcium nitrate, ammonium nitrate, monomethylammonium nitrate and water. The results are shown in table 10 below.

1 Table 10:

Mix number	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
% AN	14.6	20.0	24.6	28.4	31.7	14.2	19.4	23.8	27.5	30.7
%CN	44.9	39.5	34.9	31.1	27.8	47.8	42.6	38.2	34.5	31.3
% SN	8	8	8	8	8	5.5	5.5	5.5	5.5	5.5
Moles AN/Moles CN	0.67	1.04	1.44	1.87	2.34	0.61	0.93	1.28	1.63	2.01
% Water	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5
% MMAN	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Crystallization point (°C)	25	19	16	18	20	6	5	-1	9	16

2

3 It is clear that in the presence of sodium nitrate as long as the ratio of the molar concentration of
4 ammonium nitrate to calcium nitrate is in the range specified for the system without sodium
5 nitrate then small amounts of sodium nitrate can be introduced, but even at these low levels it
6 has the effect of raising the crystallization point. A similar effect is seen with potassium nitrate
7 as shown in the Table 11a and Table 11b below:

8

9 Table 11a:

Mix number	KN1	KN2	KN3	KN4	KN5	KN6	KN7	KN8	KN9	KN10
% AN	14.4	15.5	19.6	24.1	27.8	31.0	14.0	16.4	19.2	23.5
%CN	43.6	42.5	38.4	33.9	30.2	27.0	47.0	44.6	41.8	37.5
% Potassium nitrate	9.5	9.5	9.5	9.5	9.5	9.5	6.5	6.5	6.5	6.5
Moles AN/Moles CN	0.68	0.75	1.05	1.46	1.89	2.35	0.61	0.75	0.94	1.28
% Water	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5
% MMAN	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Crystallization point (°C)	0	<-6	-4	2	12	21	1	<-6	<-6	-3

10

11 Table 11b:

Mix number	KN11	KN12	KN13	KN14	KN15	KN16	KN17	KN18	KN19
% AN	27.1	30.2	14.0	15.0	17.1	20.6	25.2	29.1	32.5
%CN	33.9	30.8	38.3	37.3	35.2	31.7	27.1	23.3	19.8

% Potassium nitrate	6.5	6.5	15.2	15.2	15.2	15.2	15.2	15.2	15.2
Moles AN/Moles CN	1.64	2.01	0.75	0.82	1.00	1.33	1.91	2.57	3.36
% Water	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5
% MMAN	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Crystallization point (°C)	8	18	12	10	11	20	26	32	36

Emulsion products were then prepared from solutions B4 and K3 in order to investigate their effectiveness as an explosive. These two solutions were chosen since they both crystallized at 4°C and both contained the same quantity of water but differing quantities of monomethylammonium nitrate in order to check the effect of the monomethylammonium nitrate on the explosive properties of the resulting emulsion explosive. The final products had the following analyses.

Table 12:

Mix number	Emulsion B4	Emulsion K3
% AN	18.9%	21.6%
% CN	38.8%	44.2%
% MMAN	12.6%	2.9%
% Water	19.8%	19.4%
PIBSA Emulsifier	1.0%	1.0%
Soya bean oil	5.8%	7.8%
Glass microspheres*	3.1%	3.1%
Oxygen balance	-0.75%	-0.04%
Theoretical net explosive energy	2.874 MJ/kg	2.950 MJ/kg
Product density	1.19 g/cm ³	1.19 g/cm ³

* K20 microspheres made by 3M

The emulsions were each made into 50mm diameter cartridges, 600mm long, by loading into plastic lay-flat tubing (100 micron thick) and initiated with a 15g pentolite booster. Emulsion B4 initiated and detonated over its entire length at constant velocity as demonstrated by a witness

1 pipe placed in contact with the cartridge which was flattened completely over the full length of
2 the cartridge. Emulsion K3 failed to maintain detonation and most of the product was recovered.
3 This trial indicates that the monomethylammonium nitrate not only improves the solubility of the
4 salts at progressively lower water levels it also assists in the sensitivity of the final emulsion.

5

6 This invention opens the way to transporting the aqueous oxidizer solution, the oil and emulsifier
7 mixture and the gassing reagent separately to the mine. And then transporting them from
8 surface to the underground workings through relatively small diameter pipelines, over any
9 desired length, directly to the face to be blasted and then only mixing the three liquids (oxidiser
10 solution, oil/emulsifier solution and gassing reagent) to form an explosive emulsion as they are
11 pumped into the hole. It might also be feasible to emulsify the gassing reagent into the
12 oil/emulsifier mixture and in this way only transport two liquids underground for mixing at the
13 blast face. The point is that throughout there would be no need to keep the solution heated in
14 heated storage vessels or heated and jacketed pipelines as would be needed with oxidizer
15 solutions of the prior art.

16

17

CLAIMS

1. An aqueous oxidizer solution consisting of a mixture of dissolved oxidizing nitrate salts and water, for use in the preparation of explosives formulations, which has a crystallization point of 10°C or less; said solution consisting of:
 - between 12% and 24% by mass water;
 - an alkylamine nitrate or monoethanolamine nitrate in an amount of 10% to 18% by mass; and
 - ammonium nitrate and calcium nitrate or mixture of calcium nitrate and magnesium nitrate;
 - wherein the molar concentration of ammonium nitrate to calcium nitrate or mixture of calcium nitrate and magnesium nitrate is between 0.75:1 and 1.25:1.
2. The aqueous oxidizer solution claimed in claim 1, wherein the crystallization point is 0°C or less.
3. The aqueous oxidizer solution claimed in claim 2, wherein the molar concentration of ammonium nitrate to calcium nitrate is approximately 1.
4. The aqueous oxidizer solution claimed in claim 2, wherein the molar concentration of ammonium nitrate to mixture of calcium nitrate and magnesium nitrate is approximately 1.
5. The aqueous oxidizer solution claimed in claim 4, wherein the ratio of the molar concentration of the calcium nitrate to the magnesium nitrate is not less than 4:1.
6. The aqueous oxidizer solution claimed in claim 5, wherein the ratio of the molar concentration of the calcium nitrate to the magnesium nitrate is not less than 4.5:1.
7. The aqueous oxidizer solution claimed in any one of claims 1 to 6, wherein the aqueous oxidizer solution has a water content of between 17% and 22%, by mass.
8. The aqueous oxidizer solution claimed in any one of claims 1 to 7, wherein the alkylamine nitrate or monoethanolamine nitrate is present in an amount of 12% to 17% by mass.

9. The aqueous oxidizer solution claimed in claim 8, wherein, for every 1% reduction in the water content below 24%, the solution contains at least an additional 1.67% alkylamine nitrate or monoethanolamine nitrate.
10. The aqueous oxidizer solution claimed in claim 8, wherein the alkylamine nitrate or monoethanolamine nitrate is present in the solution in at least a quantity to satisfy the equation: $M > 5(24-W)/3$ (where W = the percentage water in the solution and M = the percentage alkylamine nitrate or monoethanolamine nitrate in the solution).
11. The aqueous oxidizer solution claimed in any one of claims 1 to 10, wherein the alkylamine nitrate is monomethylamine nitrate, dimethylamine nitrate or trimethylamine nitrate.
12. The aqueous oxidizer solution claimed in claim 11, wherein the alkylamine nitrate is monomethylamine nitrate ($\text{CH}_3\text{NH}_3\text{NO}_3$).
13. A method of manufacturing an explosives formulation, the method including the step of mixing the aqueous oxidizer solution defined in any one of claims 1 to 12 with a fuel.
14. An explosives formulation comprising a mixture of the oxidizer solution defined in any one of claims 1 to 12 with a fuel.