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(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.



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OXIDIZER SOLUTION

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

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

transporting the emulsion from surface to underground through a long pipeline the risk of the emulsion breaking down during transportation must be considered and if this happens the pipeline would block completely with severe economic and production consequences.

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

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

SUMMARY OF THE INVENTION

According to the present invention there is provided an aqueous oxidizer solution containing a mixture of dissolved oxidizing salts, for use in the preparation of explosives formulations, which has a crystallization point of below 30°C, preferably below 25°C, as low as 15°C or less, as low as 10°C or less, as low as 5°C or less, even as low 0°C or less, said solution containing:

- a water content of 25% by mass or less;
- ammonium nitrate; and
- calcium nitrate or mixture of calcium nitrate and magnesium nitrate, preferably calcium nitrate;

wherein the molar concentration of ammonium nitrate to calcium nitrate or mixture of calcium nitrate and magnesium nitrate is between 0.25:1 and 2:1, preferably between 0.5:1 and 1.5:1, more preferably between 0.75:1 and 1.25:1 and most preferably approximately 1.

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

When the solution comprises a mixture of calcium nitrate and magnesium nitrate, 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.

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

When the water content of the solution is 24% by mass or less, the solution preferably further contains alkylamine nitrate.

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

For every 1% reduction in the water content below 24%, the solution preferably contains at least an additional 1.67% alkylamine nitrate in order to retain a low crystallization point for the solution. Put in another way, the alkylamine nitrate is preferably present 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 in the solution).

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

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

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

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

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

DESCRIPTION OF PREFERRED EMBODIMENTS

This patent application claims priority from United Kingdom provisional patent application no. GB 1202402.2, the content of which is incorporated herein by reference.

I have invented an aqueous oxidizer solution containing a mixture of dissolved oxidizing salts with less than 25% water that does not crystallize below 30°C, at low temperatures below 25°C, 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 25% water or less;
- 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 0.25:1 and 2:1, preferably 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 8.2:1 and 1:1 and preferably 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 0.25:1 and 2:1, preferably 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 introduced as well but in this case, in order to obtain a sub-zero crystallization point, the controlling factor is the ratio of molar concentrations of the ammonium nitrate and the calcium nitrate as well as the relative water and monomethylammonium nitrate percentages and the quantity of sodium or potassium nitrate that can be introduced is determined mainly by their solubility in the available water.

This solution can then be used for manufacturing (among other things) watergel or emulsion explosives or ANE's. It can be most advantageously 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.

When using the oxidizer solutions according to the present invention for making emulsion explosives, it is possible to transport the oxidizer solution and the fuel/emulsifier mixture separately and create the emulsion at the

point of use in such a way that if the explosive is left without being used for more than a few days (for example) then the emulsion would separate and render it non-explosive due to the inherently unstable nature of any emulsion. This new system can provide a major step forward in the fight against criminal activity and terrorism, since it makes the theft of the explosives unattractive due to the extremely short shelf life of the final explosive. Obviously, since the two components of the emulsion are liquids, there is no practical limit to how far they can be transported in a pipeline and what is more the pipeline could be of a very small diameter and therefore of very low cost which is not the case with a normal emulsion type ANE.

If one were making a watergel type ANE then the solution could be thickened with a suitable thickener, such as guar gum and in this case one could use any one of the previously mentioned water soluble fuels or one of the hydrocarbon fuels. When using a hydrocarbon fuel one might want to add a surfactant of some kind to assist in keeping the hydrocarbon in suspension. Clearly one could simply thicken the oxidizer solution before transport to the point of use and then add the hydrocarbon fuel (or alcohol or polyol) as the product is pumped into the hole. Whichever method of manufacture is followed the fact that the watergel has no suspended solid means that it would be perfectly safe to drop it down a vertical pipe of virtually any length in order to get it from surface to underground. In addition the free flowing characteristics of this product is such that pumping through a long hose presents no difficulties whatsoever. In a narrow reef mining situation one could place the pumping unit in a safe location and run a hose from there to the working face. Once the charging up is complete the miner would wind the hose up and the next day, once the face has been cleaned he would unreel the hose to the new working face and charge up once more. It would probably not be necessary to move the pumping unit more than once per month making a 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

Crystallization point (°C)	53	48	25	17	9	17	27	32
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These results show that with solutions having a low water content if the content of monomethylammonium nitrate drops below a certain level the solution, while still having a minimum crystallization point when the molar ratio of ammonium nitrate to calcium nitrate is in the range 0.75:1 to 1.25:1, this minimum is no longer below 0°C. While a sub-zero crystallization point is almost certainly not needed for handling and use underground it is certainly of great benefit during transport to the mine as well as for storage both at the point of manufacture and at the mine. The point is that what has been discovered is a method of minimizing the crystallization point of an oxidizer solution while maintaining relatively low water levels which in turn allows one to produce an explosive at the point of end use which has sufficient energy to perform well when breaking rock.

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

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

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	18

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

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

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	51.9	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.

% 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	11.5	7	9	11

In Table 8 below we show results for solutions made with identical quantities of water and MMAN but without the presence of 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	-	31.3	15.1	9.7	7.0	5.4	4.3	3.6	3.0	2.5

SN										
% 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.

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

It is clear that in the presence of sodium nitrate as long as the ratio of the molar concentration of ammonium nitrate to calcium nitrate is in the range specified for the system without sodium nitrate then small amounts of sodium nitrate can be introduced, but even at these low levels it has the effect of raising the crystallization point. A similar effect is seen with

potassium nitrate as shown in the Table 11a and Table 11b below:

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

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	12.1	10.0	10.6	20.2	26.0	32.0	36.0

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

This invention opens the way to transporting the aqueous oxidizer solution, the oil and emulsifier mixture and the gassing reagent separately to the mine. And then transporting them from surface to the underground workings through relatively small diameter pipelines, over any desired length, directly to the face to be blasted and then only mixing the three liquids (oxidiser solution, oil/emulsifier solution and gassing reagent) to form an explosive emulsion as they are pumped into the hole. It might also be feasible to emulsify the gassing reagent into the oil/emulsifier mixture and in this way only transport two liquids underground for mixing at the blast face. The point is that throughout there would be no need to keep the

solution heated in heated storage vessels or heated and jacketed pipelines as would be needed with oxidizer solutions of the prior art.

CLAIMS

1. An aqueous oxidizer solution containing a mixture of dissolved oxidizing salts, for use in the preparation of explosives formulations, which has a crystallization point of below 30°C, preferably below 25°C, as low as 15°C or less, as low as 10°C or less; even as low as 0°C or less, said solution containing:
 - a water content of 25% by mass or less;
 - ammonium nitrate; and
 - calcium nitrate or mixture of calcium nitrate and magnesium nitrate, preferably calcium nitrate;wherein the molar concentration of ammonium nitrate to calcium nitrate or mixture of calcium nitrate and magnesium nitrate is between 0.25:1 and 2:1.
2. The aqueous oxidizer solution claimed in claim 1, wherein the crystallization point is below 25°C.
3. The aqueous oxidizer solution claimed in claim 2, wherein the crystallization point is 15°C or less.
4. The aqueous oxidizer solution claimed in claim 3, wherein the crystallization point is 10°C or less.
5. The aqueous oxidizer solution claimed in claim 4, wherein the crystallization point is 0°C or less.
6. The aqueous oxidizer solution claimed in any one of claims 1 to 5, wherein the molar concentration of ammonium nitrate to calcium nitrate is between 0.5:1 and 1.5:1.
7. The aqueous oxidizer solution claimed in claim 6, wherein the molar concentration of ammonium nitrate to calcium nitrate is between 0.75:1 and 1.25:1.
8. The aqueous oxidizer solution claimed in claim 7, wherein the molar

concentration of ammonium nitrate to calcium nitrate is approximately 1.

9. The aqueous oxidizer solution claimed in any one of claims 1 to 5, wherein the molar concentration of ammonium nitrate to mixture of calcium nitrate and magnesium nitrate is between 0.5:1 and 1.5:1.
10. The aqueous oxidizer solution claimed in claim 9, wherein the molar concentration of ammonium nitrate to mixture of calcium nitrate and magnesium nitrate is between 0.75:1 and 1.25:1.
11. The aqueous oxidizer solution claimed in claim 10, wherein the molar concentration of ammonium nitrate to mixture of calcium nitrate and magnesium nitrate is approximately 1.
12. The aqueous oxidizer solution claimed in any one of claims 9 to 11, wherein the ratio of the molar concentrations of the calcium nitrate to the magnesium nitrate is not less than about 4:1.
13. The aqueous oxidizer solution claimed in claim 12, wherein the ratio of the molar concentrations of the calcium nitrate to the magnesium nitrate is not less than about 4.5:1.
14. The aqueous oxidizer solution claimed in any one of the preceding claims, wherein the aqueous oxidizer solution has a water content of between 10% and 25%, by mass.
15. The aqueous oxidizer solution claimed in claim 14, wherein the aqueous oxidizer solution has a water content of between 12% and 24%, by mass
16. The aqueous oxidizer solution claimed in claim 15, wherein the aqueous oxidizer solution has a water content of between 17% and 22%, by mass.
17. The aqueous oxidizer solution claimed in any one of the preceding claims, wherein the water content of the solution is 24% by mass or less,

and the solution further contains alkylamine nitrate.

18. The aqueous oxidizer solution claimed in claim 17, wherein the alkylamine nitrate is present in an amount of 1% to 20% by mass.
19. The aqueous oxidizer solution claimed in claim 18, wherein the alkylamine nitrate is present in an amount of 10% to 18% by mass.
20. The aqueous oxidizer solution claimed in claim 19, wherein the alkylamine nitrate is present in an amount of 12% to 17% by mass.
21. The aqueous oxidizer solution claimed in claim 17, wherein, for every 1% reduction in the water content below 24%, the solution contains at least an additional 1.67% alkylamine nitrate.
22. The aqueous oxidizer solution claimed in claim 17, wherein the alkylamine 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 in the solution).
23. The aqueous oxidizer solution claimed in any one of claims 17 to 22, wherein the alkylamine nitrate is monomethylamine nitrate, monoethanolamine nitrate, dimethylamine nitrate or trimethylamine nitrate.
24. The aqueous oxidizer solution claimed in claim 23, wherein the alkylamine nitrate is monomethylamine nitrate ($\text{CH}_3\text{NH}_3\text{NO}_3$).
25. 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 24 with a fuel.
26. An explosives formulation comprising a mixture of the oxidizer solution defined in any one of claims 1 to 24 with a fuel.
27. An aqueous oxidizer solution as claimed in any one of claims 1 to 24, substantially as herein described with reference to any one of the

Examples.

28. An explosives formulation as claimed in 26, substantially as herein described with reference to any one of the Examples.