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EXPLOSIVES SUITABLE FOR SAFETY BLASTING EXPLOSIVES

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The present invention relates to the provision of new and improved ammonium nitrate detonating explosives of generally low power characteristics and is especially applicable to the production of explosives for use in gassy and dusty mines, since it is possible by means of the invention to obtain explosives of excellent safety characteristics as regards ignition of dangerous atmospheres. At the same time the explosives produced according to the invention have desirable characteristics, other than their excellent safety characteristics, for which explosives having low velocities of detonation are applicable, for instance in coal mining generally for the mining of lump coal, and in various quarrying and blasting purposes for which safety blasting explosives are frequently employed in practice.

In the hitherto known safety or permitted explosives a considerable proportion of the power producing gases is ordinarily provided by the exothermic reaction between ammonium nitrate and a non-explosive organic fuel, which is usually a vegetable carbohydrate material of organic structure, the proportions of these ingredients being such that the composition as a whole is nearly oxygen balanced, so that the gaseous products resulting from the detonation shall so far as possible be carbon dioxide, steam and nitrogen. Explosive compositions so compounded from self-explosive ingredients, ammonium nitrate and a non-explosive organic fuel, however, are still possessed of rather hot flames and of high velocity characteristics and are thus still too liable to ignite gassy or dusty atmosphere to be safe for use where these are prevalent, and it is necessary to intermingle heat absorbing flame-quenching ingredients with the exothermically reacting flame producing ingredients. Due care is therefore required to ensure that the ingredients are well mixed together.

It has been proposed in British Pat. No. 436,144 to employ as a portion of a non-detonating blasting charge within a pressure resisting vessel having a pressure-venting closure a mixture of ammonium nitrate and a fuel consisting of ammonium carbonate. This mixture, when suitably heated under confinement in the pressure resisting vessel, reacts exothermically with the production of gaseous products but without the production of any flame but such a mixture cannot be used in ordinary safety blasting cartridges owing to the volatility of the ammonium carbonate, and its action on the self-explosive ingredients.

We have now found that safety and other low power low velocity detonating explosives having an unusually favourable combination of explosive qualities and safety towards ignitions of gassy or dusty atmospheres may be obtained by the employment in conjunction with a self-explosive sensitizer and the ammonium nitrate, a fuel comprising in association a non-deliquescent ammonium salt of an inorganic acid, this ammonium salt containing insufficient oxygen in its composition to oxidize the ammonium radicle completely with the formation of nitrogen and water, and an insoluble metal carbonate, the latter being preferably present in the amount at least sufficient theoretically for metathetical transformation of the mixture into ammonium carbonate and a salt of the metal.

According to the present invention therefore detonating explosives of generally low power characteristics comprising ammonium nitrate and a self-explosive sensitizer include a fuel comprising in association a non-deliquescent ammonium salt of the kind herein defined and an insoluble metal carbonate.

Unlike the hitherto used organic fuels used in conjunction with the ammonium nitrate, mixtures of the ammonium salt of the inorganic acid as aforesaid and the insoluble metal carbonate in the proportions theoretically required for their metathetical transformation into ammonium carbonate and a salt of the metal react with the ammonium nitrate without flame and help to quench the flame from the self-explosive sensitizer, as well as producing power gases.

The heat evolved in the detonation by a mixture of the ammonium nitrate and the fuel consisting of the non-deliquescent ammonium salt of an inorganic acid, as aforesaid, and the insoluble metal carbonate is considerably less than that from ammonium nitrate compositions containing vegetable carbohydrate fuels, and in the absence of other compounds the mixture is incombustible. Moreover if the insoluble metal carbonate were omitted from the explosive composition made according to the invention, by mischance in the course of manufacture, that would not render it unsafe from the point of view of ignition in fiery or dusty mines, although unpleasant fumes would be evolved; and in the absence of any other substance a mixture of ammonium nitrate and a non-deliquescent ammonium salt of an inorganic acid as aforesaid is indeed incombustible.

By means of the invention there may be obtained a wide variety of low power detonating explosives including powder, gelatine and semi gelatine explosives suitable for the aforementioned purposes and having satisfactory storage properties.

As the non-deliquescent oxidizable ammonium salt there may be conveniently employed for instance ammonium sulphate, phosphate or chloride. As the insoluble metal carbonate there may be used any natural or artificial form of calcium carbonate, magnesium carbonate, barium carbonate, iron carbonate or the like, for instance, limestone fines, chalk, dolomite fines, witherite fines, siderite fines or marble fines. The size and shape of the particles of the ingredients, as might be expected, are not without influence on the sensitiveness characteristics of the composition, especially when the self-explosive ingredient is one capable of absorption, i. e. a liquid. Thus particles of dust-like fineness should be avoided, since if the particles are too fine they may make the composition insensitive.

Every three gram atoms of available oxygen are capable of oxidizing amounts of a mixture of insoluble metal carbonate and non-delinquescent oxidizable ammonium salt as aforesaid equivalent to 1 gram molecule of normal ammonium carbonate; so that when the other ingredients of the explosive neither contain nor consume available oxygen, an oxygen balanced explosive is obtained by the use of amounts of the insoluble metal carbonate and the non-deliquescent oxidizable ammonium salt as aforesaid theoretically equivalent to 1 gram molecule of normal ammonium carbonate for every 3 gram molecules ammonium nitrate. Reasonably small variations from zero oxygen value on either side as in ordinary explosive compositions are of course permissible.

Moreover, the use of a stoichiometric excess of the insoluble metal carbonate over the oxidizable ammonium salt as aforesaid is frequently useful since it acts as an additional cooling or flame quenching agent without producing any objectionable flames, although it somewhat reduces the sensitiveness to initiation. Various other flame quenching or cooling ingredients may be likewise included. It is sometimes desirable to include such excess of insoluble metal carbonate or other flame quenching or cooling ingredients, as when, for instance an explosive of especially low velocity of detonation, low power and high safety characteristics is required; or when a gelatine or semi-gelatine explosive of good safety characteristics is required, since in this case the attainment of the requisite consistency necessitates the use of higher proportions of liquid self-explosive ingredients than need be present in the case of powder explosive compositions.

It is also sometimes desirable to include in the detonating explosive a small amount of an acid buffer salt as for example sodium or ammonium dihydrogen phosphate, or of a non-alkaline mixture of buffer salts as for example one or more alkali metal dihydrogen orthophosphates and one or more dialkali metal orthophosphates in such relative proportions as to give neutral mixtures of these salts.

It is also sometimes desirable to include a small quantity of fibrous or bulky material, for example about one per cent of asbestos, to prevent any tendency of setting of the detonating explosives.

The explosives prepared in accordance with the present invention yield unobnoxious products of detonation, and are of higher density than explosives made with ammonium nitrate and fuels composed of the customary carbohydrate materials or organic structure.

The ammonium nitrate, the insoluble metal carbonate and the non-deliquescent oxidizable ammonium salt may be used as individual materials, of which the particles are brought into simple admixture with one another and with the self-explosive ingredients, but it is also possible to use composite granules prepared for instance in the wet way or by fusion, and containing the ammonium nitrate and non-deliquescent oxidizable ammonium salt as aforesaid in intimate association with one another and with the insoluble metal carbonate. In some cases there is a tendency for reactions to occur with evolution of ammoniacal vapours during the heating in the course of the preparation of the composite granules in either of these ways, and in such cases a suitable buffer salt may be included in the mixture in order to minimize the alkalinity, for instance ammonium dihydrogen phosphate.

The invention is further illustrated by the following examples, wherein the parts and percentages mentioned are by weight unless otherwise indicated.

Example 1

48.6 parts ammonium nitrate, 21.3 parts ammonium chloride, and 20.1 parts limestone fines, of the undernoted grists, are intimately mixed in an Atlas mixer into 10 parts of a jelly made from an 80:20 mixture of nitroglycerine and ethylene glycol dinitrate and blasting soluble nitrocellulose, containing 99 per cent of the nitric esters and 1 per cent of the nitrocellulose. (Blasting soluble nitrocellulose may be defined as the product of purified cotton cops nitrated by the pot process to a nitrogen content of 11.95 to 12.25 per cent. The product is at least 95 per cent soluble in an ether-alcohol solution, and has a viscosity of 100 to 300 C. G. S. in solution of 3 gms. in 100 ml. acetone 95 per cent at 20° C.)

The ammonium nitrate nearly all passes a 20 mesh British Standard Specification screen, roughly 45 per cent being retained on a 40 mesh, 70 per cent on a 60 mesh and 95 per cent on a 100 mesh screen. The ammonium chloride nearly all passes a 40 mesh screen, roughly 15 per cent being retained on a 40 mesh, 35 per cent on a 60 mesh and practically all on a 100 mesh sieve. The limestone fines all passes a 40 mesh screen, roughly 55 per cent being retained on a 100 mesh and 75 per cent on a 120 mesh screen.

The resulting powder safety explosive when cartridged to a bulk density of 1.1 grams per cubic centimetre can be detonated easily by commercial detonators; and when it was tested a few days after its manufacture a 1¼" x 8" cartridge could be detonated by a No. 1 detonator, which is the weakest detonator commercially available; and in a double cartridge test in which two cartridges, each in an ordinary wrapper are arranged co-axially at prearranged distances and enclosed in paper rolled tightly round them both so that their relative positions are maintained, one of the two cartridges being primed with a detonator at the end remote from the other cartridge, the detonation was transmitted across a gap of about 15 inches. The velocity of detonation was about 1,400 metres per second. When a cartridge of the specified size was fired from a gun into a 9 per cent methane-air mixture (by volume) and into a coal dust air mixture, according to the conditions prescribed for the official gallery tests, no ignitions resulted. In a gallery test in which a 1¼″ diameter cartridge was fired suspended in a 9 per cent (by volume) methane-air mixture the charge limit was about 14 ozs. The explosive had a power amounting to about 45 per cent that of blasting gelatine as determined by the ballistic mortar method. Moreover, the safety characteristics of the explosive were not substantially lowered by storage.

Example 2

The ingredients and the method of preparation were the same as in Example 1, but the proportion of limestone fines was increased at the expense of the other salts so that the final composition contained 85 per cent of the mixture of salts in the proportions shown in Example 1, with 5 per cent extra limestone fines and 10 per cent of the jelly. When cartridged at a bulk density of 1.17 and tested after a few days the sensitiveness in the double cartridge gap test was approximately 12 inches and the viscosity of detonation roughly 1,500 metres per second. The cartridges failed to give ignition in gallery tests conducted as prescribed for the official gallery tests and in the test in which the cartridge is suspended in the methane-air mixture the charge limit was about the same as that of the cartridges made according to Example 1. The power was roughly 40 per cent of that of blasting gelatine.

Example 3

43.2 parts ammonium nitrate, 18.9 parts ammonium chloride and 17.9 parts limestone fines of the same grists as in Example 1 are mixed with 20 parts pentaerythritol tetranitrate. When cartridged at a density of 0.99 the resulting powder explosive is sensitive to initiation by a small commercial detonator, and has a velocity of about 2,500 meters per second and a power of about 53 per cent of that of blasting gelatine.

Example 4

32.4 parts ammonium nitrate, 14.2 parts ammonium chloride and 28.4 parts limestone fines, all of the same grists as in Example 1, are intimately mixed in a McRoberts mixer into 25 parts of a jelly made from an 80:20 mixture of nitroglycerine and ethylene glycol dinitrate and blasting soluble nitrocellulose, containing 97 per cent of the liquid nitric esters. The resulting safety gelatine explosive can be cartridged by extrusion. When tested a few days after its manufacture a 1¼″ x 8″ cartridge could be detonated by a small commercial detonator, and in the double cartridge gap test the detonation was transmitted across a gap of about 6½ inches. The density was 1.74 grams per cubic centimetre and the velocity of detonation was about 1,800 metres per second. The cartridges failed to give ignition in gallery tests conducted as prescribed in the official gallery tests, and in the tests which the cartridges were suspended in the methane-air mixture the charge limit was about 14 ozs. The power of the explosive was about 46 per cent of that of blasting gelatine.

Example 5

A strong solution in hot water was formed from 45.2 parts ammonium nitrate, 25.0 parts ammonium sulphate and 1.0 part ammonium dihydrogen phosphate. 18.8 parts limestone fines of the same grist as that used in Example 1 were suspended in the solution, and the mixture was evaporated to dryness and granulated by keeping it in motion during the evaporation of the water. The dry granules were nearly all fine enough to pass the 20 B. S. S. screen, about 55 per cent being retained on a 40 mesh screen, about 65 per cent on a 60 mesh screen and about 90 per cent on a 100 mesh screen. 90 parts of these granules were mixed with 10 parts of the jelly containing the liquid nitric esters and nitrocellulose as described in Example 1. When cartridged to a bulk density of 1.2 grams per cubic centimetre and tested after a few days the sensitiveness of the resulting powder explosive in the double cartridge gap test was approximately 17 inches, and the velocity of detonation roughly 2,500 metres per second. The cartridges failed to give ignition in gallery tests as prescribed in the official gallery tests, and in the test in which the cartridge is suspended in methane-air mixture the charge limit was about 4 ozs.

Example 6

The materials used and the procedure were the same as in Example 5, except that the ratio of the graulated mixture of salts to the jelly was increased to 95:5. When cartridged to a bulk density of 0.95 and tested after a few days it was sensitive to initiation by a small commercial detonator. The velocity of detonation was about 1,400 metres per second.

Example 7

Ingredients used were ammonium nitrate, ammonium chloride and limestone fines of the grists indicated in Example 1 and were used in the same relative proportions. These ingredients were first mixed together and then granulated by a fusion process. The granules passed a 20 B. S. S. screen, and were thereafter mixed with the liquid nitric ester-nitrocellulose jelly as used in Example 1. When the ratio of the granules to the jelly was 93:7 and the packing density was 0.93, the corresponding velocity of detonation was about 1,500, and when the ratio was 95:5 and the packing density 0.92 the velocity of detonation was about 1,300. In each case the cartridges failed to give ignitions in gallery tests conducted as prescribed for the official gallery tests.

They were sensitive to the smallest sizes of commercial detonator.

We claim:

1. Low power explosive compositions comprising at least 30% by weight of the explosive of ammonium nitrate, a less proportion of detonating explosive sensitizer ingredient, an oxidizable ammonium salt selected from the group consisting of ammonium chloride, ammonium sulphate, and ammonium phosphate, and an insoluble metal carbonate, said oxidizable ammonium salt and metal carbonate being present in amounts sufficient to provide two ammonium radicals and at least one carbonate radical for every three molecules of ammonium nitrate.

2. Low power explosive compositions as claimed in claim 1, wherein the amount of metal carbonate is in excess of that required to provide one carbonate radical for every three molecules of ammonium nitrate.

3. Low power explosive compositions as claimed in claim 1, wherein the oxidizable ammonium

salt is ammonium chloride, and the metal carbonate is calcium carbonate.

4. Low power explosive compositions as claimed in claim 1, wherein a small amount of an acid buffer salt is included.

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