V.O.D. VS \( \text{NH}_4\text{NO}_3 : \text{HNO}_3 \) RATIO

FOR COMPOSITIONS AT OXYGEN BALANCE

WITH DNT

TRANSITION FROM LIQUID TO SOLID AT 5°C

LIQUID COMPOSITION AT 5°C

SOLID COMPOSITION AT 5°C

CHANGE IN V.O.D. WITH ADDITION OF METHYLENE BIS-(MONOMETHYL NAPHTHYLENE SODIUM SULPHONATE) IN 53/47 AN/HNO_3 COMPOSITIONS AT OXYGEN BALANCE WITH DNT.
FIG. 4

CHANGE IN V.O.D. WITH ADDITION OF CREOSOTE IN 53/47 AN/HNO₃ COMPOSITIONS AT OXYGEN BALANCE WITH DNT

NOTE: AVERAGE V.O.D. IN 2 5" DIAMETES.

FIG. 5

CHANGE IN V.O.D. WITH ADDITION OF ACETONE IN 53/47 AN/HNO₃ COMPOSITIONS AT OXYGEN BALANCE WITH DNT

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AGENT
NITRIC ACID EXPLOSIVE COMPOSITION CONTAINING INORGANIC NITRATE OXIDIZER AND NITRATED AROMATIC COMPOUND

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Filed Apr. 13, 1966, Ser. No. 542,247
Claims priority, application Canada, Apr. 21, 1965, 928,749
7 Claims. (Cl. 149—56)

This invention relates to improved explosive compositions of the Sprengel type which consist essentially of one or more oxidizing constituents and one or more organic fuel constituents.

It was found by Hermann Sprengel in British patent specification No. 921 dated April 6, 1871, that explosive compositions of high strength could be manufactured by mixing combustible organic fuel ingredients, which were themselves non-explosive, with a non-explosive oxidizing agent such as concentrated nitric acid. The principal advantage of such explosive compositions could be found in the fact that since both the fuel ingredient and the oxidizing ingredient were non-explosive materials, each might be transported without danger of detonation to the blasting site where they then could be combined in appropriate proportions just before use.

These Sprengel explosives have been shown to combine low cost, high strength, a high velocity of detonation and a high level of sensitivity, and yet they have not enjoyed any commercial success. Because of the nature of the oxidizing material normally employed, for example, concentrated nitric acid, these explosives were inconvenient, unpleasant and especially hazardous to handle. In addition, because of the generally low viscosity of the fluid Sprengel mixtures, large quantities could be lost into fissured rock if the explosives were placed directly into boreholes. Additionally, Sprengel explosives generally possess little or no resistance against penetration and dilution by water which may be present in the boreholes, which dilution may render the explosives non-detonatable.

In addition, when employed in boreholes in rock of an alkaline nature, for example, limestone or similar carbonate rock, vigorous chemical reaction between the carbonate rock and nitric acid may occur causing the formation of water, an evolution of gas and consequent possible ejection of the explosives from the boreholes.

Where in the past, as disclosed, for example, in United States Patent No. 2,525,065, a pre-mixed Sprengel type explosive was prepared, special acid-proof containers were required in which the explosive could be packaged safely for transportation and use. Similarly, where a thickened Sprengel explosive was employed as disclosed, for example, in British patent specification No. 883,918, the explosive required packaging in metal or plastic containers.

It has now been discovered that many of the disadvantages of prior art Sprengel nitric acid explosives, that is, low viscosity, lack of water resistance, the need for acid resistant packaging means and the need for thickening agents or stabilizers, may be overcome by employing as the oxidizing ingredient a mixture of concentrated nitric acid and an inorganic nitrate, preferably ammonium nitrate.

It is therefore the primary object of this invention to provide a nitric acid explosive which may be simply and economically manufactured.

Still another object of this invention is to provide a nitric acid explosive which may be simply compounded to provide a wide range of explosive properties.

Other objects of the invention will appear hereinafter.

The improved nitric acid explosive composition of this invention comprises at least one inorganic nitrate, concentrated nitric acid and an organic fuel which is miscible with and does not react with nitric acid.

It has been found that a mixture of an inorganic nitrate and concentrated nitric acid, when combined in liquid form at specific temperatures with an organic fuel such as, for example, molten, partially nitrated derivatives of toluene, to give an approximately oxygen-balanced mixture, will form a solid water-resistant high strength explosive sensitive to a No. 6 blasting cap.

It is thus now possible to prepare useful and powerful nitric acid explosives under controlled conditions and so eliminate the disadvantages heretofore associated therewith.

In order to more fully understand the composition of the nitric acid explosive of the invention, it is advantageous to examine the chemical reactions which occur when strong or concentrated nitric acid is combined with ammonium nitrate. It has been disclosed, for example, in Chemical Abstracts, volume 29, pages 561 and 3789, that a trinitrate of ammonium can be formed when ammonium nitrate and concentrated nitric acid are combined in the ratio of one mole of ammonium nitrate to two moles of nitric acid. For pure materials, this ratio is 38.8 parts by weight of ammonium nitrate to 61.2 parts by weight of nitric acid. The trinitrate salt so formed, NH₂NO₃·2HNO₃, has a melting point of 29.6°C. It has also been disclosed in United States Patent No. 1,997,927 that an ammonium trinitrate may be produced by mixing ammonia or ammonium nitrate with nitric acid containing 90 to 99% of HNO₃ and cooling the solution to or below the crystallization point of the ammonium trinitrate. The ammonium trinitrate salt so formed may then be separated from the mother liquor.

It will be obvious to one skilled in the chemical art that various ratios by weight of ammonium nitrate to concentrated nitric acid will yield a range of mixtures of reactants and reaction products. To demonstrate the unique characteristics of the oxidizing ingredient of the explosive compositions of the invention reference is made to the accompanying drawings wherein:

FIG. 1 is a phase diagram for an ammonium nitrate-nitric acid system;

FIG. 2 is a graphical representation of the velocity of detonation obtained using various ratios of ammonium nitrate/HNO₃ in the explosive of the invention at oxygen balance with dinitrotoluene; and

FIGS. 3, 4 and 5 are graphical representations showing how the velocity of detonation can be varied as desired by using gas generating additives in the explosives of the invention.

Referring to FIG. 1, there is shown a phase diagram which demonstrates the physical character of an ammonium nitrate-98% HNO₃ system for various ammonium nitrate/HNO₃ ratios over a range of temperatures.

Graph line ABC represents the point of the solidification point of solids obtained at the ratios and temperatures indicated. Line DE represents the stoichiometric proportions of 38 parts of ammonium nitrate to 62 parts of 98% HNO₃ by weight. As can be seen from an examination of the phase diagram, relatively small quantities of the ammonium nitrate, for example, up to about 20 parts of ammonium nitrate, dissolved in about 80 parts by weight of strong (98%) nitric acid will yield appreciable amounts of solid ammonium trinitrate salt, only at low temperatures. At the stoichiometric ratio, solid ammonium trinitrate crystallizes at about 27°C.
point B on the graph, a ratio of 53 parts of ammonium nitrate to 47 parts of 98% HNO₃, a low melting point eutectic is formed which crystallizes at about 13° C. With an increase in the proportion of ammonium nitrate above about 53 parts by weight, a rapid increase in the crystallization temperature results. It will, of course, be appreciated by those familiar with the art that small amounts of water (less than 1%) present in the strong nitric acid has a pronounced effect on the freezing temperature of the system because, as crystallization progresses, the freezing point of the remaining fluid phase gets progressively lower due to the gradual increase in proportion of water. It has been found, using ratios around the stoichiometric proportion, that ammonium trinitrate does not usually start to crystallize until the reactants have been super cooled to about 3° C. However, once started, crystallization takes place rapidly and the heat of crystallization released causes the temperature to rise immediately to about 27° C. If, on the other hand, the solution is seeded with a few crystals of ammonium trinitrate at around 27° C, freezing will take place immediately as the temperature is lowered.

It has indeed been surprisingly discovered that when an organic fuel which is miscible with and does not react with nitric acid is added to an ammonium nitrate/98% nitric acid, at a specific temperature, the system remains fluid only momentarily, then rapid crystallization of the mixture takes place and the composition sets up in a semi-frozen state in a matter of seconds. On further cooling, a solid, water resistant explosive is formed which may be detonated with a No. 6 blasting cap. By mixing the two components at optimum temperatures, the explosive is completely fluid only momentarily and thickens rapidly due to crystallization. This feature obviates the need for thickening or gelling agents to prevent loss into fissured rock. The solid explosive composition thus formed may be described as a substantially homogeneous mixture of very fine needle-like crystals of ammonium nitrate, ammonium trinitrate and organic fuel. The crystals comprising the solid explosive composition may be identified under microscopic examination.

It has been unexpectedly found that the addition of the miscible organic fuel to the low melting point eutectic nitrate/nitric acid solution has the surprising effect of causing the crystallization of salts of the system outside the temperature ranges shown in the phase diagram of FIG. 1. The addition of the miscible organic fuel causes, in effect, a displacement in position of plot line ABC in FIG. 1 in a direction to the left of the diagram. Although the mechanism of the crystallization of the system is not fully understood, it is postulated that the addition of the miscible organic fuel ingredient to the ammonium nitrate/nitric acid solution has the effect of absorbing or taking up some of the nitric acid present as it crystallizes on cooling. This taking up of a portion of the nitric acid thereby alters the effective ratio of ammonium nitrate to nitric acid in the remaining solution, causing the above-mentioned shift in the phase relationship, and results in rapid crystallization of some of the ammonium nitrate. As the resultant semi-frozen explosive composition further cools to, for example, normal rock temperature of about 5° C, a particularly dense solid crystal state is achieved as indicated by the area below the line FG in FIG. 1 of the drawings, at 13° C. It has been found essential to produce a structure of fine needle-like crystals in the solid explosive of the invention if adequate detonation sensitivity is to be maintained. As is well known in the art, very fine crystals of, for example, ammonium nitrate can be produced from solutions by rapid cooling. Slow cooling on the other hand, tends to result in crystal growth. Similarly, in the solid explosive compositions of this invention, too high temperatures results in slow cooling producing compositions of large crystal structure which will not detonate except in large diameter charges and by use of excessively strong priming charges. In addition, such slow-cooled, large crystal compositions tend to segregate into separate salt and fuel layers which may result in mixtures that will not detonate. It is then advantageous to employ as the oxidizing ingredient a mixture of ammonium nitrate and 98% nitric acid at a low enough temperature to facilitate the crystallization when mixed with the warm, liquid organic fuel ingredient. Such a composition comprises about 53 parts by weight of ammonium nitrate to 47 parts by weight of 98% nitric acid. This composition of the oxidizing ingredient may be referred to as a low melting point eutectic and corresponds to point B in the phase diagram of FIG. 1. Such a mixture has a crystallization point of about 13° C and may be maintained in a fluid condition in the field at only a slightly higher temperature. When, for example, a fluid miscible organic fuel which has been warmed to maintain fluidity is added to the relatively low temperature eutectic, the consequent increase in temperature of the mixture is not sufficient to inhibit the rapid production of fine needle-like crystals of both components. If, on the other hand, a nitrate/acid mixture is employed with a higher acid content than that of the eutectic, supercooling or gelation of the mixture to produce compositions of adequate sensitivity. Unless additional cooling is provided, the resultant composition may comprise large growth crystals which may be insensitive to usual detonation means or may fail to propagate after initiation.

Preferred nitric acid explosive compositions of this invention contain as an oxidant at least one inorganic nitrate and concentrated nitric acid in the approximate concentration range of about 30 parts by weight of nitrate salt/70 parts by weight of acid to about 70 parts by weight of nitrate salt/30 parts by weight of acid, and from 10% to 45%, by weight of the total compositions, of an organic fuel which is miscible with and does not react with nitric acid.

By “inorganic nitrate” is meant the salt produced by the action of nitric acid upon the metals or upon metallic oxides and hydruxides or, additionally, ammonium nitrate. A very suitable inorganic nitrate for inclusion in the explosive composition of this invention is ammonium nitrate. It may in some cases be advantageous to replace some or all of the ammonium nitrate by other inorganic nitrates such as potassium nitrate. The particle size of the inorganic salt is not critical, since the salt is dissolved in the nitric acid and granulated, prilled or crystalline forms, coated or uncoated, may be used.

The acid component of the explosive of this invention is preferably an acid containing 98% HNO₃ although an acid containing from 90% by weight HNO₃ and up to the highest strength commercially available may be employed. An acid of a strength less than about 95% appreciably lowers the fusing or freezing temperature of the composition. However, this can be compensated for by using lower mixing temperatures.

A suitable organic fuel which is miscible with and which does not react with nitric acid is preferably dinitrotoluene (DNT) but other partially nitrated aromatic compounds may be used. With dinitrotoluene, maximum blasting efficiency results with amounts of DNT which give oxygen-balanced compositions.

Some or all of the organic fuel may consist of a molten acid-inert organic explosive such as, for example, TNT. In the case where TNT is employed either alone or in mixtures as an organic fuel, the safety advantage of using a non-explosive fuel is foregone.

As mentioned herebefore, the nitric acid explosive of the invention may be simply prepared. In use in the field, the two liquid ingredients, mixing is not exact, but the resulting mixture is the nitrate/HNO₃ solution and the liquid organic fuel, need only be poured simultaneously at specific tempera-
tures and in appropriate proportions into the borehole where, at normal rock temperatures, solidification of the composition rapidly takes place. No special mixing equipment is required, and the resultant composition achieves a high borehole loading density with a good degree of water resistance on hardening. No special precautions other than those associated with the normal handling of strong nitric acid are required. Since the preferred individual constituents are not explosive until combined together in the borehole, a particular margin of safety may be enjoyed. Similarly, because of the non-explosive nature of the preferred primary constituents, no costly magazine storage facilities are required. The ingredients may be transported easily to the blasting site by means of, for example, a motor vehicle with appropriate tanks or holding vessels from which they may be simply dispensed. Each of the components in the fluid state may, for example, be discharged simultaneously at controlled rates from a holding vessel by means of hoses, the ends of which have been placed below the collar of a borehole. The nitrate/HNO₃ solution and the liquid fuel are thus combined in the borehole where rapid solidification takes place and a cap sensitive explosive is formed. Until the two components have been combined in the borehole, no explosive has been employed thereby permitting a wide margin of safety in the use of such compositions. While the explosive compositions of the invention lend themselves particularly to on-site mixing or mixing in the boreholes, this is not to say that the explosives may not be prepared and packaged in the explosive factory. Such factory manufacture will necessitate the use of special packaging since the compositions are highly acidic. Controlled temperature storage of the packaged product would also be required.

Referring to FIG. 2, the results may be seen in graphical form of the velocity of detonation (VOD) of a wide range of nitrate/HNO₃ ratios oxygen balanced with DNT. The VOD, shown in meters per second, was measured in the standard manner by means of a counter-chronograph. The charges comprised 2000 gram samples in 2.5" diameters packaged in polyethylene tubes. Primers comprising 160 grams of a 50/50 mixture of PETN/TNT (pentolite) were employed to detonate each charge at a temperature of 5°C. It will be noted from FIG. 2 that ammonium nitrate/HNO₃ ratios from 0/100 to about 20/80 oxygen balanced with DNT remained liquid at normal rock temperature of 5°C. Although such compositions may be used, they are not practical for commercial purposes because of their fluidity. Similarly ammonium nitrate/HNO₃ ratios from about 20/80 to 30/70 are in a transient state from liquid to solid and are likewise unattractive for use. Ammonium nitrate/HNO₃ ratios, however, between 30/70 and 70/30 oxygen balanced with DNT form solid compositions at temperatures above 5°C and are the preferred compositions of explosives of the invention. Such compositions, as can be seen in FIG. 2, possess VOD's in the range of about 6200 to about 1800 meters per second.

The following examples illustrate the improved compositions of this invention but the latter is in no manner to be limited in scope to the embodiments described.

EXAMPLE 1.—42/58 NH₄NO₃/HNO₃ AT OXYGEN BALANCE WITH DNT

30.2 parts by weight of ammonium nitrate dissolved in 41.8 parts by weight of 98% nitric acid were cooled to 23°C and seeded with a few NH₄NO₃·2HNO₃ crystals. This was mixed with 28 parts by weight of DNT at 60°C. The mixture was completely fluidly momentary, allowing for the two components to obtain. Due to a negative heat of solution of the NH₄NO₃·2HNO₃ crystals in the tertiary system an equilibrium temperature of 18°C resulted and the composition set up in a semi-frozen condition in 20 to 25 seconds. When cooled to normal rock temperature of about 5°C the explosive was homogeneous in texture, hard and dry. A 2000 gram sample of the composition in 2.5 inch diameter initiated with a 160 gram pentolite primer propagated at a velocity of detonation of 2715 meters per second.

EXAMPLE 2.—53/47 NH₄NO₃/HNO₃ AT OXYGEN BALANCE WITH DNT

A low melting point eutectic comprising 39.3 parts by weight of ammonium nitrate dissolved in 34.9 parts by weight of 98% nitric acid was cooled to 14°C. The solution was not seeded and no solids were present. This was mixed with 25.8 parts by weight of DNT at 60°C. The mixture was completely fluidly momentary, allowing for miscibility of the two components to obtain at a resulting equilibrium temperature of 28°C. The composition set up in a semi-frozen condition in 10 to 15 seconds. On cooling to normal rock temperature of about 5°C, the explosive was homogeneous, hard and dry. A 2000 gram sample of the composition in 2.5 inch diameter initiated with a 160 gram pentolite primer propagated with a detonation velocity of 2110 meters per second per second; and two similar samples primed with No. 1 fulminate-chlorate caps detonated at velocities of 2530 and 2410 meters per second.

EXAMPLE 3.—60/40 NH₄NO₃/HNO₃ AT OXYGEN BALANCE WITH DNT

45.4 parts by weight of ammonium nitrate were dissolved in 30.2 parts by weight of 98% nitric acid by heating and the solution was cooled to 25°C. At this temperature about 11% nitrate crystals were present. This crystal-solution mixture was combined with 24.4 parts by weight of DNT at 60°C. The composition reached an equilibrium temperature of 32°C immediately on mixing and appeared to be completely fluidly momentary, allowing for miscibility to obtain. Fudging or freezing to a semi-frozen state took place in 5 to 10 seconds, and on cooling to 5°C the explosive was homogeneous, hard and dry. A 2000 gram sample of the composition in 2.5 inch diameter, initiated with a 160 gram pentolite primer, propagated at a velocity of detonation of 1870 meters per second.

EXAMPLE 4.—44/56 KNO₃/HNO₃ AT OXYGEN BALANCE WITH DNT

A stoichiometric, 1:2 mole solution of potassium nitrate in 98% nitric acid was prepared by dissolving 30 parts by weight of KNO₃ in 38.5 parts by weight of acid. The solution was cooled to 18°C and seeded with a few crystals of potassium trinitrate. A small amount of nascent trinitrate crystal was formed. The crystal-solution mixture was combined with 31.5 parts by weight of DNT at 60°C. The composition immediately reached an equilibrium temperature of 15°C and was momentarily completely fluid but set up in a semi-frozen state in about 30 seconds. On cooling to 5°C, the explosive was homogeneous, hard and dry. A 2000 gram sample of the composition in 2.5 inch diameter initiated with a 160 gram primer propagated with a detonation velocity of 3240 meters per second.

EXAMPLE 5.—53/47 NH₄NO₃/HNO₃ AT OXYGEN BALANCE WITH TNT

A low melting point eutectic comprising 34.8 parts by weight of ammonium nitrate dissolved in 30.8 parts by weight of 98% nitric acid was heated to 60°C. This solution was mixed with 34.4 parts by weight of TNT at 85°C. The composition set up in a semi-frozen condition in 15 to 30 seconds and on further cooling to 5°C was homogeneous, dry and hard. A 2000 gram sample of the explosive in 2.5 inch diameter, initiated with a 160 gram pentolite primer, propagated at a velocity of detonation of 6020 meters per second.
EXAMPLE 6.—53/47 \(\text{NH}_4\text{NO}_3/\text{HNO}_3\) AT OXYGEN BALANCE WITH 30/70 MNT/TNT

A low melting point eutectic of 38.7 parts by weight of ammonium nitrate dissolved in 33.8 parts by weight of 98% nitric acid was combined with 16.8 parts by weight of dinitrotoluene and 11.2 parts by weight of DNT at 60°C. The composition was completely fluid immediately, allowing for miscibility of the components to obtain a resulting equilibrium temperature of 28°C. The composition set up in a semi-frozen condition in 15-20 seconds and, on cooling to 5°C, was homogeneous, hard and dry. A 2000 gram sample of the composition in 2.5 inch diameter, initiated with a 160 gram pentolite primer, detonated at a velocity of 2290 meters per second.

EXAMPLE 7.—53/47 \(\text{NH}_4\text{NO}_3/\text{HNO}_3\) AT OXYGEN BALANCE WITH 60/40 DINITROBENZENE/DNT

A low melting point eutectic of 38.2 parts by weight of ammonium nitrate dissolved in 33.8 parts by weight of 98% nitric acid was combined with 16.8 parts by weight of dinitrotoluene and 11.2 parts by weight of DNT at 60°C. The composition was completely fluid momentarily, allowing for miscibility of the components to obtain a resulting equilibrium temperature of 28°C. The composition set up in a semi-frozen condition in 15-20 seconds and, on cooling to 5°C, was homogeneous, hard and dry. A 2000 gram sample of the composition in 2.5 inch diameter, initiated with a 160 gram pentolite primer, propagated with detonation velocity of 2790 meters per second.

EXAMPLE 8

In a field trial at a rock quarry, two holes each of 2½ inch diameter and five feet apart were drilled to a depth of 39 feet at a point representing about 9 feet of burden at the quarry rock face. A vortex funnel was placed at the collar of each of the bores and, through separate hoses, 74.4 parts by weight of a low melting point eutectic similar to that shown in Example 2 and 25.6 parts by weight of DNT were run into the funnel at controlled rates from holding vessels. The whirling action achieved in the funnel adequately mixed the liquid components and approximately 115 pounds of the mixed explosive composition were run into each borehole. The composition set up in a semi-frozen condition in about 10 seconds and thereafter rapidly hardened. Each borehole charge was initiated by means of a 0.5 gram pentolite primer and an explosion connecting cord. In the detonation, a clean break of rock was achieved at the quarry face with resulting good fragmentation.

Whereas, as has been shown in FIG. 2 of the drawings, a wide range of detonation velocities may be obtained when employing ratios of ammonium nitrate/HNO_3 of from 30/70 to 70/30, it has also been noted heretofore that for use in the field, a low melting point eutectic, corresponding to point B in FIG. 1, is advantageously employed. Such a low melting point eutectic, because of its relatively low crystallization point of about 13°C, may be melted and handled in the fluid state in the field at only a slightly higher temperature than 13°C. The low melting point eutectic, oxygen balanced with, for example, DNT as in Example 2 above, however, has been found to have a detonation velocity of about 2100 meters per second. It can be seen therefore that whereas handling advantages may be gained in using a low melting point eutectic of ammonium nitrate/HNO_3, such a mixture oxygen balanced with, for example, DNT is limited in usefulness because of a relatively low velocity of detonation. As is well known in the art, a range of detonation velocities is desirable, and in fact essential, if useful work is to be accomplished by explosives on rock of various characteristics to achieve specific end results. In some instances, a high velocity explosive is required where high shattering or fragmentation is required. Alternatively, where low fragmentating and a heaving effect is desired, an explosive of low detonation velocity is employed.

It has been found that the low melting point eutectic comprising a ratio of ammonium nitrate/98% HNO_3 of about 53/47 by weight oxygen balanced with, for example, DNT, may be modified in composition to provide a wide range of detonation velocities, while at the same time retaining all of the advantages mentioned heretofore. A range of detonation velocities may be achieved with the preferred explosive compositions of the present invention by incorporating in the fuel a small amount of a substance which will react with the nitrate/HNO_3 component to produce a dispersion of microscopic gas bubbles throughout the solidified explosive composition. By means of a simple variation in the quantity of gas generating substance in the fuel component of the preferred explosive of the present invention, a full range of detonation velocities may be achieved. The gas generating substance that reacts with nitric acid must not react with, but must be soluble or miscible in the fuel component of the explosive composition so as to give a molecular dispersion and consequently produce gas bubbles that are microscopic in size. The reaction between the gas generating substance and the oxidizing solution must be slow so that migration of the gas is virtually eliminated by the microscopic bubbles being held in a uniform dispersion by the freezing or crystallizing of the explosive composition.

Any material which is soluble or miscible in the fuel component of the explosive and which reacts with the oxidizing solution to give a dispersion of microscopic gas may be used. Suitable gas generating substances are, for example, naphthylamine, methylene bis-(monomethyl-naphthalene sodium sulphonate), diphenylamine, aniline, cresote, o-toluidine, p-cresol, and acetone. As mentioned heretofore, the velocity of detonation of the nitric acid explosive of the present invention may be controlled by varying the quantity of gas generating substance in the mixture. Referring to FIG. 3 of the drawings, there is shown in graphical form the velocity of detonation obtained with a preferred explosive composition of the present invention comprising a low melting eutectic of ammonium nitrate/98% nitric acid oxygen balanced with DNT fuel in which is incorporated varying proportions of methylene bis-(monomethyl-naphthalene sodium sulphonate) from 0.0 to 0.5%.

It will be noted that an increased quantity of gas generating substance results in a proportionate increase in the velocity of detonation obtained. FIG. 4 and FIG. 5 show in similar graphical form the proportional changes in detonation velocities which result from the addition of other gas generating substances. In FIG. 4, the gas generating substance employed is cresote, and in FIG. 5, acetone.

The soluble or miscible gas generating substance in the desired quantity need only be added to the liquid organic fuel ingredient and stirred briefly to effect solution. The gas generating substance/fuel mixture then need only be employed as the fuel ingredient in the manner hereinbefore described.

The velocities of detonation shown in FIGS. 3, 4 and 5 of the drawings were determined in the standard manner by means of a counter-chronograph, 2000 gram samples of explosives packaged in 2½ inch diameter polythene tubes being used. 160 grams of pentolite primers were employed to detonate each charge. As exemplified heretofore, explosive compositions of this invention are, under normal conditions of use and confinement, cap sensitive. By "cap sensitive" it is meant that the range of formulations as mentioned heretofore, oxygen balanced with for example, DNT, may be initiated by means of a No. 6 fulminate-chlorate cap. The same compositions, however, show a sensitivity to impact or metaion, negative results being shown in
the standard Drop Test and Abrasion Test used for commercial explosives.

The following example illustrates the sensitivity to cap initiation and the lack of sensitivity to impact and abrasion of the explosive composition of the invention.

EXAMPLE 9.—38/62 NH₄NO₃/HNO₃ AT OXYGEN BALANCE WITH DNT

27 parts by weight of ammonium nitrate dissolved in 44 parts by weight of 98% nitric acid were cooled to 24° C. and seeded with a few crystals of ammonium tri-nitrate. Some nascent NH₄NO₃·2H₂O crystals were formed. This was mixed with 29 parts by weight of DNT at 60° C. These quantities represent the stoichiometrical proportions of one mole of ammonium nitrate to two moles of nitric acid that combine to form ammonium tri-nitrate. On mixing, the equilibrium temperature was about 19° C., the drop in temperature being due to a negative heat of solution of ammonium tri-nitrate crystals in the tertiary system. Thickening took place quickly due to the formation of very fine crystals of both fuel and oxidant, and on further cooling the composition, it will be appreciated by the workers, that the mixture is explosive.

Samples of this explosive were subjected to standard cap detonation, drop and abrasion tests as used for commercial explosives. The results are shown in Table 1.

<table>
<thead>
<tr>
<th>Test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Cap test</td>
<td>2 of 3 fired with one No. 1 cap.</td>
</tr>
<tr>
<td>(2) Drop test</td>
<td>5 of 5 failed to detonate at maximum fall height of 54 inches.</td>
</tr>
<tr>
<td>(3) Abrasion test</td>
<td>5 of 5 failed to detonate at maximum slide distance of 63 inches.</td>
</tr>
</tbody>
</table>

A further series of tests were conducted to investigate the possibility of ammonium nitrate/HNO₃ mixtures being detonated. A full range of ammonium nitrate/HNO₃ ratio mixtures were prepared and subjected to heavy primer charges. In no instance was there evidence of even partial detonation of the mixture.

It will be apparent from the above that the novel nitric acid explosive of the invention represents a substantial advance in the commercial explosive art. The explosive is, first of all, made from inexpensive and readily available raw materials. It is further characterized by the ease by which it may be formulated, the high borehole loading density which may be achieved, resistance to water penetration and segregation of ingredients in the borehole, high detonation sensitivity and low sensitivity to impact and abrasion, and the wide range of detonation velocities which may be provided. Because of the rapid freezing of the composition after mixing, the need for thickening or gelling agents is obviated. Neither is there any appreciable chemical reaction with carbonate rock since solidification in the borehole takes place nearly immediately after the components are combined. Additionally, it will be appreciated by the commercial user of explosives that a wide margin of safety may be enjoyed since no self-explosive is handled by the workers, the composition becoming explosive only after mixing in the borehole. No costly magazine storage facilities are required and the ingredients may be moved, for example, by vehicle directly to the blasting site for use.

What we claim is:

1. An explosive composition comprising essentially at least one inorganic nitrate selected from the group consisting of ammonium nitrate and potassium nitrate, concentrated nitric acid and an organic fuel selected from the group consisting of nitrotoluenes and nitrobenzenes, which is miscible with and does not react with nitric acid.

2. An explosive composition comprising essentially an inorganic nitrate selected from the group consisting of ammonium nitrate and potassium nitrate, and concentrated nitric acid in a ratio of from 30 parts by weight of inorganic nitrate/70 parts by weight of acid to 70 parts by weight of inorganic nitrate/30 parts by weight of acid, in admixture with an organic fuel selected from the group consisting of nitrotoluenes and nitrobenzenes which is miscible with but does not react with nitric acid.

3. An explosive composition as claimed in claim 1 wherein the organic fuel contains a gas-generating substance selected from the group consisting of naphthylamine, methylene bis-(monomethylglycylhydroxy sodium sulphonate), diphenylamine, analine cresote, p-toluidine, p-cresol and acetone.

4. An explosive composition as claimed in claim 2 comprising from 55% to 90% by weight of the mixture of inorganic nitrate and concentrated nitric acid and from 10% to 45% by weight of the organic fuel.

5. An explosive composition according to claim 2 wherein the strength of the nitric acid is at least 90%.

6. A process for manufacturing a high strength, high density, low cost explosive composition which comprises mixing together an inorganic nitrate selected from the group consisting of ammonium nitrate and potassium nitrate, and nitric acid of not less than 90% strength in a weight ratio of nitrate/acid of from 30/70 to 70/30, and thereafter incorporating with said mixture from 10% to 45%, by weight of the total composition, of an organic fuel selected from the group consisting of nitrotoluenes and nitrobenzenes, which is miscible with but does not react with nitric acid, the temperatures of the nitrate/acid component and the organic fuel component being sufficiently low that the composition sets up in a semi-frozen state nearly immediately after mixing and becomes hard and dry on cooling to normal rock temperature of from about 5° C. to about 13° C.

7. A process according to claim 6 wherein there is additionally added from 0.01% to 1.0% by weight a gas generating substance selected from the group consisting of naphthylamine, methylene bis-(monomethylglycylhydroxy sodium sulphonate) diphenylamine, analine cresote, p-toluidine, p-cresol and acetone.

References Cited by the Examiner

UNITED STATES PATENTS

3,164,503 1/1965 Gehrig ———— 149—74
3,242,019 3/1966 Gehrig ———— 149—74

CARL D. QUARFORTH, Primary Examiner.

BENJAMIN R. PADGETT, Examiner.

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