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(54) A stable single phase liquid explosive.

(57) Liquid explosives comprising nitric acid and, as a fuel, one or more of nitromethane, nitroethane, nitropropane, nitrobenzene, nitrotoluene, dinitrobenzene and dinitrotoluene, are stabilised by the inclusion therein of at least 0.1% by weight of ammonium ions. The ammonium ions preferably are added in the form of an ammonium salt, which constitutes less than 35 weight percent of the explosive composition. An explosive composition which has been stabilised by the addition of ammonium ions can be de-stabilised by the addition of more nitric acid and/or fuel.

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A STABLE SINGLE PHASE LIQUID EXPLOSIVE

This invention relates to a chemically and physically stable single phase liquid explosive and, more particularly, to an explosive in which the sensitivity to detonation can be adjusted by the addition of a desensitizer, and to a method of making the said explosive.

Hermann Sprengel disclosed in 1871 that explosive compositions 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 the Sprengel explosives could be found in the fact that since both the fuel ingredient and the oxidizing ingredient were non-explosive materials, each could be transported without danger of detonation to the blasting site where they were combined in appropriate proportions just before use.

The Sprengel explosives have been shown to have low cost and a high detonation velocity and yet they have not enjoyed significant commerical success. One disadvantage which has limited use of these explosives is the high shock sensitivity or instability of the explosive once formed from the non-explosive ingredients.

We have now found that the sensitivity of such explosive compositions can be modified. In particular, we have found that the sensitivity of an explosive composition comprising nitric acid and an organic fuel comprising a nitroparaffin containing from 1 to 3 carbon atoms and/or certain nitroaromatic compounds, can be controlled by the addition of a desensitizer to the explosive composition. The desensitizer comprises a source of soluble ammonium ions, and is mixed with the nitric acid and organic fuel in an amount sufficient to provide an ammonium ion concentration of at least about 0.1 percent by weight of the total explosive composition comprising the nitric acid, organic fuel and desensitizer. The desensitizer should comprise less than about 35 percent by weight of the total explosive composition to permit the formation of a chemically and physically stable single phase liquid. The effect of the desensitizer upon the shock stability of the explosive composition can be reversed by the addition of an additional quantity of nitric acid organic fuel or both to the explosive composition to reduce the concentration of the ammonium ions in the composition.

According to the invention, there is provided a chemically and physically stable single phase liquid explosive composition comprising: nitric acid; an organic fuel comprising at least one of nitromethane, nitroethane, nitropropane, nitrobenzene, nitrotoluene, dinitrobenzene, and dinitrotoluene; and a desensitizer comprising a soluble source of ammonium ions present in an amount sufficient to provide an ammonium ion concentration of at least about 0.1 percent by weight of said explosive composition, whereby the shock sensitivity of said explosive composition is reduced, said desensitizer comprising less than about 35 percent by weight of said explosive composition.

The invention also includes a method of preparing a chemically and physically stable single phase liquid explosive composition comprising: admixing a quantity of a nitric acid solution with a desensitizer comprising a soluble source of ammonium ions present in an amount sufficient to provide an ammonium ion concentration of at least about 0.1 percent by weight of said explosive composition, whereby the shock sensitivity of said explosive composition is reduced, to form a mixture, said desensitizer comprising less than about 35 percent by weight of said explosive composition; and admixing said mixture with a quantity of an organic fuel comprising at least one of nitromethane, nitroethane, nitropropane, nitrobenzene, nitrotoluene, dinitrobenzene, and dinitrotoluene, to form said chemically stable single phase liquid explosive composition.

The nitric acid component of the present explosive composition comprises a solution of nitric acid containing from about 65 percent to about 100 percent by weight of nitric acid. Preferably, the solution contains in excess of about 70 percent by weight of nitric acid and most preferably in excess of about 90 percent by weight of nitric acid. Nitric acid having a concentration of less than about 65 percent by weight yields a product which is insensitive to normal detonation means. The term "insensitive" as used herein means the composition is insensitive to detonation by a No. 6 electrically fired detonator or blasting cap. A No. 6 blasting cap contains the equivalent of 3.7 grains of pentaerythritol tetranitrate (PETN) as a base charge.

The nitric acid solution comprises from about 30 percent to about 75 percent by weight of the explosive composition of the present invention. Preferably, the nitric acid solution comprises from about 40 to about 65 percent by weight of the composition.

The organic fuel of the present invention comprises at least one member selected from a group consisting of nitroparaffins and nitroaromatics. The nitroparaffins are selected from the group having from 1 to 3 carbon atoms such as nitromethane and nitropropane. The nitroaromatics useful in the present invention are selected from those having at least one nitro group attached to the hydrocarbon ring compound. The nitroaromatics which will form the chemically and physically stable single phase liquid explosive composition of the present invention include nitrobenzene, dinitrobenzene, nitrotoluene, and dinitrotoluene. The organic fuel can comprise mixtures of the nitroparaffins and nitroaromatics. The use of nitroparaffins as the organic fuel is preferred and, most preferably, nitropropane is utilized as the organic fuel.

The organic fuel comprises from about 15 percent to about 75 percent by weight of the explosive compositions of the present invention. Preferably, the organic fuel comprises from about 20 percent to about 40 percent by weight of the composition.

The use of organic fuels containing a larger number of carbon atoms than those set forth hereinabove generally results in the formation of a physically unstable two phase liquid which will not provide uniform detonation propagation upon initiation by an appropriate detonation means such as an electrical blasting cap.

The nitric acid and organic fuel components in the explosive composition of the present invention preferably should be present in such quantities as to give an "oxygen balanced" composition. By "oxygen balanced" is meant the availability of sufficient oxygen in the composition to oxidize the fuel components to their most chemically stable oxidation state. That is, sufficient oxygen is provided to completely convert, on a theoretical basis, all of the available carbon to carbon dioxide and hydrogen to water. While oxygen balance is preferred, a chemically and physically stable single phase liquid explosive composition having reduced shock sensitivity can be prepared having an oxygen deficiency of about 40 percent and detonation can be achieved. The explosive composition of the present invention also can be prepared having an oxygen excess of about 20 percent and detonation can be achieved.

The desensitizer utilized to chemically stabilize and reduce the shock sensitivity of the explosive composition of the present invention comprises a soluble source of ammonium ions. Suitable ammonium-containing desensitizer compounds comprise ammonium acetate, ammonium sulfate, ammonium phosphate, ammonium nitrate, ammonium chloride and the like. While ammonium chloride can be utilized as the desensitizer in the explosive compositions of the present invention, its use is undesirable because the ammonium chloride reacts with the nitric acid upon contact to form chlorine gas which creates undesirable health hazards for personnel handling the explosive compositions.

The desensitizer in the explosive composition of the present invention must be present in an amount sufficient to provide an ammonium ion concentration of at least about 0.1 percent by weight of the total explosive composition to chemically stabilize the composition and reduce the shock sensitivity. The desensitizer should not be present in an amount in excess of about 35 percent by weight of the explosive composition. Preferably, the desensitizer is present in an amount less than about 25 percent by weight of the total explosive composition. Surprisingly, it has been found that when the desensitizer is present in an amount of about 35 percent by weight or more of the explosive composition, an undesirable physically unstable two phase composition forms rather than the desired chemically and physically stable single phase liquid which has reduced shock sensitivity of the present invention. The formation of two phases has been found to occur regardless of the composition of the desensitizer.

The explosive composition of the present invention generally can be produced by admixing an effective amount of the desensitizer with the nitric acid to dissolve the ammonium-containing compound comprising the desensitizer prior to addition of the organic fuel. Alternatively, the desensitizer can be added to the mixture of nitric acid and organic fuel. However, when the quantity of desensitizer in the explosive composition is such that the concentration of ammonium ions is to be about 4 percent by weight or more of the total explosive composition, the desensitizer preferably should be admixed with the nitric acid prior to addition of the organic fuel to form a chemically and physically stable single phase liquid explosive composition having reduced shock sensitivity.

In yet another method of producing the explosive composition, the desensitizer can be dissolved in water and then combined with the organic fuel. The aqueous desensitizer and organic fuel are substantially immiscible. Nitric acid then is admixed with the organic fuel and aqueous desensitizer to form the homogenous mixture comprising the chemically and physically stable single phase liquid explosive composition having reduced shock sensitivity of the present invention.

The desensitizing effect of the ammonium ions on the shock sensitivity of the explosive composition can be reversed by decreasing the concentration of the ammonium ions in the explosive composition. The reduction in concentration can be achieved by adding nitric acid, organic fuel or both to the explosive composition in an amount sufficient to reduce the concentration of the ammonium ions in the composition.

The explosive composition produced by the method of the present invention is stable against separation of components when stored at temperatures as high as about 150°F. (66°C) over extended periods of time.

The present invention provides a practical and economical way of producing chemically and physically stable single phase liquid explosive compositions. The explosive compositions can be used for wellhead severing tools and pipeline cutter tools employing linear shaped charges.

A preferred use of the chemically and physically stable single phase liquid explosive composition is in trenching operations either on dry land or in laying pipe lines beneath bodies of water. The explosive compositions can be used in the production of "shaped" charges, that is, explosive charges contained in a vessel having a liner which has a specific geometrical configuration to effect a controlled directional movement of the liner material by the explosive force produced upon detonation of the charge. The single phase liquid explosive composition of the present invention can be stored for a substantial period of time in any metal or plastic container that is not affected by the components of the explosive composition or a glass container. For example, stainless steel containers or polyethylene containers can be utilized for long-term storage, but copper, which is dissolved by nitric acid, should not be utilized except for storage of short duration.

The following examples are presented for the purpose of illustration of the present invention and are not intended as limitations thereof.

Example I

In the experiments described below, several different explosive compositions were utilized to demonstrate the advantages provided by the explosive composition of this invention. Table I lists the explosive compositions utilized and provides the content of each component in terms of percent by weight of each in the composition. The number in parenthesis below each component indicates the approximate purity of each component actually used in the tests. Explosive compositions A through Q, except explosive composition F, were chemically stable solutions and were not emulsions or suspensions. Explosive composition F was a damp solid.

Each composition utilized was approximately oxygen balanced which means that oxidizers were added in an amount sufficient to provide the amount of oxygen necessary to theoretically completely convert all available carbon to CO_2 and all available hydrogen to H_2O.

Explosive compositions D, E, G, H, I, J, K, and O are within the scope of this invention with examples of the preferred form of the invention being compositions D, E, G, H, I, J, and K.

Explosive compositions A, B, C, F, L, M, N, P and Q are not within the scope of this invention. Explosive composition A is a prior art liquid explosive composition which currently enjoys wide commercial use. Nitric acid was not present in explosive composition F. As shown in Table II, the effect of the absence of nitric acid on the performance of the compositions is clearly evident. Explosive compositions L, M, N and Q did not include the desensitizer of the present invention and, therefore, as shown in Table III in Example II, demonstrate the effect of the ammonium ion as a desensitizer when compared with compositions G, H, K, and O, respectively, which did include ammonium ions.

It is to be noted that each component of each explosive composition A through Q is not considered to be an explosive in and of itself, as defined in current Department of Transportation regulations. Accordingly, each component can be separately shipped as a non-explosive, although other shipping regulations may be applicable. ((49 CFR 100 to 177, (Rev. 10/1/81) 171,172.101)).

Tests were performed to indirectly determine the detonation pressure of each of several explosive compositions wherein the impression or dent produced in a steel target by the detonation of an explosive composition was an indication of detonation pressure. The test results are shown in Table II wherein it is evident that explosive compositions within the scope of this invention (See Table I) developed much greater detonation pressures than the explosive compositions not within the scope of this invention.

In performing the tests, the following procedure and apparatus were employed:

Apparatus:

Each explosive composition was detonated against a witness plate which consisted of a 1020 mild carbon steel plate one inch (2.54cm) in thickness and having a length and width of three inches (7.6cm). Each composition detonated was held in a small, cylindrical polystyrene container referred to as a phial. Each phial had an inside diameter of about 1-1/8 inches (2.86cm) and was about 2¼ inches (5.7cm) tall. Such a container is sometimes referred to as a 15 dram vial. Each phial was equipped with a closure cap which was drilled in the center thereof to accept a Number 6 electrically fired detonator otherwise referred to as a blasting cap. A Number 6 blasting cap, as used in the tests, contains 3.7 grains of PETN as a base load. Each explosive composition tested was, of course, initiated by detonation of the blasting cap. As a direct result of the explosive detonation, a dent or depression was produced in each witness plate by the detonation pressure of the explosive composition. The extent of the detonation pressure was determined by measuring the depth of the dent produced in the witness plate. The instrument utilized to measure the depth of each dent was a Sterrett Depth Micrometer Model Number 445.

Procedure:

Fifty grams of explosive composition were placed in each phial. The phial was covered and the blasting cap was placed in the hole in the closure cap and inserted far enough into the phial so that the tip end of the blasting cap was immersed in the composition. The phial containing the composition and the detonator was placed in the center of a 3-inch (7.6cm) face of a witness plate. Thereafter each composition was detonated. (The explosive compositions were not confirmed in any sort of pressure or containment vessel when detonated.) After each detonation, the witness plate was recovered and the dent or depression produced by the detonation was measured with the depth micrometer and the depth was recorded in Table II.

TABLE I

EXPLOSIVE COMPOSITIONS

Percent Component by Weight of Explosive Composition

Explosive Compositions	Nitromethane (100%)	2-Nitropropane (100%)	Nitric Acid (90%)	Diethylene Triamine (100%)	Dinitro-toluene (100%)	Desensitizer Component	
							Compound
A	95	0	0	5	0	0	
B	0	29.76	70.24	0	0	0	
C	59.22	0	40.78	0	0	0	
D	0	25.18	49.87	0	0	24.95	NH_4NO_3
E	53.13	0	31.25	0	0	15.62	NH_4NO_3
F	0	12.92	0	0	0	87.08	NH_4NO_3
G	0	23.61	69.45	0	0	6.94	$NH_4(OOCCH_3)$
H	0	27.63	65.79	0	0	6.58	$(NH_4)_2HPO_4$
I	0	27.63	65.79	0	0	6.58	$(NH_4)_2SO_4$
J	0	27.63	65.79 (98% nitric acid)	0	0	6.58	$(NH_4)_2SO_4$
K	0	25.93	61.73	0	0	12.34	$(NH_4)_2SO_4$
L	0	25.93	61.73	0	0	12.34	H_2SO_4*
M	0	23.61	69.45	0	0	6.94	CH_3COOH*
N	0	27.63	65.79	0	0	6.58	H_3PO_4*
O	0	0	64.94	0	28.57	6.49	$(NH_4)_2SO_4$
P	0	0	68.36	0	31.74	0	
Q	0	0	64.94	0	28.57	6.49	H_2SO_4*

*Not an ammonium-containing desensitizer of the present invention. Included for comparison purposes.

TABLE II
PERFORMANCE TESTS

Explosive Composition	Dent Produced In Test Block (mm)	(Inches)
A	2.41	0.095
B	2.67	0.105
C	3.05	0.120
D	3.30	0.130
E	3.56	0.140
F	0.64	0.025
G	2.90	0.114
H	2.92	0.115
I	2.92	0.115
J	3.07	0.121
O	3.81	0.150
P	3.68	0.145
Q	3.53	0.139

Referring now to Table II, it is evident that all compositions within the scope of the invention produced substantially greater depressions in the witness plates and thus produced greater detonation pressures than did either of compositions A and F which are not within the scope of the invention. Furthermore, the explosive compositions of this invention which did include an ammonium component (D, E, G, H, I, J, and O) enhanced to some degree the detonation pressure of those compositions in comparison to those outside the scope of this invention which did not include an ammonium component (B and C).

Example II

Tests were performed to determine the shock sensitivity or shock stability of certain explosive compositions listed in Table I. The purpose of the tests was to determine whether a given explosive composition would or would not be detonated by the shock produced by the detonation of a Number 6 blasting cap placed a given distance from the explosive composition. An explosive composition having a high shock sensitivity can be detonated from a greater distance by the detonation of the blasting cap than a composition having low shock sensitivity. Of course, the designations "high" and "low" are not very informative other than being an indicator of the safe handling characteristics of a given explosive composition. Thus, a low shock sensitive composition is safer to handle than a high shock sensitive composition.

In order to help quantify the shock sensitivity level and to better inform those persons having skill in the art, the shock sensitivity of the explosive compositions of this invention were compared to the shock sensitivity of explosive composition A, a widely used commercial explosive.

In performing the tests, the following procedure and apparatus were employed:

Apparatus:

Steel witness plates, 15 dram vials and Number 6 blasting caps, all as described in connection with the performance tests were utilized in the shock sensitivity tests.

Procedure:

Twenty milliliters of explosive composition were placed in each phial. This quantity was sufficient to fill each phial to a liquid depth of about one inch (2.54cm). The phial was covered and the blasting cap was placed in the hole in the closure cap and inserted far enough into the phial such that the tip end of the blasting cap was set at a given distance from the liquid surface of the explosive composition. This distance is referred to in Table III as the "Cap Distance". (In instances where the Cap Distance was greater than 1½ inches (3.81cm), two phials were taped together mouth-to-mouth.) Each phial containing a composition and positioned detonator was placed in the center of a 3-inch (7.6cm) face of a witness plate. Thereafter, each blasting cap was detonated and a record was made of whether or not the explosive composition was also detonated. In Table III it is indicated that a detonated explosive composition "Fired" but that a composition not detonated or not exploded or not deflagrated was a "No Fire".

TABLE III
SHOCK SENSITIVITY TESTS

Explosive Composition	Cap Distance (cm)	Cap Distance (Inches)	Result
A	5.08	2	Fired
B	10.16	4	Fired
D	3.81	1½	No Fire
G	3.81	1½	No Fire
H	3.81	1½	No Fire
I	3.81	1½	No Fire
K	3.81	1½	No Fire
L	5.08	2	Fired
M	5.08	2	Fired
N	5.08	2	Fired
O	3.81	1½	No Fire
P	5.08	2	Fired
Q	5.08	2	Fired

A review of the data set forth in Table III discloses that explosive composition A, the explosive composition widely used in the prior art, detonated at a Cap Distance of 2 inches (5.1cm). Accordingly, for purposes of comparison, the other compositions tested were compared to the 2 inch (5.1cm) Cap Distance of explosive composition A to determine the shock sensitivity of the other compositions relative to that of composition A. Those explosive compositions which did include the desensitizer, that is compositions D, G, H, I, K and O, which were subjected to the shock sensitivity test, did not fire at a cap distance of $1\frac{1}{2}$ inches (3.8cm), which means that such compositions are low shock sensitive compositions and thus safer to handle than the widely used prior art explosive composition A. Also, compare explosive composition B with explosive composition D and notice the effect on shock sensitivity produced by the addition of the ammonium-containing desensitizer compound. Explosive composition B, not containing the desensitizer was very shock sensitive in that the composition detonated at a Cap Distance of 4 inches (10.16cm), whereas explosive composition D, having an ammonium-containing desensitizer component, did not detonate at a cap distance of $1\frac{1}{2}$ inches (3.81cm). Similar comparisions can be made as between explosive composition B and explosive compositions G, H, I and K. Explosive compositions G, H, I, and K, which included an ammonium component, did not detonate at a distance of $1\frac{1}{2}$ inches (3.81cm), whereas explosive composition B, which did not include the desensitizer, detonated at a cap distance of 4 inches (10.16cm). Accordingly, the inclusion of the desensitizer does render a given explosive composition less shock sensitive than one not having the desensitizer of the present invention. Similar observations will be made with respect to explosive composition O.

A comparison of explosive compositions G and M, H and N, and K and L clearly illustrates that it is the ammonium portion of the desensitizer and not the anion from that same compound which affects the shock sensitivity of a given explosive. With respect to the above comparisons, explosive compositions including the desensitizer exhibited low shock sensitivity whereas those compositions having the common anion but not including the ammonium ion of the desensitizer were not desensitized.

Accordingly, it is surprising that the ammonium-containing desensitizer acts both as a desensitizer, that is, reduces the shock sensitivity of an explosive composition, as well as a detonation pressure enhancer. In other words, with an ammonium-containing desensitizer present in the explosive composition of this invention, the composition is more powerful than the composition would be without the desensitizer and it is less shock sensitive than it is without the desensitizer.

CLAIMS:

1. A chemically and physically stable single phase liquid explosive composition comprising: nitric acid; an organic fuel comprising at least one of nitromethane, nitroethane, nitropropane, nitrobenzene, nitrotoluene, dinitrobenzene, and dinitrotoluene; and a desensitizer comprising a soluble source of ammonium ions present in an amount sufficient to provide an ammonium ion concentration of at least about 0.1 percent by weight of said explosive composition, whereby the shock sensitivity of said explosive composition is reduced, said desensitizer comprising less than about 35 percent by weight of said explosive composition.

2. A composition according to claim 1, wherein said nitric acid comprises from about 30 percent to about 75 percent by weight of the explosive composition.

3. A composition according to claim 1 or 2, wherein the organic fuel comprises from about 15 percent to about 75 percent by weight of said explosive composition.

4. A composition according to claim 1, 2 or 3, wherein said desensitizer comprises at least one of ammonium acetate, ammonium sulfate, ammonium phosphate and ammonium nitrate.

5. A method of preparing a chemically and physically stable single phase liquid explosive composition comprising: admixing a quantity of a nitric acid solution with a desensitizer comprising a soluble source of ammonium ions present in an amount sufficient to provide an ammonium ion concentration of at least about 0.1 percent by weight of said explosive composition, whereby the shock sensitivity

of said explosive composition is reduced, to form a mixture, said desensitizer comprising less than about 35 percent by weight of said explosive composition; and admixing said mixture with a quantity of an organic fuel comprising at least one of nitromethane, nitroethane, nitropropane, nitrobenzene, nitrotoluene, dinitrobenzene, and dinitrotoluene, to form said chemically stable single phase liquid explosive composition.

6. A method according to claim 5, wherein said nitric acid solution comprises from about 30 percent to about 75 percent by weight of said explosive composition.

7. A method according to claim 5 or 6, wherein said nitric acid solution contains from about 90 percent to about 100 percent by weight nitric acid.

8. A method according to claim 5, 6 or 7, wherein the organic fuel comprises from about 15 percent to about 75 percent by weight of said explosive composition.

9. A method according to claim 5,6,7 or 8, wherein said desensitizer comprises at least one of ammonium acetate, ammonium sulfate, ammonium phosphate, and ammonium nitrate.

10. A single phase liquid explosive composition which comprises a composition as claimed in any of claims 1 to 4, to which has been added a further quantity of one or both of the nitric acid and organic fuel, to reverse the said effect of the desensitizer.