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3,419,443
**HYDRAZINE CONTAINING EXPLOSIVE
 COMPOSITIONS**

Michel E. Maes, Bellevue, Wash., assignor to Explosives Corporation of America, Issaquah, Wash., a corporation of Washington
 No Drawing. Filed Apr. 17, 1967, Ser. No. 631,123
 31 Claims. (Cl. 149—1)

ABSTRACT OF THE DISCLOSURE

Explosive compositions characterized by a nominally liquid condition and a very high detonation velocity, and with low freezing point, low viscosity and low impact sensitivity characteristics, said explosive composition comprising as essential ingredients an at least principally hydrazinium oxidizer salt (e.g., hydrazinium nitrate and mixtures thereof with hydrazinium perchlorate), hydrazine, and ammonia, and comprising as optional additives various compatible desensitizers, gelling agents, wetting agents, self-sterilizing components, freezing point depressants, low gas producing substituents, and waterproofing agents. Also presented are modes of preparation of the compositions, involving either premix of the ingredients, or mixing thereof in place at the situs of use. Relative proportions by weight of the essential ingredients are as follows: $N_2H_5NO_3$, from about 40% to about 92%; $N_2H_5ClO_4$, from 0% to about 40%; N_2H_4 , from about 6% to about 15%; and NH_3 , from about 2% to about 15%. Optionally, minor proportions of the nitrate and perchlorate salts can be metallic salts.

BACKGROUND OF THE INVENTION

Field of the invention

The invention pertains to low impact sensitivity, high detonation velocity explosive compositions containing hydrazine in admixture with a hydrazinium salt, together with a controlled amount of ammonia, the latter functioning primarily as a modifying agent with regard to the physical properties of the composition, namely the density, viscosity, and freezing point thereof.

Description of the prior art

Explosive and propellant compositions are generally known which involve mixtures of hydrazine and hydrazinium nitrate, also known as hydrazine nitrate or hydrazine mononitrate, such as disclosed in Audrieth et al. U.S. Patent No. 2,943,927, wherein the hydrazine-hydrazinium nitrate system is noted as having a characteristically low freezing point and having utility for use as a fuel in conjunction with conventional oxidizers such as hydrogen peroxide, fuming nitric acid or liquid oxygen, the hydrazine-hydrazinium nitrate in this instance including at least about 18% hydrazine by weight, and optimally about 50% or more by weight of hydrazine, to provide a freezing point for the fuel of some $-50^\circ C$. In the Audrieth et al. fuel, and as above noted, the proportionation of the hydrazine-hydrazinium nitrate mix is determined solely by consideration of freezing point depression, and not by any consideration of stoichiometric balance or maximal efficiency as an explosive composition, at least in part for the reasons that the fuel contemplated by Audrieth et al. is intended for use as a fuel constituent with an external oxidizer, and because the exothermic reaction is one of combustion, rather than explosive detonation.

Also known are prior explosive compositions involving ammonium nitrate, together with a hydrogen-containing solvent therefor, such as liquid ammonia, and with a

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metallic fuel constituent such as aluminum particles, such as disclosed in Hradel U.S. Patent No. 3,124,495. In these compositions the liquid ammonia or like solvent for the ammonium nitrate is present in a proportion of from about 2% to about 35% by weight, as compared with the ammonium nitrate present in the proportion of about 10% to about 83% by weight, and the metal constituent present in the amount from about 15% to about 60% by weight. In the Hradel explosive composition, as will be observed, the principal fuel constituent is the particulated metal ingredient, and the particle size of the metal in the Hradel composition is stated to be essentially greater than 20 U.S. standard seive, in order that the composition be satisfactorily insensitive from the point of view of avoidance of premature detonation during handling. In addition to the sensitivity problem when using a metallic particle fuel in conjunction with a nitrate or like oxidizer constituent, it is a well known disadvantage of explosives incorporating metallic fuel particles that such create substantial smoke upon detonation, and are difficult to maintain uniformly dispersed in a liquid system, particularly if of a sufficient particle size to have a reasonably tolerable insensitivity to impact detonation. Also the substantial presence of metal particles constitutes a sacrifice in detonation velocity and brisance. Further, with regard to the Hradel explosive system, which is basically an ammonium nitrate solution in conjunction with contained metal particles, and while Hradel presents a general statement as to the hydrazine-containing solvent for the ammonium nitrate being either liquid ammonia, water, ammonium hydroxide, or hydrazine (with all examples presented involving ammonia as the solvent), Hradel makes no distinction with regard to various solvents, nor any comprehension of any particularly advantageous physical properties or detonation characteristics of particular combinations of ammonia and hydrazine with a nitrate and in the absence of metallic particles, such as characterizes the present invention.

SUMMARY OF THE INVENTION

In general, explosive compositions according to the present invention at least principally comprise a preferably substantially stoichiometric combination of a hydrazinium salt as the oxidizer reactant, coupled with hydrazine which functions as an exothermically decomposable constituents, yielding decomposition products which in turn coact as reducer reactants and undergo explosive decompositions with the oxidizer reactant upon detonation of the composition, such oxidizer-reducer system further including a controlled amount of ammonia functioning prior to detonation as a modifying agent with regard to the physical properties of the composition, to reduce the viscosity thereof, and to reduce the freezing point of the composition. In the absence of the ammonia, the hydrazine-hydrazinium salt system in approximately stoichiometric proportions has an impractically high freezing point and a solid form at normal temperatures of use. On the other hand, if the proportion of ammonia present in the system is excessive, significant reductions in detonation velocity and explosion energy result.

In explosive compositions of the present invention, the oxidizer reactant comprises either hydrazinium nitrate, or mixtures of hydrazinium nitrate with hydrazinium perchlorate, with a cationic metal radical substituted for a minor portion of the hydrazinium radical in some instances. For simplicity, much of the following discussion of the invention simply refers to the oxidizer reactant as an "oxidizer salt" or "hydrazinium salt." However, in more particular terms, it will be understood that the oxidizer constituent contemplated by the present invention is selected from the group consisting of nitrate salt(s) and mixtures thereof with a minor amount of per-

chlorate salt(s) (where the perchlorate anionic radical is desired to increase sensitivity). Further it will be understood that such oxidizer constituent is a nitrate or nitrate/perchlorate salt wherein the cationic radical is either hydrazinium or is a mixture of hydrazinium radical with a minor amount of a metal radical (where the metal salt is desired to reduce foaming during composition preparation). Suitable substituent metallic salt(s) are characteristically nonreactive when stored in admixture with hydrazine and can be sodium nitrate, sodium perchlorate, potassium nitrate, potassium perchlorate, calcium nitrate, calcium perchlorate, aluminum nitrate, and/or aluminum perchlorate, for example.

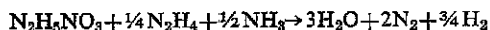
In general, it has been determined that considerable variation in proportions of the hydrazinium salt/hydrazine/ammonia explosive system of the present invention can be utilized, consistent with the obtaining of various advantageous physical properties of the explosive prior to detonation. Characteristic advantageous physical properties are; availability in liquid form, low freezing point, low viscosity, low impact sensitivity, and good field mixability. Characteristic advantageous detonation characteristics are; very high detonation velocities, low detonation temperatures, detonation by conventional means, little or no light generation, no smoke residue by reason of an absence of carbon and an absence of metallic particles, and non-corrosive and non-particulate detonation products.

Compositional constituents of explosives according to the invention can be varied as follows:

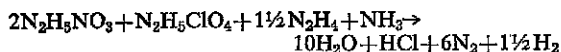
Constituent:	Range, percent
$N_2H_5NO_3$	About 70 to about 92 (including perchlorate and metal salt substituents, if any)
N_2H_4	About 6 to about 15
NH_3	About 2 to about 15

In order to optimize the detonation characteristics of explosive compositions according to the present invention, it is desirable to maintain an approximately stoichiometric balance as between the oxidizer constituent(s) and the hydrazine, and exclusive of the ammonia content.

In the case where the oxidizer salt is entirely hydrazinium nitrate, the theoretical detonation reaction is as follows:



In the case where the oxidizer salt incorporates substantial hydrazinium perchlorate with the hydrazinium nitrate, the detonation reaction is typically as follows:



A listing of various specific typical examples of explosive compositions according to the invention is set forth in Table I, as follows:

Examples	$N_2H_5NO_3$ (percent)	$N_2H_5ClO_4$ (percent)	N_2H_4 (percent)	NH_3 (percent by weight)
.....	91	0	7	2
2.....	88	0	7	5
3.....	84	0	7	9
4.....	79	0	7	14
5.....	79	0	13	8
6.....	68	19	9	7
7.....	59	24	10	7
8.....	42	40	11	7

The above explosives are either water white or clear, and all are liquids at room temperature, with freezing

point variations occurring principally as a function of ammonia content, as illustrated in Table II:

Formulation example	Percent NH_3 by weight	Density	Deton. Veloc.	Freezing point ($^{\circ}F.$) (crystal)	Viscosity (cps.)
1.....	2	1.42	8,600	58	22
2.....	5	1.39	8,500	38	20
3.....	9	1.35	8,300	15	19
4.....	14	1.31	8,100	-8	12

Viscosity also varies a function of ammonia content in these compositions, and is typically 8 centipoises or higher, depending on the type of viscosity modifying agent added, as discussed in more detail below. Density of the explosive compositions is also a function of ammonia content, as also shown in Table II above.

The explosive characteristics of the compositions are a function of compositional makeup. In general, detonation velocity is in the range of 8,000 to 8,600 meters per second. Detonation velocity is characteristically a function of density and the variation in detonation velocity with ammonia content are also shown in Table II above.

Detonation temperature of the explosives of the invention is characteristically low because no carbon products are formed. Detonation products are water and nitrogen in the stoichiometrically balanced formula and in cases where excess hydrazine and/or ammonia are added some hydrogen is formed. Based upon theoretical calculations, the detonation temperature of these compositions appears to be approximately $\frac{1}{2}$ to $\frac{2}{3}$ that of conventional nitrated hydrocarbon explosives such as TNT, dynamite or tetryl. A consequence of low detonation temperature and absence of carbon products is the virtual absence of any light produced upon detonation. Since they contain no carbon or other solid materials, the detonation products are exceptionally clean, non-corrosive and non-particulate.

The impact sensitivity of the explosives of the invention is a function of hydrazinium perchlorate content. The basic explosive compositions containing no perchlorate (as in Examples 1-5) have an impact sensitivity on the Olin-Mathieson liquid propellant drop weight tester of 75 to 85 kilogram centimeters. In comparison, nitroglycerin has an impact sensitivity of 2 kilogram centimeters. Impact sensitivity on the drop weight tested of certain specific explosive compositions is as listed in Table III, as follows:

TABLE III.—IMPACT SENSITIVITY

Example	Percent ClO_4 by weight	Impact sen. kg.-cm.
2.....	0	85
6.....	10	75
7.....	24	70
8.....	40	45
X*.....	76	8
Nitroglycerine.....	2

*Example X: 76% $N_2H_5ClO_4$, 17% N_2H_4 , 7% NH_3 .

As will be seen in Table III, the perchlorate substituent, when used in the explosive composition, functions basically as a sensitizing agent, making the explosive more sensitive to low level initiation, and reducing the explosive's critical diameter (the minimum diameter at which a propagation will take place in a continuous tube of length).

Explosive compositions have been manufactured which consist entirely of hydrazine perchlorate and hydrazine in typical percentages of 76% hydrazinium perchlorate and 17% hydrazine (with 7% ammonia, to provide direct comparison with explosives characterizing the present invention) as reflected by Example X of Table III above. As will be noted in Table III, such explosive composition is comparatively quite dangerous, having an impact sensitivity of 8. This is because hydrazinium perchlorate, in the absence of a desensitizer, is a somewhat unstable salt, decomposing easily under the influence of low level mechanical shock or relatively low

heat, and having an impact sensitivity similar to that of raw nitroglycerin. The explosive of comparative Example X is therefore not considered as a practical explosive for field use. However, hydrazine perchlorate is sufficiently stable when combined with hydrazinium nitrate and hydrazine, in percentages up to about 45% of the total weight of a mixture, and the impact sensitivity of this composition is still at a reasonably safe level for field use. Importantly, also, this nitrate-perchlorate type composition has certain unique characteristics, such as enabling detonation of very low concentrations of explosive (typically as little as 7% by weight of explosive to 93% by weight of porous media), enabling detonation of thin films of the explosive on solid surfaces (e.g. films less than 1 millimeter thick). Since the partial substitution of hydrazinium perchlorate for hydrazinium nitrate does little to change the energy content of the explosive, the percentage of hydrazinium perchlorate used is therefore basically a function of the desired sensitivity of the explosive and the detonation propagation characteristics desired for the explosive. Preferably, however, the proportion of perchlorate is less than the proportion of the nitrate constituent.

The principal function of the ammonia in the composition is to act as a freezing point depressant. Explosive compositions composed of 92% hydrazinium nitrate and 8% hydrazine, have been determined to have a freezing point of about +120° F., which of course renders such in solid form at room temperature. However, it has been found that as low as 2% ammonia by weight reduces the freezing point of this mix to about 58° F. (as in Example 1 above). Addition of 15% ammonia by weight reduces the freezing point to about -8° F. (as in Example 4 above). The only detrimental effect caused by the addition of ammonia is a progressively small to moderate reduction in the explosive density and detonation velocity, and therefore a reduction in the energy density or effective power of the explosive. The percentage of ammonia can therefore be varied a considerable degree, to selectively optimize the freezing point, detonation velocity and/or energy per unit weight of the explosive for any particular field application.

Additional freezing point depressants can be added to the composition if desired, such as hydrazinium thiocyanate (N_2H_5SCN) or monomethyl hydrazine ($CH_3N_2H_3$) in percentages in the case of the thiocyanate of up to 30% by weight and in the case of the monomethyl hydrazine in percentages up to 50% by weight of the total liquid ingredients.

Several desensitizing agents can be added to the explosive compositions of the present invention, to reduce the basic sensitivity of the compositions, either during the manufacturing process or after the explosive has been manufactured or put in place. Water is an effective desensitizer and can be added to progressively desensitize the explosive to a point where it is no longer detonatable by a blasting cap (when the water content is in excess of 50%). The effect of impact sensitivity on explosives of the invention and containing various percentages of water is shown in Table IV, as follows:

TABLE IV

Composition:	Impact sensitivity
Ex. 2 -----	85
Ex: 2 plus 10% H_2O by weight -----	120
Ex. 2 plus 20% H_2O by weight -----	>140

Other effective desensitizing agents are glycerin, glycol, and various hydrocarbon oils, for example. The oils are not miscible with the explosives but can be formed into emulsion and do effectively desensitize the explosive when in emulsions in concentrations less than 10% by weight. Typical hydrocarbon oils for the purpose are stove oil and motor oil. With oil concentrations of 10% by weight or more, the explosive nature is no longer cap sensitive, but is sensitive to initiation by a 50 gram tetryl pellet

type booster. A second benefit of the use of a material such as glycerin or glycol as a desensitizing agent is that the vapor pressure of the diluent is very low when the explosive is left standing, as when in storage. Once the explosive is mixed and left exposed to the ambient, the hydrazine slowly vaporizes away, leaving behind the crystalline hydrazinium salt(s). These crystals when exceptionally dry become relatively sensitive to initiation or detonation by either mechanical impact or friction. A means of maintaining prolonged desensitization of these crystals is to add some impactively inert, substantially non-volatile liquid ingredient such as oil, glycerin, or glycol (in the amount of about 2-6% by weight, for example). In general, any liquid, non-volatile material which exhibits storage stability in admixture with the hydrazine/hydrazinium salt mixture, can act as a desensitizer for the explosive when added in minor concentrations.

In certain applications it is desirable to modify the normal, free flowing liquid state of the explosive, to provide a solid form explosive either prior to placement or after placement of the explosive at the point of use. This can be accomplished by a variety of gelling agents which are added to the explosive in quantities of about ½% to 15% by weight, for example, in order to achieve the desired result. Typical gelling agents are Cab-O-Sil (a finely divided SiO_2 thickening agent, suitably usable in proportions up to about 10% by weight) and Guartec 503 (a cross linking gelling agent, suitably used in proportions up to about 5% by weight). After standing for 2 hours, the resulting mixture has a putty-like consistency similar to pizza dough or so-called "Silly Putty." It is a highly moldable somewhat sticky material which can be formed and emplaced very easily. The stickiness and the rigidity of the material can be varied by varying the percentage of Cab-O-Sil and/or Guartec. Other useful gelling agents are Carbopol and methyl acetate, for example. If gelling in place is desired, up to 5% Guartec 503 can be added to the explosive just prior to placement and 1% to 2% water can be added after placement to accelerate the rigidization of the explosive. With this mix a rheological state similar to hard "Jello" occurs within 30 minutes. In order to enhance the addition of the gelling agent powder to the liquid explosive and to form a homogeneous mixture of the gelling agent throughout the explosive, the particulated gelling agent can be mixed prior to addition to the explosive with a material such as Freon, glycol, or ammonium nitrate. Mixture of the gelling agent with the other material assists in dispersing the gelling agent and prevents congealing of lumps of the gelling agent upon contact with the liquid explosive.

The addition of Guartec 503 to the explosive is also advantageous in terms of waterproofing the explosive for ground placed applications. Since the explosive is desensitized by water, its use in wet soil requires protection against leaching by the moisture and gradual desensitization of the explosive to the point of its being nondetonatable after a period of time. The addition of from ½% to 3% Guartec 503 prior to placement in the ground forms a barrier to water penetration of the explosive body. when the explosive containing the water-activated gelling agent is poured onto the wet ground, immediate complexing of the gelling agent takes place, forming an effective barrier to further penetration of water, with adsorption of some of the local water in the process. Another suitable waterproofing agent is Polyox resin.

In certain applications utilizing liquid explosive, it is desirable to have the explosive adsorbed readily and rapidly by porous media. Certain wetting agents can be added to the explosive in percentages of about ½% to 5% by weight, to enhance the ability of the liquid explosive to be adsorbed in porous media. The use of a wetting agent also is helpful in forming thin films of explosive for thin film detonation applications. Typical suitable wetting agents are dimethyl sulfoxide, dimethyl formamide, ethanol, propanol, and fatty acids such as Alkanox.

In certain applications of explosives of the invention, it is desirable to vary the detonation velocity of the explosives. In general, detonation velocity can be reduced by reducing the density of the explosive reactants or by adding a diluent which reduces the energy density of the explosive. Addition of a liquid medium such as water serves to reduce the detonation velocity of the explosive, and addition of an inert solid medium such as sand also is effective to reduce detonation velocity.

A unique phenomenon of explosive of the invention is that they can possess two stable detonation velocity regimes. A high detonation velocity regime on the order of 8,000 to 8,600 meters per second is achieved for the basic composition when initiated by a number 8 detonator or a booster. A low detonation velocity regime at approximately 2,000 to 2,500 meters per second is achieved in the explosive compositions containing 20% or more water by weight when initiated with a No. 6 or smaller detonator. Characteristically, low level initiation of the explosive detonation results in an abrupt, discontinuous change in detonation velocity from the 8,000 meter per second range to the 2,000 meter per second range. Other detonation velocities, between 2,500 meters per second and 8,000 meters per second, can be achieved by the addition of certain inert materials such as sand but with corresponding reduction in explosive energy.

Certain materials can be added to the explosives which cause self-sterilization or self-destruction of the explosives in place. Mixtures of strong oxidizing agents such as iodine pentoxide or nitrogen tetroxide will cause hypergolic deflagration, and under even slight confinement immediate detonation, of the explosive. If a time delay is required, the desensitizing agent or self-destruction agent can be encapsulated in a soluble plastic capsule. Plastic capsules can be typically polyurethane for rapid solubility in hydrazine or polycarbonate for slow solubility. When the explosives dissolve the capsule, the agent is released into the explosive, causing either desensitization (such as release of water) or deflagration or detonation (such as by release of the indicated strong oxidizers).

An important characteristic of explosives of the invention is that they can be mixed easily from ammonium nitrate or a mixture of ammonium nitrate and ammonium perchlorate, with liquid hydrazine or with a mixture of hydrazine with a small amount of ammonium nitrate or hydrazinium nitrate added. The ammonium salts can be added either as granular salts, tartars, cakes, tablets or plastic encapsulated lumps. A slurry of the ammonium salts and a relatively high vapor pressure carrier such as Freon or high vapor pressure hydrocarbon oil can be used for continuous mixing processes or for more rapid blending of the two materials in the field. The relatively high vapor pressure carrier (such as benzene) for the solids would not be miscible with the liquid and would vaporize away from the surface of the liquid explosive after mixing takes place.

Preparation of the constituents for the two component field mix version of the explosives can involve prepackaging the solid ammonium salt(s), drying them out when necessary, or blending them with a carrier such as Freon when a slurry blending process is to be used. In the case of the liquid hydrazine, the addition of 20% of hydrazinium nitrate to the hydrazine results in a liquid which is still nondetonatable but which does not release as much gas when combined with the ammonium salt(s). In the mixing process the addition of the ammonium salt(s) to the liquid hydrazine results in an immediate conversion of the ammonium salt(s) to the hydrazinium salt(s) with the subsequent release of ammonia gas. The release of the ammonia gas can be very violent under certain circumstances. The addition of 20% hydrazinium nitrate to the hydrazine has been shown experimentally to result in far less gaseous ammonia evolution during mixing of the explosive compositions.

Large quantities of the explosives can be field mixed by

pouring the liquid ingredient into the solid, or vice versa, from large bulk containers. Agitation can be accomplished either by rolling the containers after the ingredients have been combined or by agitating with a Lightening type or other rotating mixer. In continuous field mix processes, the ammonium salt(s) can be either in free-flowing granular form or can be mixed with some high vapor pressure diluent to form a slurry and then combined with the liquid as a liquid-liquid mix operation, in a typical rotating continuous batch blender, such diluent being relatively high vapor pressure Freon or hydrocarbon oil. Further examples of structural arrangements for mixing the two basic components of the explosive will be found in my application Ser. No. 703,994, entitled Field Sensitized Explosive Devices and Sensitizing Method, and filed Feb. 8, 1968.

In certain cases it is possible to impregnate a material with the solid component or to retain the solid component in an end use container. The liquid component is then added and little or no agitation applied to form the explosive in place. A typical example is the impregnation of a plastic sponge or cloth with ammonium nitrate/ammonium perchlorate mixture and the subsequent spraying of the cloth with hydrazine to form a cloth or sponge-like material which is soaked with explosive. In this process no explosive is handled at all prior to the formation of the explosive in the cloth or sponge which is put in place prior to mixing. Effective self-mixing occurs because the liquid is rapidly and effectively absorbed by the solid crystals. The crystals subsequently dissolve in the liquid resulting in a substantially homogeneous liquid mix. Another unique characteristic of the explosive of the invention is the ability to be absorbed in porous media such as cloth and earth and remain detonatable in place.

In certain field applications of explosives according to the invention, it is desirable to minimize the gas release upon mixing of the explosive ingredients. This is particularly appropriate in connection with certain in-place mixing techniques. In these cases some sacrifice in explosive energy may be tolerated and the use of a compatible metal nitrate and/or metal perchlorate oxidizing salt such as sodium, potassium, calcium or aluminum nitrate or perchlorate may be substituted for a minor part of the ammonium salt from which the hydrazinium salt constituent of the explosive composition is prepared.

In order to prevent serious degradation of performance and in order to prevent serious sensitivity problems, such substitution should be in percentages of less than about 50% by weight, and preferably less than about 25% by weight, relative to the hydrazinium salt content of the final composition.

The explosives of the invention can be manufactured by either adding preformed hydrazinium salt(s) to hydrazine with a subsequent addition of ammonia gas by bubbling the gas through the mix to permit complete solubility of the hydrazinium salt(s) in the hydrazine, or more preferably by the addition of the counterpart ammonium salt(s) to liquid hydrazine. The addition of the ammonium salt(s) to hydrazine has a dual benefit; firstly, no sensitive explosive material is handled during the manufacturing process prior to mixing and, secondly, adequate ammonia is automatically introduced into the mix by the transition of the ammonium salt(s) to the hydrazine salt(s) with the release of ammonia gas. Selective control of the proportion of ammonia can then be achieved, if desired, by pumping the ammonia gas out of the mixed explosive or by raising the temperature of the mixed explosive causing the ammonia gas to vaporize away rapidly. Pumping can be either by a vacuum pumping system or, in the case of the raised temperature, by merely exhausting the ammonia by means of fans or gas phase circulation. An alternate technique is to bubble dry nitrogen through the liquid explosive, stripping the ammonia out of solution. A typical manufacturing technique involves preweighing ammonium nitrate and liquid hydra-

zine in separate containers. Liquid hydrazine is then poured into the ammonium nitrate container and agitated by means of a small paddle mixer. Addition of the hydrazine to the ammonium nitrate does not involve any exothermic reaction. On the contrary, if rapid mixing is to take place, a small amount of heat should be applied to the container since mixing and subsequent dissolving of the ammonia in the mix is slightly endothermic. The addition of the hydrazine to the ammonium nitrate or vice versa should be started slowly to avoid foaming, but after approximately 25% to 30% of one ingredient is added to the other more rapid blending can occur without danger of foaming. Once the container contents are blended, the entire container is placed in a vacuum chamber for the desired partial removal of the dissolved ammonia. A heater coil is immersed in the liquid container to provide heat of vaporization for the ammonia to speed the ammonia removal process.

A substantial number of modifications can be made on the explosive formula either at the time of manufacture or after the explosive is manufactured and even after it has been put in place. This is a significant advantage of the liquid state of the explosives.

In certain applications involving large field usage of the explosive, ammonium nitrate can be poured directly into a blast hole or over a large exposed surface, such as ground terrain, which is to be covered with explosive and the liquid hydrazine either poured or dumped over the surface, to accomplish in-place mixing of the explosive.

Another application where explosive compositions of the present invention can be advantageously mixed in place is in the field of explosive forming of metallic articles such as laminate coin stock. In this case the thin metallic sheet to be laminated to a metallic substrate first receives a coating of the oxidizer salt (applied evenly over the metal surface either directly or onto a pre-placed adsorbent flocc or the like) and the oxidizer is then evenly sprayed with an appropriate amount of liquid hydrazine to complete the explosive mix which may then be detonated on demand.

Field mixing of the explosive composition can also be accomplished in plastic tubes filled with a solid, large container which will act as an explosive charge after the explosive is mixed. In a typical application in large bulk containers, a diaphragm separating the liquid from the solid is designed to be broken by external impact, which causes self-mixing inside the container.

From the foregoing, various further modifications, adaptations, modes of preparation, and fields of application of the present invention will be apparent to those skilled in the art to which the invention is addressed, within the scope of the following claims.

What is claimed is:

1. An explosive composition comprising:

(a) an oxidizer reactant selected from the group consisting of

(1) hydrazinium nitrate, and

(2) mixtures of hydrazinium nitrate with

(a) hydrazinium perchlorate, and/or

(b) metal salt(s) selected from the group consisting of alkali metal nitrates, calcium nitrate, aluminum nitrate, alkali metal perchlorates, calcium perchlorate, aluminum perchlorate, and mixtures thereof,

with the hydrazinium radical being at least the principal cationic radical of the reactant, by weight, and with the nitrate radical being at least the principal anionic radical of the reactant, by weight;

(b) hydrazine, present in at least approximately stoichiometric proportion with respect to said oxidizer reactant; and

(c) ammonia, present in an amount less than 15% by weight.

2. The explosive composition according to claim 1, with ammonia present in the amount of from about 5 to about 9% by weight.

3. An explosive composition according to claim 1, wherein said oxidizer reactant is substantially entirely hydrazinium nitrate.

4. An explosive composition according to claim 1, wherein said oxidizer reactant consists essentially of a mixture of hydrazinium nitrate and hydrazinium perchlorate, the proportion of nitrate to perchlorate being from about 4:1 to about 1:1 by weight, and the proportion of hydrazinium salts to hydrazine being about 7:1 to about 10:1 by weight.

5. An explosive composition according to claim 1, wherein said oxidizer reactant consists essentially of hydrazinium salt(s) together with metal salt(s) in minor proportion.

6. An explosive composition according to claim 5, wherein said metal salt(s) are present in the amount of less than 25% of the oxidizer reactant by weight.

7. An explosive composition according to claim 1, further comprising a minor proportion of desensitizing agent, selected from the group consisting of water, glycerin, glycol, and hydrocarbon oil, and mixtures thereof.

8. An explosive composition according to claim 1, further comprising a water activated gelling agent, present in the amount of less than about 10% by weight.

9. An explosive composition according to claim 1, further comprising a wetting agent, present in the amount of less than about 5% by weight.

10. An explosive composition according to claim 1, further comprising a self-sterilization constituent in a hydrazine soluble capsule in contact with the explosive composition.

11. An explosive composition according to claim 10, wherein said self-sterilizing agent is a desensitizer.

12. An explosive composition according to claim 10, wherein said self-sterilization agent upon direct exposure to the explosive composition undergoes hypergolic decomposition therewith.

13. An explosive composition according to claim 1, further comprising a waterproofing agent, present in the amount of less than about 10% by weight.

14. An explosive composition comprising the following constituents in the following relative proportions by weight:

$N_2H_5NO_3$, from about 40% to about 92%;

$N_2H_5ClO_4$, from 0% to about 40%;

N_2H_4 , about 6% to about 15%; and

NH_3 , from about 2% to about 15%.

15. The explosive composition according to claim 14, wherein the hydrazinium salt(s) and the hydrazine are present in approximately stoichiometric proportions, and the ammonia is present in the amount of from about 5 to about 10%.

16. An explosive composition according to claim 14, comprising from about 70% to about 92% $N_2H_5NO_3$.

17. An explosive composition according to claim 14, wherein said oxidizer reactant consists essentially of hydrazinium salt(s) together with metal salt(s) in minor proportion.

18. An explosive composition according to claim 17, wherein said metal salt(s) are present in the amount of less than 25% of the oxidizer reactant by weight, and are selected from the group consisting of alkali metal nitrates, calcium nitrate, aluminum nitrate, alkali metal perchlorates, calcium perchlorate, aluminum perchlorate, and mixtures thereof.

19. An explosive composition according to claim 14, wherein said hydrazinium salt(s) consists essentially of a mixture of hydrazinium nitrate and hydrazinium perchlorate, the proportion of nitrate to perchlorate being from about 4:1 to about 1:1 by weight, and the proportion

of hydrazinium salts to hydrazine being about 7:1 to about 10:1 by weight.

20. An explosive composition according to claim 19, further comprising a minor proportion of the desensitizing agent, selected from the group consisting of water, glycerin, glycol, and hydrocarbon oil, and mixtures thereof.

21. An explosive composition according to claim 19, further comprising a water activated gelling agent, present in the amount of less than about 10% by weight.

22. An explosive composition according to claim 19, further comprising a wetting agent, present in the amount of less than about 5% by weight.

23. An explosive composition according to claim 19, further comprising a waterproofing agent, present in the amount of less than about 10% by weight.

24. An explosive composition at least principally comprising:

- (a) an oxidizer reactant, at least the major portion of which is hydrazinium nitrate;
- (b) hydrazine, present in at least approximately stoichiometric proportion with respect to the oxidizer reactant and functioning as an exothermically decomposable constituent, yielding decomposition products which in turn function as reducer reactants undergoing explosive decomposition with said oxidizer reactant upon detonation of the composition; and

- (c) ammonia, present in sufficient amount to materially reduce the viscosity and freezing point of the composition.

25. The method of forming an explosive composition at the point of use, said method comprising:

- (a) emplacing at the point of use a predetermined amount of an oxidizer reactant at least principally comprised of ammonium salt(s) selected from the group consisting of ammonium nitrate and mixtures thereof with ammonium perchlorate;
- (b) admixing with the ammonium salt(s) an amount of hydrazine calculated to autogenously convert the ammonium salt(s) to hydrazinium salt(s) and provide a substantial proportion less than about 15% of free ammonia dissolved in the hydrazine, together with an amount of unreacted hydrazine at least sufficient to realize an approximately stoichiometric balance between the hydrazine and the oxidizer reactant.

26. The method of forming an explosive composition comprising:

- (a) gradually mixing liquid hydrazine with an oxidizer reactant at least principally comprised of ammonium salt(s) selected from the group consisting of ammonium nitrate and mixtures thereof with ammonium perchlorate, the admixed amount of liquid hydrazine being sufficient to dissolve the ammonium salt(s) in the hydrazine and convert the ammonium salt(s) to hydrazinium salt(s) with evolution of free ammonia; and

- (b) selectively reducing the proportion of ammonia dissolved in the mixture to a predetermined amount more than about 2% and less than about 15% by weight of the total mixture.

27. The method of forming an explosive composition in-place at the point of use, said method comprising:

- (a) substantially covering an atmospherically exposed solid surface of substantial area with a substantially uniform layer of an oxidizer reactant at least principally comprised of ammonium salt(s) selected from the group consisting of ammonium nitrate and mixtures thereof with ammonium perchlorate; and

- (b) substantially uniformly applying an amount of liquid hydrazine to convert at least most of the ammonium salt(s) to hydrazinium salt(s) with evolution of free ammonia, and to provide sufficient hydrazine in the explosive composition so that the hydrazine is in approximately stoichiometric proportion with respect to the formed hydrazinium salt(s).

28. The method of claim 27, wherein such solid surface is a porous media, and the formed explosive composition contains sufficient ammonia to be in essentially liquid state so as to permeate and penetrate into the porous media.

29. The method of claim 27, wherein said solid surface is a metallic sheet.

30. The method of claim 27, comprising placing on the exposed solid surface a layer of absorbent material in which the oxidizer reactant is substantially uniformly distributed; and spraying the liquid hydrazine onto the emplaced absorbent material.

31. The method of explosively laminating a metal sheet to a solid substrate, said method comprising:

- (a) forming an explosive coating on one surface of a metal sheet in accordance with the method of claim 27;
- (b) superposing the coated metal sheet on the substrate with the uncoated surface thereof in contact with the substrate; and
- (c) detonating the explosive.

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CARL D. QUARFORTH, *Primary Examiner.*

M. J. SCOLNICK, *Assistant Examiner.*

U.S. Cl. X.R.

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