United States Patent Office 3,205,103 Patented Sept. 7, 1965

3,205,103

HIGH ENERGY EXPLOSIVE AND PROPELLANT COMPOSITIONS

Milka Radoicich Zhivadinovich and Radivoje Zhivadinovich, both of 2079 28th Ave., San Francisco, Calif.

No Drawing. Filed Nov. 26, 1962, Ser. No. 240,134
5 Claims. (Cl. 149—23)

This application is a continuation-in-part of our application Serial No. 722,154, filed March 18, 1958, entitled "High Energy Fuel and Explosive," now U.S. Patent No. 3,066,139, issued November 27, 1962.

This invention relates to combustible mixtures, more particularly to those containing both a fuel component and an oxidizer component to support combustion.

In rocket fuels and the like intended to burn and provide thrust for a non-airbreathing vehicle or missile it is necessary, of course, to provide both a fuel and an oxidizer. The fuel is preferably rich in hydrogen because of the greater heat of combustion of hydrogen per unit of weight compared to most other elements. Many fuels proposed heretofore have been expensive, toxic or hazardous to use. Many oxidizers proposed heretofore have also been expensive, toxic or dangerous. As a result many of the combustible mixtures proposed or employed heretofore for the purpose have been expensive, or toxic or dangerous to store and handle, or have had a combination of such disadvantages.

It is an object of the present invention to provide improved combustible mixtures of the character described.

It is a further object of the invention to provide combustible (i.e., fuel plus oxidizer) materials which are effective for such purposes as a propellant and/or an explosive and which are economical to manufacture.

A further object of the invention is to provide a combustible mixture of the character described which is safe to manufacture and safe to handle.

A still further object of the invention is to provide a combustible mixture of the character described which is nontoxic in character or which has such low toxicity that it can be prepared and handled safely.

It is a particular object of the invention to provide a high energy fuel in a form which is highly susceptible to the action of an added oxidizer.

The above and other objects of the invention will be apparent from the ensuing description and the appended claims.

We have discovered that certain nitrogen compounds and certain polyvalent metal salts can be united in the form of addition compounds which are combustible and in which the fuel component is in a form which can be oxidized very readily by an added oxidizer.

We have discovered that certain nitrogen compounds react with certain hydrated polyvalent metal salts to form addition compounds which provide high energy fuels. These fuels are in a colloidal or highly dispersed form which reacts with oxidizers with a high degree of efficiency. The oxidizer may be added to the addition compound after the latter has been formed or it may be incorporated by an in situ method as explained hereinafter. Also other fuels, such as powdered or flaked metals, may be added to the compositions.

As stated, the fuel component of the compositions of the present invention are addition compounds or reaction products (formed by separate addition, or by an in situ process) of (1) a nitrogen compound and (2) a polyvalent metal salt, which will now be generally characterized.

The nitrogen compound (which may be a single compound or a mixture of any two or more of such compounds) has the following characteristics: It is water soluble or highly water-absorptive. It is combustible and is a good fuel. It forms an addition compound with basic aluminum nitrate in the manner described hereinafter. Examples of suitable nitrogen compounds are as follows:

Hexamethylenetetramine; aliphatic, aromatic and mixed aliphatic-aromatic amines such as any of the isomers of propyl amine, butyl amine and amyl amine; benzylamine; α- and β-phenyl ethyl amines; polyamines such as ethylene diamine, tetramethylene diamine, hexamethylene diamine, o-, m- and p-phenylene diamines; hydrazine and its derivatives such as methyl and ethyl hydrazines, symmetrical and asymmetrical dimethyl hydrazines, phenylhydrazine; guanidine and its derivatives such as 1-amino guanidine, methyl and ethyl guanidines and biguanide; pyridine and its derivatives such as the α-, β- and γ-picolines, the various dimethyl pyridines, and α-, β- and γ-amino pyridines; pyrazine and 2,5-dimethyl pyrazine; piperazine and 2,5-dimethyl piperazine; piperidine and its derivatives such as 2-ethyl piperidine and the 1-, 2-, 3- and 4-methyl piperidines; pyrrolidine; the hydrogenated methyl and ethyl pyrroles; quinoline and 4-amino quinoline; hydrazino pyridines; morpholine; and compounds (hydrazine derivatives) of the type $NH_2 \cdot NH \cdot X$ wherein X is a heterocyclic radical containing nitrogen in the heterocyclic nucleus. These and other suitable nitrogen compounds are water soluble to at least some substantial degree; they have a low volatility; and they are rich in fuel elements (C and H) and preferably contain relatively little oxygen. Also they are basic and are capable of forming a double compound with $Al(NO_3)_3 \cdot 9H_2O$ of the general type

$$(Y)_a \cdot Al(OH)_b(NO_3)_c$$

wherein Y is the nitrogen compound, and *a*, *b* and *c* are integers each not less than unity.

The polyvalent metal salt component is a salt of a polyvalent, amphoteric metal such as aluminum, gallium, beryllium, indium and thallium. Certain metals (e.g., beryllium) are toxic, hence will be so avoided except in systems or end uses where toxicity is not important or where adequate safeguards exist. Other metals are relatively expensive. The preferred metal is aluminum. The selected metal is used in the form of the salt of an oxidizing anion, and the salt is in the form of a hydrate, preferably a polyhydrate; that is, it is in the form $(M)_a(X)_b \cdot nH_2O$ wherein M represents the metal, X the anion, *a* and *b* their combining ratios and *n* is an integer greater than unity. Salts of this type have the property, when they are mixed with a nitrogen compound of the character described, of undergoing hydrolysis to form a basic salt of the type $M_a(OH)_cX_d$ wherein *a*, *c* and *d* represent the combining ratios. The significance of this reaction is that the basic salt formed by the reaction is colloidal and presents a large amount of surface with which the nitrogen compound forms an addition compound, thereby making a very large surface available for the added oxidizer which is sorbed on the addition compound. The oxidizing anion X also has an oxidizing effect, and the hydrolyzed salt $M_a(OH)_c(X)_d$ may act as a combustion catalyst.

The hydrolysis referred to above is effected by reason of the water of hydration of the salt and the basic nature and water absorptive property of the nitrogen compound. The nitrogen compound should have a pH greater than 7 and should produce a mixture with the salt having a pH not less than 6; otherwise the salt is stabilized in the form $M_aX_b \cdot nH_2O$ and does not hydrolyze, or hydrolyzes at an undesirably low rate.

Any polyvalent metal salt of an oxidizing anion may be used which is stable in storage, which exists as a hydrate and which is amphoteric; e.g., the nitrate, chlorates and perchlorates of aluminum, gallium, beryllium, indium

and thallium. Certain of these metals (e.g., beryllium) are toxic and others are rather expensive, but where toxicity and/or expense can be tolerated, they can be used.

Examples of suitable salts are as follows:

$Be(NO_3)_2 \cdot 3H_2O$, $Be(NO_3)_2 \cdot 4H_2O$
$Ga(NO_3)_3 \cdot 8H_2O$
$In(NO_3)_3 \cdot 4\frac{1}{2}H_2O = 2In(NO_3)_3 \cdot 9H_2O$
(also: $In(NO_3)_3 \cdot 3H_2O$
$Tl(NO_3)_3 \cdot 3H_2O$
$Al(ClO_3)_3 \cdot 6H_2O$, $Al(ClO_3)_3 \cdot 9H_2O$
$Be(ClO_4)_2 \cdot 4H_2O$
$Al(ClO_4)_3 \cdot 6H_2O$, $Al(ClO_4)_3 \cdot 9H_2O$, $Al(ClO_4)_3 \cdot 15H_2O$
$Ga(ClO_4)_3 \cdot 6H_2O$
$In(ClO_4)_3 \cdot 8H_2O$

The preferred hydrated polyvalent metal salt is aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$, but other metal salts may be used as explained hereinafter. This preferred salt is stable and economical and it is very effective for the purpose.

Any of a large number of oxidizers may be incorporated in the addition compounds above described. Potassium chlorate is preferred but other suitable oxidizers include potassium perchlorate, potassium nitrate, ammonium perchlorate, lithium nitrate, lithium perchlorate and in general any of the known solid oxidizers, preferably those which are stable in storage. Liquid oxidizers may also be used in suitable environments and systems, e.g., where pressure is applied to prevent evaporation; examples of liquid oxidizers being liquid oxygen, liquid fluorine and $ClO_3 \cdot F$. The quantity of oxidizer is preferably such that it will oxidize all of the fuel in the mixture, but more or less may be added.

As stated, other fuels may be added such as powdered metals (e.g., powdered aluminum, boron, magnesium, silicon and charcoal, etc.). These added fuels economize in the use of the more expensive organic nitrogen-polyvalent metal salt addition compounds of the invention.

Our investigations have been carried further in connection with hexamethylenetetramine and aluminum nitrate nonahydrate; but our observations and conclusions with respect to this pair of reactants are applicable generally.

We have found that hexamethylenetetramine and aluminum nitrate nonahydrate react to form an addition compound when each is dissolved in alcohol and the alcoholic solutions are mixed. A precipitate forms immediately which is white and flocculent but which, on filtering, washing with alcohol and drying in a dessicator becomes a white powder. Analysis has shown that the aluminum nitrate exists in the form of a basic nitrate, approximately $Al(OH)_2NO_3$, but probably a mixture of $AlOH(NO_3)_2$ and $Al(OH)_2NO_3$, with the latter predominating. The presence of hexamethylenetetramine is shown by the fact that when water is added insoluble aluminum hydroxide forms and hexamethylenetetramine dissolves. The precipitate formed with hexamethylenetetramine and aluminum nitrate nonahydrate is, therefore, an addition compound. The precipitate is insoluble in organic solvents such as alcohol, benzene, toluene, petroleum ether and carbon tetrachloride. Its approximate formula is

(I) $$[(CH_2)_6N_4]_2 \cdot Al(OH)_2NO_3$$

which is apparently formed by the reaction

(1) $$2(CH_2)_6N_4 + Al(NO_3)_3 \cdot 9H_2O \rightarrow [(CH_2)_6N_4]_2 \cdot Al(OH)_2NO_3 + 2HNO_3 + 7H_2O$$

It is of interest that this addition compound can be ignited to form a very highly dehydrated and active form of alumina. We believe that this results from the fact that the basic aluminum nitrate from which the alumina is formed is in a colloidal, highly dispersed and very active state. It is this highly active, colloidal basic aluminum nitrate which provides a substrate, base or medium to accept and disperse an added oxidizer, to hold the hexamethylenetetramine in highly dispersed form, and to provide a very efficient high energy, self-oxidizing composition when an oxidizer is added.

Although the addition compound above described may be formed by precipitation, we have found that it is preferable to form it by a dry method in which the hexamethylenetetramine and hydrated aluminum nitrate are mixed dry. If these compounds are mixed in 2:1 molar ratio (i.e., 2 mols of hexamethylenetetramine and one mol aluminum salt), a thick viscous mass forms, which dries overnight in an ordinary dry atmosphere to a friable solid. If a 2.5:1 ratio is employed, the mixture first assumes a damp consistency, then a damp, granular consistency rather than the viscous consistency of the 2:1 ratio product.

It is an advantage of the dry method that an oxidizer such as $KClO_3$ may be added to the reactants at the outset, although it may be added subsequently to the addition compound. If the oxidizer is incorporated in situ, i.e., by adding it to the reactants before forming the addition compound, it becomes more efficiently dispersed. Apparently the oxidizer dissolves in the water of crystallization which is expelled (cf. Equation 1 supra) and is adsorbed on the addition compound. In this way, a very intimate contact—a maximum interfacial area—is formed between the hexamethylenetetramine and the oxidizer.

At this point it should be noted that the addition compounds of the invention, such as compound I supra, are not by themselves in most cases highly effective as explosives or as self-sustaining combustible material. Hexamethylenetetramine by itself decomposes on heating without exploding; likewise hydrated aluminum nitrate. Compound I without any added oxidizer is different in this respect in that it ignites easily and burns with a puffing effect, but it does not sustain combustion in the absence of air. However, upon adding an oxidizer such as $KClO_3$, an easily ignited product (i.e., easily ignited by heat) is formed which, if left in the open will burn rapidly in the absence of air and which, if confined, will explode violently.

Thus Compound I and other nitrogen compound-polyvalent metal salt addition compounds of our invention provide high energy fuels to which oxidizer can be added to yield a very efficient combustible system.

Among the advantages of these addition compounds, there may be mentioned the following: The raw materials are inexpensive; they can be produced in large volume; and they are nonexplosive and nontoxic. The addition compounds are nontoxic and relatively insensitive to shock and friction. In the dry method no solvents are used, hence solvent recovery is not required. It will be understood that these advantages apply to our preferred addition compounds which are the result of reacting approximately 2 to 2½ mols of hexamethylenetetramine with 1 mol of aluminum nitrate nonahydrate. With other embodiments of our invention some of these advantages are lacking or are present in diminished degree.

The following specific examples will serve further to illustrate the practice and advantages of our invention:

Example 1

2 gram mols of hexamethylenetetramine, 1 gram mol of $Al(NO_3)_3 \cdot 9H_2O$ and 40% of $KClO_3$ based on the combined weight of hexamethylenetetramine and aluminum nitrate were mixed together. During the mixing period it was noted that the mixture became moist, then honey-like in consistency, then hard and malleable. Finally after keeping in a desiccator it becomes friable enough to powder. At the end of this time a white, caked friable product was formed which, unlike any of the ingredients, would ignite easily, would burn steadily and at a relatively rapid rate and would explode if heated within a confined space. An 0.1 gram sample heated in an open test tube at the rate of 5° C. per minute exploded at 85–91° C.

Example 2

The same procedure was employed as in Example 1 except that the ratio of hexamethylenetetramine to aluminum nitrate nonahydrate was 2½ to 1 instead of 2 to 1. The product differed from that of Example 1 in that it burned faster but exploded at 163–168° C. in the heating test described in Example 1.

Higher ratios of hexamethylenetetramine than 2½ to 1 and lower ratios than 2 to 1 may be employed. By employing higher ratios, the addition compound formed by reaction (1) contains more fuel value and can therefore, utilize more oxidizer. Ratios greater than 3:1 are not preferred. Lower ratios than 2:1 lead to products having reduced flammability and explosiveness.

Example 3

The ingredients were 2 moles of pyridine, 1 mole of $Al(NO_3)_3 \cdot 9H_2O$ and 0.5 gram of $KClO_3$ per gram of pyridine-$Al(NO_3)_3 \cdot 9H_2O$ mixture. The solid ingredients were first powdered in a mortar and mixed together, first $KClO_3$ and pyridine. On adding aluminum nitrate a thick "fog" is formed that nearly immediately disappears, and on continued mixing the mass soon becomes quite fluid with small crystals (aluminum nitrate and potassium chlorate being not yet dissolved) dispersed therein. On continued mixing a colloid starts forming (after about 5–10 minutes), and its formation proceeds slowly; it also slowly becomes thicker, until after about an hour-and-a-half the colloid is thick. On standing the mass solidifies or sets.

On ignition this mixture burns vigorously and evenly and has good propellant properties.

Example 4

The ingredients were 2 moles of piperazine hexahydrate, 1 mole of $Al(NO_3)_3 \cdot 9H_2O$ and 0.5 gram of $KClO_3$ per gram of the hydrated piperazine-hydrated aluminum nitrate mixture. The ingredients were first powdered and piperazine and aluminum nitrate first mixed, at which time a white "fog" appeared. On the addition of $KClO_3$ the mixture immediately becomes damp, then changes into a thick wet mass which slowly becomes thinner. The formation of the colloid starts after 15–20 minutes, and it slowly thickens into a cream. On standing it sets.

On ignition this mixture burns vigorously and evenly and has good propellant properties.

Example 5

The ingredients were 2 moles of hydrazine monohydrate, 1 mole of $Al(NO_3)_3 \cdot 9H_2O$ and 0.4 gram of $KClO_3$ per gram of hydrazine hydrate-hydrated aluminum nitrate mixture. The solid ingredients were powdered and mixed and then hydrazine was added; the mass immediately became liquid owing to the dissolution of the solids. A reaction took place; there was foaming and a gas evolved. After about 15 minutes the pH was shown to be below 3 (indicator paper), too low for the formation of a gel.

By increasing the ratio of hydrazine hydrate to 4 moles of hydrazine hydrate to 1 mole of $Al(NO_3)_3 \cdot 9H_2O$, the pH was about 3 at the start of reaction.

Example 6

8 moles of hydrazine hydrate and 1 mole of

$$Al(NO_3)_3 \cdot 9H_2O$$

were mixed. The pH at the start was about 7. On mixing a gel starts forming almost immediately and the mass is semi-liquid. After about half-an-hour all the small crystals dispersed therein seemed to have dissolved and reacted. The mass is of the consistency of a smooth soft cream. On standing, about another hour, it becomes considerably thicker. As such it is too wet to be inflammable; but upon drying in a dessicator it is inflammable.

Example 7

The ingredients were 2 moles of hexamethylenetetramine, 4 moles of hydrazine hydrate, 1 mole of

$$Al(NO_3)_3 \cdot 9H_2O$$

and 0.4 gram of $KClO_3$ per gram of the other three components.. Hydrazine hydrate was added to the solid powdered mixture of the other ingredients; the pH was 6, but already a gel started to form as the hexamethylenetetramine continued to dissolve; the mass slowly became semi-liquid. After about 15 minutes a fine colloidal cream was formed which was becoming thicker. Towards the end 0.6 gram of powdered NH_4ClO_4 per gram mass was added. The NH_4ClO_4 was not added at the beginning so that the pH would remain high enough for the formation of a colloid.

In all of the above examples (and in the example below) the end product could be ignited readily and, when ignited, burned steadily and with good energy release, suitable for propellant usage.

Example 8

As an example of a product containing added metallic fuel, 8 moles of hydrazine hydrate and 1 mole of

$$Al(NO_3)_3 \cdot 9H_2O$$

were mixed with 0.4 gram of $KClO_4$, 0.2 gram of ammonium perchlorate and 0.1 gram of powdered aluminum (these last three ingredients being used in the stated amounts per gram of hydrazine hydrate-hydrated aluminum nitrate). The powdered aluminum and ammonium perchlorate were added toward the end of the reaction.

It will, therefore, be apparent that novel explosive and propellant compositions have been provided wherein the principal (or a principal) fuel element is a nitrogen compound; an oxidizer such as potassium chlorate is included; and a partially hydrolyzed polyvalent salt is present in the form of an addition compound with the nitrogen compound, such salt providing an excellent surface for combustion.

We claim:

1. Addition compounds of basic, hydrogen-containing water-soluble organo nitrogen compounds and hydrated polyvalent metal salts, said polyvalent metal salt being present in the addition compound in the form of a basic salt, said addition compounds being combustible, said addition compounds being in admixture with an oxidizer, said oxidizer forming a stable mixture with the addition compound at room temperature and being effective, upon heating the mixture, to oxidize the addition compound rapidly and in a self-sustaining manner.

2. The compounds of claim 1 in which the metal salt is a hydrated aluminum nitrate.

3. A composition of matter consisting essentially of (1) an addition compound of a nitrogen base and a polyvalent metal salt and (2) an oxidizer; said nitrogen base being water-soluble and basic, being capable of forming an addition compound with aluminum nitrate nonahydrate and being a combustible fuel; said polyvalent metal salt being present in the addition compound in the form of a partially hydrolyzed hydrated salt of an amphoteric polyvalent metal and an oxidizing anion; said oxidizer being a solid salt of a metal and an oxidizing anion.

4. A composition of matter consisting essentially of (1) an addition compound of (a) a nitrogen base and (b) a polyvalent metal salt, and (2) an oxidizer; said polyvalent metal salt being a partly hydrolyzed polyvalent metal salt of the type $M_a(OH)_bX_c$ derived from

a hydrated salt of the type $M_aX_{b+c}\cdot nH_2O$ wherein *a*, *b*, *c* and *n* are integers not less than unitl, X is an oxidizing anion and M is selected from the group consisting of aluminum, gallium, indium, beryllium, thallium; said nitrogen base being basic and water-soluble and being capable of forming an addition compound of said character with $Al(NO_3)_3\cdot 9H_2O$ upon admixture therewith; said oxidizer being a metal salt of the type Me_aY_b wherein Me is a metal, Y is an oxidizing anion and *a* and *b* are small integers not less than unity.

5. The composition of claim 4 wherein the polyvalent metal salt is aluminum nitrate nonahydrate.

References Cited by the Examiner

UNITED STATES PATENTS

957,307 5/10 Claessen ---------- 149—45 X

CARL D. QUARFORTH, *Primary Examiner.*

REUBEN EPSTEIN, *Examiner.*