

1

3,066,139

**HIGH ENERGY FUEL AND EXPLOSIVE**

Milka Radoicich Zhivadivovich and Radivoje Zhivadivovich, San Francisco, Calif.

No Drawing. Filed Mar. 18, 1958, Ser. No. 722,154  
5 Claims. (Cl. 260—242)

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 nonairbreathing 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.

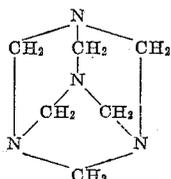
It is a particular object of the invention to provide a high energy fuel in the form which is highly susceptible to the action of an added oxidizer.

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.

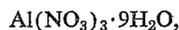
The preferred nitrogen compound is hexamethylenetetramine, which has the formula



2

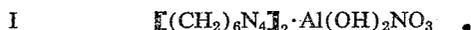
but other nitrogen compounds may be used as explained hereinafter.

The preferred hydrated polyvalent metal salt is aluminum nitrate nonahydrate,

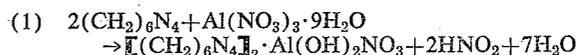


but other metal salts may be used as explained hereinafter.

We have found that the preferred reactants (hexamethylene tetramine 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 desiccator becomes a white powder. Analysis has shown that the aluminum nitrate exists in the form of a basic nitrate, approximately  $\text{Al}(\text{OH})_2\text{NO}_3$ , but probably a mixture of  $\text{AlOH}(\text{NO}_3)_2$  and  $\text{Al}(\text{OH})_2\text{NO}_3$ , 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



which is apparently formed by the reaction



It is of interest that the addition compound of our invention 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 2½:1 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  $\text{KClO}_3$  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 absorbed 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  $\text{KClO}_3$ , 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  $2\frac{1}{2}$  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  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 40% of  $\text{KClO}_3$  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  $5^\circ \text{C}$ . per minute exploded at  $85\text{--}91^\circ \text{C}$ .

*Example 2.*—The same procedure was employed as in Example 1 except that the ratio of hexamethylenetetramine to aluminum nitrate nonahydrate was  $2\frac{1}{2}$  to 1 instead of 2 to 1. The product differed from that of Example 1 in that it burned faster but exploded at  $163\text{--}168^\circ \text{C}$ . in the heating test described in Example 1.

Higher ratios of hexamethylenetetramine than  $2\frac{1}{2}$  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.

Other nitrogen compounds may be used in place of hexamethylenetetramine and other polyvalent metal salts in place of aluminum nitrate nonahydrate. Referring to Equation 1 above, it is required that the nitrogen compound replacing the hexamethylenetetramine be highly water-absorptive; and it is required that the metal salt replacing aluminum nitrate nonahydrate be hydrated and that it give up its water of crystallization to the nitrogen compound and in so doing form a colloidal or highly surface active substrate for added oxidizer.

In place of hexamethylenetetramine, other amines, both aliphatic and aromatic, also hydrazine and lower

alkyl substituted hydrazines, hydroxylamine and guanidine may be used provided they react with the polyvalent metal salt in the manner described. Examples of suitable organo nitrogen compounds are methylamine, aniline, hydrazine, mono and dimethyl hydrazines, hydroxylamine and guanidine. However, hexamethylenetetramine is preferred. It forms an addition compound with basic aluminum nitrate with ease; it has a very high hydrogen-to-carbon ratio; and it is inexpensive and nontoxic.

In place of aluminum nitrate nonahydrate, lower hydrates of aluminum nitrate may be used, also other hydrated metal nitrates which tend to hydrolyze in the presence of water, e.g., hydrated nitrates of beryllium, gallium, ferric iron, trivalent chromium, nickel, cobalt, zinc and magnesium. Other salts than nitrates may be used, e.g., chlorates such as  $\text{Al}(\text{ClO}_3)_3 \cdot 9\text{H}_2\text{O}$  and perchlorates such as  $\text{Al}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ . However, aluminum nitrate nonahydrate is preferred because of the ease with which it reacts with hexamethylenetetramine to form an additional compound; because of the lightness of aluminum compared to most other polyvalent metals, because of the cheapness and availability of this particular salt; because of its lack of toxicity and its lack of any dangerous storage and handling qualities; and because of its strong tendency to hydrolyze to yield a colloidal basic nitrate.

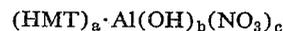
Other oxidizers may be used in place of  $\text{KClO}_3$ , e.g.,  $\text{KNO}_3$ , ammonium nitrate, lithium nitrate, lithium perchlorate, ammonium perchlorate, potassium perchlorate and fluorine oxidizers such as  $\text{ClO}_3 \cdot \text{F}$  and liquid fluorine. The quantity of oxidizer is preferably such that it will oxidize substantially all of the nitrogen compound, an excess being preferred.

It will, therefore, be apparent that, addition compounds have been provided which constitute high energy fuels and which are in a physical form which is uniquely adapted to function with added oxidizer. The preferred addition compounds are advantageous because of the economical, nontoxic, nonexplosive starting materials; the ease with which they can be formed; the relatively non-hazardous and nontoxic character of the addition compounds; and their high energy value and advantageous physical state.

Although the products of our invention in their preferred form are addition compounds, it will be understood that intimate physical mixtures may be employed which may not be, technically speaking, true addition compounds. It will also be understood that the composition is variable. Thus the ratio of reactants will govern the ratio of components in the final product. Also other factors such as choice of solvent in the wet method (precipitation from combined solutions) will govern the composition.

We claim:

1. Addition compounds of hexamethylenetetramine and aluminum nitrate nonahydrate.
2. Compounds having the formula



in which HMT represents hexamethylenetetramine,  $a$  is not less than about 2 and not greater than about 3 and  $b$  and  $c$  are integers greater than zero whose sum is 3.

3. The method of producing a high energy fuel which comprises forming separate solutions of hexamethylenetetramine and aluminum nitrate nonahydrate, mixing the two solutions to precipitate an addition compound of hexamethylenetetramine and basic aluminum nitrate and drying the additional compound.

4. The method of producing a high energy fuel which comprises mixing hexamethylenetetramine and aluminum nitrate nonahydrate in the dry state to form an addition compound of hexamethylenetetramine and basic aluminum nitrate and drying the addition compound.

5. A method of forming combustible material which

5

comprises reacting hexamethylenetetramine with aluminum nitrate nonahydrate to form an addition compound of hexamethylenetetramine with a hydrolysis product of the aluminum nitrate.

## References Cited in the file of this patent

## UNITED STATES PATENTS

|           |             |               |    |
|-----------|-------------|---------------|----|
| 2,019,121 | De Rewal    | Oct. 29, 1935 |    |
| 2,480,743 | Krantz      | Aug. 30, 1949 |    |
| 2,628,561 | Sage et al. | Feb. 17, 1953 | 10 |

2,682,461  
2,735,858

5 338,427

6

Hutchison ----- June 29, 1954  
Bergman ----- Feb. 21, 1956

## FOREIGN PATENTS

Germany ----- June 17, 1921

## OTHER REFERENCES

Galzolari: Atti della Reale Accademie Lincei, 21, Part I, 563-68, p. 567 (1912).  
Vanino et al.: Chem. Abs., 9, 1049<sup>s</sup> (1915).  
Sarkar: Chem. Abs., 22, 4074-75 (1928).