United States Patent Office 3,211,720 Patented Oct. 12, 1965

3,211,720

HYDRAZINE BASED SOLID PROPELLANT

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No Drawing. Filed Aug. 8, 1958, Ser. No. 753,886
21 Claims. (Cl. 260—239)

This invention relates to new and useful fuels and propellants which are normally solids, and to the methods for making same and the uses thereof in the production of motion; and in particular to that class of solid propellants designated as monopropellants of the single compound type, and to the employment of such single compound solid propellants as fuel in turbo engines and reaction motors, particularly in rockets and the like.

In turbo type engines of the turbo jet and turbo prop designations, the fuel is employed to provide the motive power for the turbines. In the turbo jet engine only enough gas expansion is permitted as is necessary to drive the turbine to perform its prime function as a gas compressor. The residual energy in the expanding gases from the combustion chamber is then used to drive the engine by jet action. In a turbo prop engine all of the energy of the expanding gases is expended through and manifested in the work done by the propellers. The fuels normally employed for such engines are usually designated as those of the bipropellant type; that is, a mixture of a burnable material which is usually organic in nature, as for example gasoline and the like, and an oxidizing agent which in its simplest form may be air. In the combustion chamber of the engine, gasoline is burned or combusted, giving rise to large volumes of gases at elevated temperatures; the continued expansion of the gases providing the driving force. Control of this type of combustion is relatively simple as evidenced by the well known gasoline internal combustion engine, but unfortunately the energy levels of such a fuel combination are very low, and it is not feasible or indeed even possible to use such fuels to obtain controlled, very high velocities as is required in the modern turbo engines and reaction motors. In both of these fields there is a constant striving towards development of higher energy fuels, and there have been many prior suggestions whereby the energy level or B.t.u. rating of the fuel might be increased.

In rocketry where the motive power is of the pure propulsion type, there is a dire need for safe, controllable, stable, and otherwise improved high energy propellants. In this field propellants are conventionally divided into two main types; those characterized as monopropellants and other combinations known as bipropellants. As the terms imply, the monopropellants consist essentially of single compounds which are capable under proper conditions to evolve large volumes of gases. With such propellants there is no need for any auxiliary agents such as air, oxygen and the like. The bipropellants are similar to those used and described above with respect to the turbo type engines, and in the rocket field similarly comprise a burnable material and a powerful oxidizing agent; the combination being capable of tremendous energy releases as are necessary for the attainment of the extremely high velocities. The measure of energy of rocket and jet fuels and propellants is set forth as the specific impulse of the fuel. The higher the specific impulse, the greater the thrust per unit of fuel employed. The use of bipropellant fuels has to date predominated in all fields of motive power and even in the rocket and jet propulsion fuels, but in order to achieve the necessary high energy levels required in rocketry it has been necessary to effect combinations of materials which are extremely dangerous to handle. Such combinations include for example the

hydrocarbon fuels such as kerosene and the like together with liquid oxygen. Other powerful oxidizing agents which have been used are nitric acid, hydrgen peroxide, fluorine and the like. Such materials are obviously extremely dangerous to handle, and are usually very corrosive thus accounting for numerous unfortunate accidents.

In addition to these bipropellant combinations, the use of hydrogen peroxide as a monopropellant has been proposed. Other suggested monopropellants are nitroparaffins and ethylene oxide. Each of these materials, however, suffers from one or more disadvantages of the type discussed above, namely, lack of stability, danger of handling, corrosiveness, etc.

I have now discovered however, that by chemically combining a powerful oxidizing acid and a fuel capable of undergoing "combustion," and effecting polymerization of the resulting combination, a solid, stable and otherwise improved propellant may be prepared. By varying the organic fuel and the amount and type of oxidizing acid, different polymeric products may be obtained, tailored to fit the needs of the solid propellant applications. By such variations it is also possible to obtain most any desired energy level of fuel combination from about a specific impulse of 200 to over 400. The physical properties of the resulting polymeric materials will vary depending upon the particular selection of organic intermediates employed. Thermoplastic materials varying from balsam-like materials to hard glass-like products can be obtained. In addition, thermosettable compositions whose physical propetries will remain virtually unchanged up to the temperature of decomposition may be prepared; again depending upon the proper selection of starting materials.

It is therefore an object of this invention to provide new and useful propellant compositions.

Another object of this invention is to provide new and useful propellant compositions for use in reaction motors and the like.

It is still another object of this invention to provide methods for the preparation of new and useful polymeric compositions suitable for use as propellants in reaction motors.

It is still another object of this invention to provide new and useful polymeric materials which give outstanding thrust energy levels when used as fuels.

Other objects will appear hereinafter as the present description proceeds.

I have found that hydrazine and certain derivatives thereof, in combination with inorganic oxidizing acids, may be condensed with compounds which are polyfunctional and capable of undergoing a polymerization process, to yield high molecular weight polymers containing integrally bonded within the basic recurring unit of the polymer the inorganic oxidizing acid moiety. Upon proper activation as by the use of elevated temperature, the polymeric materials herein contemplated give rise to a tremendous evolution of gaseous products which manifest themselves in the development of high impulse energy levels. The inorganic oxidizing acids which are contemplated for use in the present invention are well known and include nitric acid, perchloric acid, sulfuric acid and phosphoric acid. In addition to hydrazine itself and such simple derivatives as hydroxy alkyl substituted hydrazines, and a specifically diethylol hydrazine and the cyclic derivatives, specifically N-aminoethyleneimine, other hydrazines which may be employed for salt formation with the oxidizing acids described above are unsaturated derivatives, such as allyl hydrazine, vinyl hydrazine, unsymmetrical diallyl hydrazine, unsymmetrical divinyl hydrazine, and unsymmetrical allyl vinyl hydrazine.

Each of the aforementioned nitrogen compounds contains a primary amino group which is capable of reacting with an acid to form a stable salt. This resultant salt is then subjected to reaction whereby polymeric materials are obtained. The type of reaction employed to effect polymerization depends upon the particular hydrazine derivative utilized as the starting material. Hydrazine itself in the form of its salt may be reacted with a polybasic acid of the aliphatic or aromatic series such as oxalic acid, malonic acid, succinic acid, adipic acid, phthalic acid, terephthalic acid, naphthalene dicarboxylic acid and other higher molecular weight dicarboxylic acids such as sebacic acid, to form polyhydrazides of the corresponding dibasic acids; each hydrazide unit containing an equivalent amount of salt forming oxidizing acid. As pointed out above, by varying the polybasic acid used, the ratio of oxidizing acid to oxidizable material can be changed to fit any specifically desired energy level. Instead of using the polybasic acid itself, it is also possible to employ the anhydride or acid halide thereof. It is also contemplated that instead of the saturated aliphatic polyfunctional acids above described which give rise to thermoplastic polymeric materials, one may employ unsaturated aliphatic polybasic acids or a mixture of saturated and unsaturated acids. The use of the unsaturated acids as described above leads to products which may be cross-linked to yield thermosettable compositions. The use of mixtures of acids gives rise to products of intermediate physical properties.

In addition to the use of hydrazine and its aforementioned derivatives in the form of the oxidizing salt thereof for reaction with the polybasic acids, it is also contemplated to form condensation products of the said hydrazines with carbonyl containing compounds such as monoaldehydes, mono-ketones, poly-aldehydes and poly-ketones. As suitable carbonyl compounds there may be employed formaldehyde, acetaldehyde, propionaldehyde, dimethyl and diethyl ketones, and the like. The first stage condensation products are fusible masses which upon further polymerization by means of heat and/or catalysts and/or reaction with additional carbonyl form non-fusible, readily decomposable compositions. The catalysts employed in the initial condensation stage are preferably acidic catalysts such as hydrochloric acid, sulfuric acid, acid salts e.g. sodium bisulfate, ammonium dihydrogen phosphate etc. In the reactions equi-molar amounts of hydrazine (or derivative) salt and carbonyl are condensed with about 0.25 mole of acid at temperatures of from about 60° to 150° C. The products so produced are fusible intermediates which upon further heating, preferably under vacuum, and especially in the presence of additional carbonyl, set to a substantially infusible mass.

The cyclic hydrazine compound N-aminoethyleneimine, mentioned above, may be polymerized in the absence of any additional reagents similarly as ethylene oxide may be polymerized to yield high molecular weight thermoplastic compositions. By chemically combining an inorganic acid moiety with the free amino group of this organic compound, a polymeric salt may be obtained which is readily liquefiable and may be molded into any preferred shape or form in the manner of the usual thermoplastic substances.

In addition to the use of a single acid to effect formation of the desired polymeric salt, one may employ a mixture of acids; again for the purpose of varying the energy level development of the resultant propellant composition. Where hydroxy derivatives of hydrazine are employed in lieu of hydrazine itself, the resultant esters, instead of being polyimides, are polyesters. Where one employs ethylenically unsaturated substituted derivatives of hydrazine such as the vinyl or allyl compounds mentioned above, the polymerization occurs in the usual addition manner similar to other vinyl type polymerizations.

As described above, the hydrazine compound which contains at least one basic, primary, salt-forming amine group is reacted with at least one equivalent (i.e. at least in equimolecular proportions) of the strong oxidizing acid resulting in a chemical combination containing sufficient oxidizing potential by way of combined acid to convert all of the hydrazine compound to gaseous decomposition products at suitable and selected temperatures and pressures. In general the condensation polymers derived from hydrazine or diethylol hydrazine and a polycarboxylic acid or carbonyl require temperatures above about 250° C. to effect the desired decomposition almost instantaneously. The addition type polymers from N-aminoethyleneimine salts and the ethylenically unsaturated hydrazine salts undergo satisfactory gas formation at somewhat lower temperatures, that is above about 180–200° C.

The decomposition of the polymeric salts of this invention may be carried out in the reaction motor or other energy conversion mechanisms by any suitable means. Thus, the polymer mass may be heated either internally or externally by electrical means or by any indirectly applied heat exchange medium such as steam, hot gases, molten metals and the like. Once the critical decomposition temperature has been reached the reaction is self-sustaining and usually no further heating is necessary.

The following examples will serve to illustrate the present invention without being deemed limitative thereof:

Example 1

To one mole of N-aminoethyleneimine there is slowly added one mole of perchloric acid. Salt formation is accompanied by the evolution of heat and the reaction is kept cooled to below 50° C. during the acid addition. The perchlorate salt is then polymerized by heating it in the presence of a cadmium acetate catalyst at a temperature of 100–110° C. for four hours. The resultant polymer is an amorphous, brown solid. Upon heating the polymer to 200° C. there is an instantaneous decomposition to gaseous products.

Example 2

To one mole of hydrazine, one mole of perchloric acid is added slowly. The resultant hydrazine perchlorate is heated for five hours at 170° C. with one mole of adipic acid. After this period of time the evolution of water ceases and the reaction mass is then further heated in a vacuum at 200° C. for six hours. A thermoplastic polymer results. A small portion of the polymer salt is heated to 300° C. and at this temperature there is an instantaneous and complete decomposition to gaseous products.

Example 3

Example 2 is repeated except that an equivalent amount of diethylol hydrazine is substituted for hydrazine itself. There results, similarly, a polymeric substance which is thermoplastic and which decomposes above 260° C.

Example 4

To one mole of vinyl hydrazine, one mole of perchloric acid is slowly added with adequate cooling to maintain a reaction temperature of below about 60° C. The resultant salt is dissolved in 1 liter of N-methyl pyrrolidone and polymerized in an autoclave at a temperature of 95° C. and a pressure of 10 atmospheres in the presence of a copper acetate catalyst. There results a rubber-like, thermoplastic polymer which completely decomposes at 180° C.

Example 5

Example 4 is repeated except nitric acid is used in lieu of perchloric acid. The results are comparable.

Example 6

Example 4 is repeated except that sulfuric acid is used in place of perchloric acid and the catalyst employed is cadmium naphthenate. The results are comparable to those of Example 4.

Example 7

Example 2 is repeated using however maleic anhydride in place of adipic acid. The resultant polymer after pressure molding is not thermoplastic. Similar decomposition of the polymer, however, is effected by heating to 310° C.

Example 8

Example 2 is repeated using a mixture of equal parts by weight of phthalic anhydride and succinic acid in lieu of adipic acid. The results are comparable to Example 2.

Example 9

Example 3 is repeated employing in place of adipic acid a mixture of equal parts by weight of glutaric acid and phthalic anhydride. The resultant polymer decomposes at 275° C.

Example 10

Example 9 is repeated except that the acid salt is prepared using phosphoric acid (100% H_3PO_4). A polymer results which decomposes at about 300° C.

Example 11

The procedure of Example 2 using the reagents of Example 7 is repeated except that in the vacuum heating step, 1% benzoyl peroxide is added. A cross-linked polymer results which is stable up to 400° C. Complete decomposition occurs above this temperature.

Example 12

The procedure of Example 2 is repeated employing nitric acid (95%) in place of perchloric acid. A readily decomposable, thermoplastic polymer results.

Example 13

Example 11 is repeated employing nitric acid in place of perchloric acid. Similar results are obtained.

Example 14

Example 4 is repeated using unsymmetrical diallyl hydrazine. A glass-like polymer results.

Example 15

Example 14 is repeated using nitric acid in place of perchloric acid. Similar results are obtained.

Example 16

One mole of hydrazine and one mole of perchloric acid are slowly mixed to form the perchlorate salt. The salt (1 mole) is gently heated under reflux with 1 mole of formaldehyde and 0.25 mole of hydrochloric acid for 4 hours. An amorphous product is isolated from the reaction mass. This product upon further heating for 3 hours at 6 mm. vacuum forms a hard, non-fusible resin. The resin when heated to 260° C. spontaneously degenerates to gaseous products.

In addition to the organic dicarboxylic acids, both aliphatic and aromatic, described in the above examples, it is also possible to employ any of the polycarboxylic acids heretofore employed in the preparation of polyamide, alkyd and polyester type resins. Other aldehydes in addition to formaldehyde may also be used. While the catalysts described are preferred, others well known in the polymerization and condensation arts may be used.

What is claimed is:

1. A method of making a polymer characterized by its ability to decompose to evolve sufficient quantity of gaseous products as to render the polymer useful as a rocket fuel and the like, which comprises

neutralizing hydrazine with an inorganic oxidizing acid selected from the group consisting of perchloric acid, nitric acid, sulfuric acid, phosphoric acid and mixtures thereof,

condensing the salt thus formed by heating the same in contact with a polyfunctional compound selected from the group consisting of $(CH_2)_x(COOH)_2$, $(CH_2)_x(COY)_2$, $(CH_2)_x(COOOC)$ and mixtures thereof where x is 0 to 8, Y is a halogen, and wherein the hydrazine, the oxidizing acid and polyfunctional compound are selected to give a carbon-oxygen balance which affords substantially complete decomposition of the polymer,

and continuing such heating to render the condensation reaction substantially complete.

2. A method of making a polymer characterized by its ability to decompose to evolve sufficient quantity of gaseous products as to render the polymer useful as a rocket fuel and the like, which comprises

neutralizing a hydroxy alkyl hydrazine with an inorganic oxidizing acid selected from the group consisting of perchloric acid, nitric acid, sulfuric acid, phosphoric acid and mixtures thereof,

condensing the salt thus formed by heating the same in contact with a polyfunctional compound selected from the group consisting of $(CH_2)_x(COOH)_2$, $(CH_2)_x(COY)_2$, $(CH_2)_x(COOOC)$ and mixtures thereof where x is 0 to 8, Y is a halogen, and wherein the hydrazine, the oxidizing acid and polyfunctional compound are selected to give a carbon-oxygen balance which affords substantially complete decomposition of the polymer,

and continuing such heating to render the condensation reaction substantially complete.

3. A method of making a polymer characterized by its ability to decompose to evolve sufficient quantity of gaseous products as to render the polymer useful as a rocket fuel and the like, which comprises

neutralizing N-aminoethyleneimine with an inorganic oxidizing acid selected from the group consisting of perchloric acid, nitric acid, sulfuric acid, phosphoric acid and mixtures thereof, wherein the N-aminoethyleneimine and the oxidizing acid are selected to give a carbon-oxygen balance which affords substantially complete decomposition of the polymer,

and heating such salt to break the N-aminoethyleneimine ring and form the polymer.

4. A method of making a polymer characterized by its ability to decompose to evolve sufficient quantity of gaseous products as to render the polymer useful as a rocket fuel and the like, which comprises

neutralizing an unsaturated hydrazine derivative selected from the group consisting of allyl hydrazine, vinyl hydrazine, unsymmetrical diallyl hydrazine, unsymmetrical divinyl hydrazine, unsymmetrical allyl vinyl hydrazine and mixtures thereof with an inorganic oxidizing acid selected from the group consisting of perchloric acid, nitric acid, sulfuric acid, phosphoric acid and mixtures thereof, wherein the unsaturated hydrazine derivative and the oxidizing acid are selected to give a carbon-oxygen balance affording substantially complete decomposition of the polymer,

and heating such salt to form the polymer.

5. A method of making a polymer characterized by its ability to decompose to evolve sufficient quantity of gaseous products as to render the polymer useful as a rocket fuel and the like, which comprises

neutralizing hydrazine with an inorganic oxidizing acid selected from the group consisting of perchloric acid, nitric acid, sulfuric acid, phosphoric acid and mixtures thereof,

condensing the salt thus formed by heating the same in contact with a carbonyl compound having the structure R_1COR_2 where R_1 and R_2 are selected from the group consisting of lower alkyls and hydrogen, wherein the hydrazine, oxidizing acid and carbonyl compound are selected to give a carbon-oxygen balance affording substantially complete decomposition of the polymer,

and continuing such heating to render the condensation reaction substantially complete.

6. The method of making high energy level propellants which comprises mixing one mole of N-aminoethyleneimine with one mole of perchloric acid to form a salt, and heating such salt in the presence of a cadmium acetate catalyst at a temperature of 100–110° C. for four hours.

7. The method of making high energy level propellants which comprises mixing one mole of hydrazine with one mole of perchloric acid to form a salt, heating such salt, with one mole of adipic acid, for five hours at 170° C., and then vacuum heating the reaction mass for six hours at 200° C.

8. The method of making high energy level propellants which comprises mixing one mole of diethylol hydrazine with one mole of perchloric acid to form a salt, heating such salt, with one mole of adipic acid, for five hours at 170° C., and then vacuum heating the reaction mass for six hours at 200° C.

9. The method of making high energy level propellants which comprises mixing one mole of vinyl hydrazine with one mole of perchloric acid to form a salt, dissolving said salt in one liter of N-methyl pyrrolidone, and autoclaving the dissolved salt at a temperature of 950° C. and a pressure of 10 atmospheres in the presence of a copper acetate catalyst.

10. The method of making high energy level propellants which comprises mixing one mole of vinyl hydrazine with one mole of nitric acid to form a salt, dissolving said salt in one liter of N-methyl pyrrolidone, and autoclaving the dissolved salt at a temperature of 950° C. and a pressure of 10 atmospheres in the presence of a copper acetate catalyst.

11. The method of making high energy level propellants which comprises mixing one mole of vinyl hydrazine with one mole of sulfuric acid to form a salt, dissolving said salt in one liter of N-methyl pyrrolidone, and autoclaving the dissolved salt at a temperature of 950° C. and a pressure of 10 atmospheres in the presence of a cadmium naphthenate catalyst.

12. The method of making high energy level propellants which comprises mixing one mole of hydrazine with one mole of perchloric acid to form a salt, heating such salt, with one mole of maleic anhydride, for five hours at 170° C., and then vacuum heating the reaction mass for six hours at 200° C.

13. The method of making high energy level propellants which comprises mixing one mole of hydrazine with one mole of perchloric acid to form a salt, heating such salt, with one mole of a mixture of equal parts by weight of phthalic anhydride and succinic acid, for five hours at 170° C., and then vacuum heating the reaction mass for six hours at 200° C.

14. The method of making high energy level propellants which comprises mixing one mole of hydrazine with one mole of perchloric acid to form a salt, heating such salt, with one mole of a mixture of equal parts by weight of glutaric acid and phthalic anhydride, for five hours at 170° C., and then vacuum heating the reaction mass for six hours at 200° C.

15. The method of making high energy level propellants which comprises mixing one mole of hydrazine with one mole of nitric acid to form a salt, heating such salt, with one mole of adipic acid, for five hours at 170° C., and then vacuum heating the reaction mass for six hours at 200° C.

16. The method of making high energy level propellants which comprises mixing one mole of diethylol hydrazine with one mole of phosphoric acid to form a salt, heating such salt, with one mode of a mixture of equal parts by weight of glutaric acid and phthalic anhydride, for five hours at 170° C., and then vacuum heating the reaction mass for six hours at 200° C.

17. The method of making high energy level propellants which comprises mixing one mole of hydrazine with one mole of perchloric acid to form a salt, heating such salt, with one mole of maleic anhydride, for five hours at 170° C., adding one percent benzoyl peroxide and vacuum heating the reaction mass for six hours at 200° C.

18. The method of making high energy level propellants which comprises mixing one mole of hydrazine with one mole of nitric acid to form a salt, heating such salt, with one mole of maleic anhydride, for five hours at 170° C., adding one percent benzoyl peroxide and vacuum heating the reaction mass for six hours at 200° C.

19. The method of making high energy level propellants which comprises mixing one mole of unsymmetrical diallyl hydrazine with one mole of perchloric acid to form a salt, dissolving said salt in one liter of N-methyl pyrrolidone, and autoclaving the dissolved salt at a temperature of 950° C. and a pressure of 10 atmospheres in the presence of a copper acetate catalyst.

20. The method of making high energy level propellants which comprises mixing one mole of unsymmetrical diallyl hydrazine with one mole of nitric acid to form a salt, dissolving said salt in one liter of N-methyl pyrrolidone, and autoclaving the dissolved salt at a temperature of 950° C. and a pressure of 10 atmospheres in the presence of a copper acetate catalyst.

21. The method of making a high energy level propellant which comprises mixing one mole of hydrazine with one mole of perchloric acid to form a salt, refluxing said salt with one mole of formaldehyde and 0.25 mole of hydrochloric acid for four hours to isolate an amorphous product from the reaction mass, and vacuum heating such amorphous product for three hours.

References Cited by the Examiner

UNITED STATES PATENTS

2,016,026	10/35	Shinkle	260—2
2,084,927	6/37	Towne	260—2
2,395,642	2/46	Prichard	260—558
2,744,380	5/56	McMillan et al.	60—35.4
2,764,570	9/56	Kowolik et al.	260—561
2,765,617	10/56	Gluesenkamp et al.	60—35.4
2,901,886	9/59	Doerner	60—35.4
2,926,750	3/60	Nelson	60—35.4

OTHER REFERENCES

Audrieth et al.: "Chemistry of Hydrazine," published by John Wiley and Sons, Inc., New York; note pp. 175–177 and 219–223.

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