United States Patent Office

3,031,839
Patented May 1, 1962

3,031,839
ROCKET PROPELLANTS

Olaf E. Larson, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

No Drawing. Filed Sept. 4, 1958, Ser. No. 759,102
21 Claims. (Cl. 60—35.4)

This invention relates to rocket propellants. In one aspect this invention relates to the addition of small amounts of organic amine salts to a nitric acid oxidizer to enhance rocket motor performance characteristics when said nitric acid is used as the oxidizer with a normally liquid hydrocarbon fuel in a rocket motor. In another aspect this invention relates to a stabilized nitric acid.

Rocket motors are operated by burning a mixture of fuel and oxidant in combustion chamber and causing the resulting gases to be expelled through a nozzle at high velocity. Liquid propellants are frequently preferred over solid propellants where it is necessary to vary thrust during flight. Liquid propellants can be classified as bipropellants and as monopropellants and the latter are either a single compound or mixtures of compounds. The principal elements of a rocket motor utilizing a liquid fuel comprise a combustion chamber, exhaust nozzle, an injection system, and propellant control valves. The propellent gases are produced in the combustion chamber at pressures governed by the chemical characteristics of the propellant, its rate of combustion, and the cross-sectional area of the nozzle throat. The gases are ejected into the atmosphere through the nozzle with supersonic velocity. The function of the nozzle is to convert the pressure of the propellent gases into kinetic energy. The reaction of the discharge of the propellent gases constitutes the thrust developed by the rocket motor.

The present invention relates to utilizing a liquid bipropellant system in a rocket motor. In the operation of rocket motors utilizing this system of propellants, it is usually desirable to inject the oxidizer component and the fuel component into the combustion chamber of the rocket motor as separate streams. If the fuel component is a hypergolic fuel, it is necessary that said fuel component and said oxidizer component be introduced as separate streams so that the initial contact occurs in the combustion chamber because spontaneous ignition occurs upon said initial contact. If, however, the fuel component is a non-hypergolic fuel, the oxidizer component and the fuel component can be mixed immediately prior to introduction into the combustion chamber and the introduced mixture, which is introduced as a single stream, can be ignited by any suitable ignition means, such as an electrical igniter.

A number of problems have been encountered in the development of liquid bipropellant rocket motors using hydrocarbon fuels and nitric acid oxidizers. Rapid and smooth ignition and stable combustion are two major problem areas related to the physical and chemical compositions of the reactants. Most hydrocarbons, and hydrocarbon blends such as the JP-type fuels, are non-hypergolic with nitric acid oxidizers and require an independent source of energy for ignition. Both low frequency and high frequency combustion oscillations in the combustion chamber, such as those referred to as chugging and screaming respectively, and which may result in unstable operation of the rocket motor, or even flame out, are forms of combustion instability that are effected by fuel type.

When a nitric acid oxidizer and a liquid hydrocarbon are mixed, certain precursor reactions take place with the evolution of considerable thermal energy during the initial exothermic reactions which occur upon mixing. It has been found that a correlation exists between the amount of thermal energy released when a liquid hydrocarbon is mixed with a nitric acid oxidizer and the operation of the rocket motor when said fuel is burned therein. It has been found that the greater the amount of total thermal energy released, the more suitable the fuel is as a fuel for a rocket motor, i.e., more rapid and smooth ignition, and more stable combustion will occur in the combustion chamber of the rocket motor. The amount of thermal energy released upon mixing of a liquid hydrocarbon fuel and a nitric acid oxidizer can be determined by measuring the amount of temperature increase which occurs when said fuel is added to said oxidizer. It has been found that the rate-of-temperature rise is related to the ease of ignition of the fuel and oxidizer mixture and the over-all burning process, and the total amount of energy produced is related to the over-all combustion stability. The slope of the temperature increase vs. time curve will give the rate-of-temperature rise. The above two effects are combined wherein the area under said temperature increase vs. time curve during the first second of operation is obtained. In many instances the rate-of-temperature rise alone can be used to give an indication of the suitability of a hydrocarbon fuel.

In accordance with the invention it has been found that the performance characteristics of nitric acid as an oxidizer for liquid hydrocarbon fuels can be enhanced by incorporating in said acid an amine salt, e.g., an amine nitrate, an amine perchlorate, or an amine picrate. Increasing said performance characteristics of nitric acid also increases the performance characteristics of the rocket motor where said fuel is used. Said amine salts increase the amount of thermal energy released when the liquid hydrocarbon fuel is mixed with the nitric acid oxidizer as is shown by an increase in the rate of temperature rise when said fuel and said oxidizer are mixed.

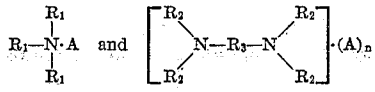
It has also been found that said amine salts, when incorporated in nitric acid in amounts of 0.1 to 10 weight percent, preferably in amounts within the range of 1 to 5 weight percent, increase the stability of the nitric acid oxidizers in storage. Nitric acids, and particularly concentrated nitric acids, decompose during storage with evolution of gases. If the acid is stored in a closed vessel, the pressure in the vessel can increase. To avoid rupture of the vessel it must be designed to withstand said pressure increases. This results in considerable inconvenience in the handling, storage, and shipping of said acids. Furthermore, the evolution of the gases will frequently render a pure anhydrous nitric acid unsuitable for certain purposes. The acid compositions of the invention, comprising nitric acid having the amine salts herein described incorporated therein, have an increased stability. The evolution of said gases during storage is decreased so that when the stabilized acid is stored in a closed container the pressure is maintained at a lower

value than when the acid does not contain the amine salt.

Thus, broadly speaking, the present invention resides in a stabilized nitric acid containing at least one of the amine salts of the invention, i.e., an amine nitrate, an amine perchlorate, or an amine picrate, dissolved therein, and the use of said stabilized acid as an oxidizer component in a nitric acid-liquid hydrocarbon bipropellant system.

An object of this invention is to provide an improved liquid bipropellant system for use in rocket motors. Another object of this invention is to provide an improved method for the operation of rocket motors utilizing a liquid bipropellant system. Still another object of this invention is to enhance the performance characteristics of nitric acid when used as an oxidizer for a liquid hydrocarbon fuel in a liquid bipropellant system. Another object of this invention is to provide a stabilized nitric acid. Other aspects, objects, and advantages of the invention will be apparent to those skilled in the art in view of this disclosure.

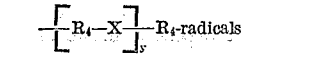
Suitable amine salts for use in the practice of the invention include those selected from the group consisting of piperidine nitrate, piperidine perchlorate, piperidine picrate, pyridine nitrate, pyridine perchlorate, pyridine picrate, 2-methylpyridine nitrate, 2-methylpyridine perchlorate, 2-methylpyridine picrate, and amine salts characterized by a formula selected from the group consisting of



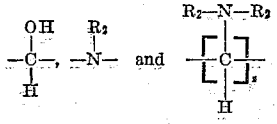
wherein: A is selected from the group consisting of nitric acid, perchloric acid, and picric acid molecules, and n is an integer of from 1 to 5; each R_1 and each R_2 is selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals containing from 1 to 8 carbon atoms, and hydrogen, at least one R_1 being one of said hydrocarbon radicals; and R_3 is selected from the group consisting of

(*a*) alkylene, alkenylene, and alkynylene hydrocarbon radicals containing from 2 to 8 carbon atoms wherein the carbon atoms attached to the nitrogen atoms are attached to adjoining carbon atoms by single valence bonds, and

(*b*)



wherein each R_4 is an alkylene radical containing from 2 to 4 carbon atoms, and X is selected from the group consisting of oxygen, sulfur, and



radicals wherein R_2 is as defined above, y is an integer of from 1 to 3, and z is an integer of from 1 to 3;

the total number of carbon atoms in the molecule does not exceed 40; and the total number of amino nitrogen atoms in the molecule does not exceed 5.

Examples of amine salts which can be used in the practice of the invention include, among others, the following:

Methylamine nitrate
Dimethylamine nitrate
Trimethylamine nitrate
Ethylamine nitrate
Diethylamine nitrate
Triethylamine nitrate
Propylamine nitrate
Dipropylamine nitrate
Tripropylamine nitrate
Isopropylamine nitrate
Tertiary butylamine nitrate
Isobutylamine nitrate
Cyclopentylamine nitrate
Cyclohexylamine nitrate
Cyclooctylamine nitrate
Dicyclohexylamine nitrate
Tricyclohexylamine nitrate
4-cyclohexenylamine nitrate
Phenylamine nitrate
Diphenylamine nitrate
Tri-n-butylamine nitrate
N,N-di-n-octyl-p-tolylamine nitrate
o-Methylbenzylamine nitrate
N,N,N',N'-tetramethylethane-1,2-diamine dinitrate
N,N,N',N'-tetraethylethane-1,2-diamine dinitrate
N,N,N',N'-tetra-n-octylethane-1,2-diamine dinitrate
N,N,N',N'-tetramethylpropane-1,2-diamine dinitrate
N,N,N',N'-tetramethylpropane-1,3-diamine dinitrate
N,N,N',N'-tetraethylpropane-1,3-diamine dinitrate
N,N,N',N'-tetrabutylpropane-1,3-diamine dinitrate
N,N,N',N'-tetrahexylpropane-1,3-diamine dinitrate
N,N,N',N'-tetramethylbutane-1,4-diamine dinitrate
N,N,N',N'-tetracyclohexylbutane-1,4-diamine dinitrate
N,N,N',N'-tetraphenylbutane-1,4-diamine dinitrate
N,N,N',N'-tetraphenyl-n-4-octene-1,3-diamine dinitrate
N,N,N',N'-tetracyclohexylhexane-2,6-diamine dinitrate
N,N,N',N'-tetramethyl-2-butene-1,4-diamine dinitrate
N,N,N',N'-tetramethyl-2-butyne-1,4-diamine dinitrate
N,N,N',N'-tetramethyl-2-octene-4,8-diamine dinitrate
N-phenyl-N'-n-octaylethane-1,2-diamine dinitrate
N,N,N',N'-tetra-n-octyloctane-1,2-diamine dinitrate
N,N'-di(2-ethylhexyl) 2-butene-1,4-diamine dinitrate
N,N,N',N'-tetraethyl-4-octyne-1,8-diamine dinitrate
Bis-(N,N-dimethylaminoethyl)ether dinitrate
Bis-(N,N-di-n-octylamino-n-butyl)ether dinitrate
N-cyclohexylaminopropyl N'-phenylaminopropyl ether dinitrate
N-2-ethylphenylaminoethyl amino-n-butyl ether dinitrate
Bis(amino-n-butyl)ether dinitrate
Bis(N,N-di-2-ethylcyclohexylamino-n-butyl)thioether dinitrate
Bis(aminoethyl)thioether dinitrate
Bis(N,N-dimethylaminoethyl)thioether dinitrate
N,N,N',N'-tetramethyl-1,3-diamine-2-propanol dinitrate
N,N,N',N'-tetraethyl-1,9-diamino-5-nonanol dinitrate
N,N',N'-tri-(2-ethylcyclohexyl)-1,4-diamino-2-butanol dinitrate
N,N,N',N',N''-pentamethyldiethylenetriamine trinitrate
N,N',N''-tricyclohexyldiethylenetriamine dinitrate
N,N,N'-tri-n-octyldiethylenetriamine trinitrate
N,N,N',N',N'',N''-hexamethylpropane-1,2,3-triamine trinitrate
$N_1,N_1,N_2,N_2,N_3,N_3,N_4,N_4,N_5,N_5$-decamethylpentane-1,2,3,4,5-pentamine pentanitrate
N_1,N_2,N_3,N_4,N_5-pentaethyltetraethylenepentamine pentanitrate
N-ethyl-2-butynylamine nitrate
N-methyl-2-butynylamine perchlorate
Di(2-butynyl)amine nitrate
N-hexyl-2-propynylamine nitrate
N-propyl-3-hexynylamine perchlorate

The majority of the above given examples are amine nitrates. It is to be understood that the corresponding amine perchlorates and amine picrates are also included as examples of compounds which can be used in the practice of the invention. Likewise, where the amine perchlorate or the amine picrate has been given as an example, the corresponding amine nitrate is also included.

The preferred compounds are the salts of primary, secondary, and tertiary mono-amines and tertiary diamines. For these preferred compounds the preferred hydrocarbon R_1 groups are alkyl groups having 1 to 6, inclusive, carbon atoms. For the tertiary diamines, the

preferred R_2 groups are alkylene groups having 3 to 6 carbon atoms. These preferred compounds generally have a greater stability in the acid solution. Presently more preferred amine salts for use in the practice of the invention include the following:

Piperidine nitrate
Pyridine nitrate
Pyridine perchlorate
Tri-n-butylamine picrate
N,N,N',N'-tetramethylethane-1,2-diamine dinitrate
N,N,N',N'-tetramethylpropane-1,2-diamine dinitrate
N,N,N',N'-tetramethylpropane-1,3-diamine dinitrate
N,N,N',N'-tetramethylbutane-1,3-diamine dinitrate
N,N,N',N'-tetramethyl hexane-1,6-diamine diperchlorate
Methylamine perchlorate
Methylamine nitrate
Dimethylamine nitrate
Dimethylamine perchlorate
Triethylamine nitrate
Triethylamine perchlorate
Triethylamine picrate
Trihexylamine nitrate

When the amine salts of the invention are used to enhance the oxidizer characteristics of nitric acid, said salts are dissolved in said acid in an amount in the range of 0.5 to 10 weight percent, preferably 1 to 5 weight percent.

Since water tends to retard combustion of the acid with the liquid hydrocarbon fuel, the nitric acid used in a propellant system is preferably substantially free of water. Thus, the presently most preferred oxidizer is anhydrous nitric acid. However, other more dilute nitric acids can be used in the practice of the invention. White fuming nitric acids and red fuming nitric acids of varying concentrations are available commercially, and all are useful in the practice of this invention. White fuming nitric acid usually contains about 90 to 99 weight percent HNO_3, from 0 to 2 weight percent NO_2, and up to about 10 weight percent water. Red fuming nitric acid usually contains about 70 to 90 weight percent HNO_3, from 2 to 25 weight percent NO_2, and up to about 10 weight percent water. Of course, mixtures of the above-described acids can be employed to give an acid having any intermediate composition, and all are useful as oxidizers in the practice of this invention. Thus, it has been found that nitric acids of all types containing at least about 70 weight percent HNO_3 are useful as oxidizers in the practice of this invention.

While the above-described nitric acids are useful in the practice of the invention as oxidizers, the class of nitric acids which can be stabilized according to the invention is much broader. It is within the scope of the invention to stabilize any nitric acid according to the practice of the invention. Thus nitric acid containing as little as 1 weight percent of HNO_3 can be effectively stabilized according to the invention. However, the stabilizing aspect of the invention finds its greatest utility in stabilizing the above-described concentrated nitric acids. For this reason, in a preferred embodiment of the invention, the acid stabilizing aspect of the invention is applied to said above-described concentrated nitric acids.

In the bipropellants used in the practice of the invention, the ratio of the liquid hydrocarbon fuel component to the nitric acid oxidizer component is preferably near stoichiometric. Said ratio can be in the range of 0.75 to 1.25 times that of the stoichiometric amount. The stoichiometric amount of oxidizer is defined as the amount required to obtain complete combustion to nitrogen, carbon dioxide, and water. In computing said stoichiometric amount of oxidizer, consideration is given to the amine salts which are dissolved in the nitric acid. Thus, the stoichiometric amount of oxidizer includes the amount necessary to oxidize said amine salts as well as the amount necessary to oxidize the fuel with which the nitric acid is mixed in the combustion chamber of the rocket motor. A slightly fuel-rich mixture is usually required to give an optimum rocket motor performance.

Amine nitrates can be prepared by several methods. One method is to react an amine with nitric acid. Another method which can be employed is to form a salt of the amine, such as a hydrochloride or an acetate, and then react said amine salt with nitric acid. Further details regarding the preparation of amine nitrates are given in Example I below.

The amine perchlorates which are employed in the practice of the invention can be prepared by reacting perchloric acid with an amine by charging the perchloric acid into the amine. The reaction should be carried out at a temperature below 20° C. The perchloric acid which is employed in this preferred method of preparation can be of a concentration of from 20 percent by weight (aqueous solution) up to concentrated perchloric acid. If concentrated perchloric acid is employed, it is preferred to utilize temperatures below —20° C. If desired, diluents can be employed to dilute the amine compound, but the diluent must be inert to perchloric acid under the reaction conditions. Other methods for preparing the amine perchlorates can be employed if desired. For example, other salts of the amines, hydrochlorides for example, can be prepared and subsequently reacted with a perchlorate such as sodium perchlorate. The amine perchlorates can thus be prepared by a displacement reaction.

The amine picrates useful in the practice of the invention can be prepared by reacting a suitable amine with picric acid. A saturated solution of picric acid in methanol is conveniently employed, and the reaction temperature is maintained below about 20° C. by cooling the reaction mixture in an ice bath. Control of the reaction temperature is facilitated by diluting the amine with methanol or other suitable solvent inert to the acid under the reaction conditions.

It is also known that the amine salts can be prepared from the amines or other amine salts by ion exchange processes. For example, a solution of the amine in suitable solvent can be contacted with an ion exchange resin which has been previously regenerated by washing with the acid or a solution of the acid corresponding to the salt which it is desired to prepare.

The following examples will serve to further illustrate the invention.

EXAMPLE I

A number of runs were made in which polyamine compounds were reacted with nitric acid to form the corresponding amine nitrates. These runs were carried out according to the following procedure.

An amount of the pure polyamine compound was charged to a flask, after which an amount of aqueous nitric acid was charged slowly to said flask by means of a dropping funnel. The temperature of the flask contents was maintained within the range of from 0 to 10° C. by means of an ice bath and by adjusting the rate of addition of the nitric acid to keep the temperature of the reaction mass below 10° C. During the addition of the nitric acid, the flask contents were stirred vigorously. After the nitric acid has been charged, the flask contents were stirred for several minutes to insure complete reaction, after which said flask contents were poured into approximately 5 times its volume of chilled acetone (—10 to —25° C.). The amine nitrate precipitated out. This precipitate was recovered by filtration, washed with cold acetone or ether, and dried in a vacuum desiccator at room temperature. The melting point and stability of the amine nitrate were then determined. None of the amine nitrates which were prepared were found to be shock sensitive to the blow of a hammer. The results of these runs are given below in Table I.

Table I

Run No.	Amine Charged	Mols Nitric Acid Charged	Percent Aqueous Acid (Wt. Percent HNO_3)	Mols Amine Charged	Yield of Amine Nitrate, Percent	M.P. of Amine Nitrate, °C
1	N,N,N',N'-tetramethylethane-1,2-diamine	0.606	40.5	0.275	96.3	220–221
2	N,N,N',N'-tetramethylpropane-1,2-diamine	0.606	33.4	0.275	92.3	177–179
3	N,N,N',N'-tetramethylbutane-1,3-diamine	0.606	40.5	0.275	95.0	115–116
3a	N,N,N',N'-tetramethylbutane-1,3-diamine	1.19	70.0	0.570	97.0	115–116
4	N,N,N',N' - tetramethyl-2-butyne-1,4-diamine.	0.6	41.0	0.285	96.4	145–146
5	N,N,N',N'-tetraethylethane-1,2-diamine	0.6	41.0	0.285	76.5	142–143
6	N,N,N',N'-tetramethylbutane-1,4-diamine	0.43	70.0	0.208	98.7	173–174
7	N,N,N',N'-tetramethylbutane-1,2-diamine	0.40	70.0	0.183	94.3	173–174
8	Bis(N,N-dimethylaminoethyl)ether	0.51	70.0	[1] 0.25	72.0	88–93
9	N,N,N',N'-tetramethyl-1,3-diamino-2-propanol.	0.51	70.0	0.25	85.2	120–124
10	N,N,N',N'-tetraethyl-1,3-diamino-2-propanol.	0.51	70.0	0.25	91.2	113–114
11	N,N,N',N',N''-pentamethyldiethylene triamine.	0.70	70.0	0.23	80.0	162–163
12	N,N,N',N',N'',N''-hexamethylpropane-1,2,3-triamine.	0.53	70.0	0.173	65.3	104–106
13	N,N'-dimethylethylene-1,2-diamine	0.505	60.0	0.5	[2]	125
14	N,N,N',N' - tetramethyl-2-butene-1,4-diamine.	0.44	70.0	0.21	88.8	179–180
15	N,N,N',N'-tetraethylpropane-1,3-diamine	0.42	70.0	0.2	97.0	157.5–159.5

[1] In this run, the amine was dissolved in an equal volume of acetone.
[2] Not recorded.

EXAMPLE II

A number of runs in which two volumes of red fuming nitric acid having 4.0 weight percent of a candidate amine salt dissolved therein were placed at ambient temperature into an enclosed mixing chamber equipped with a stirrer which extended into the acid. A thermocouple, connected through an amplifier to a temperature recorder, also extended into said acid. After said acid had been placed in the mixing chamber, the amplifier and recorder were turned on and the stirrer was started. One volume of a JP–4 liquid hydrocarbon jet fuel was then added to said acid. The increase in temperature of the mixture in said mixing chamber for each run was plotted against reaction time in seconds.

As indicated above, the rate of temperature rise is related to ease of ignition and overall burning process, and the total amount of energy produced is related to combustion stability. These two effects are combined when the area under a curve obtained by plotting amount of temperature increase vs. time. Therefore, in these runs, the area under the curve for a time of one second duration was determined.

The red fuming nitric acid employed in these tests contained 77 weight percent HNO_3, 21 weight percent NO_2, and 2 weight percent water. The JP–4 liquid hydrocarbon jet fuel used in these tests had the physical properties listed in Table II below. The results of the above-described runs are given in Table III below and compared with the average value of control runs wherein no additive was present in the acid mixed with the fuel.

Table II

A TYPICAL JP–4 JET FUEL

Distillation, F.:	
Initial B.P	162
5% evaporated	218
10%	240
20%	266
30%	290
40%	312
50%	331
60%	358
70%	381
80%	408
90%	443
95%	468
End point	500
Residue, vol. percent	1.0
Loss, vol. percent	0.0
Existent gum, mg./100 ml	1.7
Potential gum, mg./100 ml	1.8
Freezing point, F	−70
Reid vapor press., p.s.i	1.8
Density, gr./cc. at 20 C	0.7720
Sulfur, total, wt. percent	0.109
L. heat of comb., B.t.u./lb	18,651 (est.)
Aniline point, F	128.5
Aromatics, vol. percent	13.2
Bromine No	1.1
Smoke point, mm	24.5
Smoke volatility index	56.8

Table III

MIXING OF ACID AND JP–4 FUEL—EFFECT OF ADDITIVES IN ACID ON THERMAL ENERGY RELEASED

Run No.	Additive	Conc. in Acid Wt. Percent	Area Under Curve	Percent Increase Over Run No. 1
1	None (neat acid+neat fuel).	0.0	10.0	
2	N,N,N',N -tetramethylethane-1,2-diamine dinitrate.	4.0	12.2	21.5
3	N,N,N',N'-tetramethylpropane-1,2-diamine dinitrate.	4.0	11.2	11.6
4	N,N,N',N'-tetramethylpropane-1,3-diamine dinitrate.	4.0	14.6	45.4
5	N,N,N',N'-tetramethylbutane-1,3-diamine dinitrate.	4.0	11.4	13.5
6	Tri-n-butylamine picrate	4.0	20.5	104.0

The above results show that all of the candidate amine salts enhanced the performance characteristics of the nitric acid as an oxidizer for the JP–4 fuel. In all instances the amount of thermal energy was increased when an additive was present, as compared to run No. 1 when no additive was present.

As mentioned above, the amine salts used in the practice of the invention have been found to increase the stability of nitric acid during storage. This effect is demonstrated by the runs described below.

EXAMPLE III

A first sample of pure anhydrous nitric acid (containing more than 99.8 weight percent HNO_3) was placed in a glass tube constructed from ¼ inch I.D. glass pipe so that said tube was about two-thirds full. A second sample of said nitric acid containing 1.0 weight percent of tri-

ethylamine nitrate dissolved therein was placed in a second glass tube so that said second tube was about two-thirds full. A third sample of said acid containing 1.0 weight percent of triethylamine perchlorate dissolved therein was placed in a third glass tube so that said third tube was about two-thirds full. Each of said tubes was equipped with a blow-out disc which would rupture at a pressure of 200 pounds per square inch gauge. Each of said tubes was connected to a pressure recording system and then pressured to about 75 pounds per square inch gauge with nitrogen to determine if leaks were present in the systems. After ascertaining that there were no leaks in the systems, the pressure in each tube was then decreased to about 20 p.s.i.g. at room temperature (20–25° C.). The temperature of said tubes and their contents was then increased to 200° F. by placing said tubes in a constant temperature bath. Approximately 30 minutes was required for said tubes and contents to reach a temperature of 200° F. and the time at which the contents of the tube reached 200° F. was noted as the start of the run. The run was terminated for each tube when the pressure therein exceeded 100 pounds per square inch gauge or when the blow-out disc was ruptured since the pressure rise is often rapid after a pressure of 100 pounds per square inch gauge is reached. The storage life of the sample was recorded as the time taken for the pressure to increase from 20 to 100 pounds per square inch gauge at a temperature of 200° F. The results of these runs are given in Table IV below.

Table IV

STORAGE STABILITY RUNS

Run No.	Additive in Acid	Concentration of Additive, Wt. Percent	Storage Life, Hours
1	None	0.0	28
2	Triethylamine nitrate	1.0	>72
3	Triethylamine perchlorate	1.0	>432

EXAMPLE IV

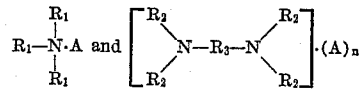
When two volumes of the nitric acid of Example II containing 4.0 weight percent of the triethylamine perchlorate tested in Example III above is added to one volume of the JP–4 liquid hydrocarbon fuel described in Table II, in the same manner as described in Example II, the increase in the net area under the curve over the area under the curve for the JP–4 fuel alone (run No. 1, Table III) is at least 11.6 percent.

While the JP–4 jet fuel described in Table II above is one of the presently preferred liquid hydrocarbon fuels for use in the practice of the invention, it is to be understood that other normally liquid hydrocarbon fuels can be so used. Thus, other hydrocarbon jet fuels can also be used. Suitable normally liquid hydrocarbons which can be used in the practice of the invention include paraffin, cycloparaffin, and aromatic hydrocarbons in the C–5 to C–30 range or mixtures thereof. Examples of such hydrocarbon fuels are normal pentane, normal hexane, normal heptane, benzene, kerosene, isooctane, 2,3-dimethylbutane, diisobutylene, cyclohexene, cyclohexane, isodecane, methylcyclohexane, toluene, hexadecane, eicosane, hexacosane, pentatricontane, gasoline, naphthas, and the like. Hydrocarbons in the C–5 to C–16 range are preferred.

Since variations and modifications of the invention can be made by those skilled in the art without departing from the scope or spirit of said invention, it is to be understood that all matter herein set forth in the above discussion is merely illustrative and does not unduly limit the invention.

I claim:

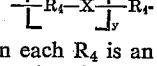
1. In the method for developing thrust by the combustion of bipropellant components in a combustion chamber of a reaction motor, wherein: an oxidizer component and a liquid hydrocarbon fuel component are injected into a combustion chamber of said motor, a mixture of said components is ignited and burned in said chamber to form products of combustion which are exhausted from said motor; the ratio of said oxidizer component to said fuel component is within the range of 0.75 to 1.25 times the stoichiometric ratio; and said oxidizer component comprises a nitric acid containing at least about 70 weight percent HNO_3; the improvement of incorporating in said nitric acid, from 0.5 to 10 weight percent of an amine salt selected from the group consisting of piperidine nitrate, piperidine perchlorate, piperidine picrate, pyridine nitrate, pyridine perchlorate, pyridine picrate, 2-methylpyridine nitrate, 2-methylpyridine perchlorate, 2-methylpyridine picrate, and amine salts characterized by a formula selected from the group consisting of



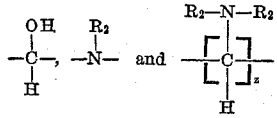
wherein: A is selected from the group consisting of nitric acid, perchloric acid, and picric acid molecules, and n is an integer of from 1 to 5; each R_1 and each R_2 is selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals containing from 1 to 8 carbon atoms, and hydrogen, at least one R_1 being one of said hydrocarbon radicals; and R_3 is selected from the group consisting of

(*a*) alkylene, alkenylene, and alkynylene hydrocarbon radicals containing from 2 to 8 carbon atoms wherein the carbon atoms attached to the nitrogen atoms are attached to adjoining carbon atoms by single valence bonds, and

(*b*)



radicals wherein each R_4 is an alkylene radical containing from 2 to 4 carbon atoms, and X is selected from the group consisting of oxygen, sulfur, and



radicals wherein R_2 is as defined above, y is an integer of from 1 to 3, and z is an integer of from 1 to 3;

the total number of carbon atoms in the molecule does not exceed 40; and the total number of amino nitrogen atoms in the molecule does not exceed 5.

2. The method of claim 1 wherein said amine salt is tri-n-butylamine picrate.

3. The method of claim 1 wherein said amine salt is N,N,N′,N′ tetramethylethane-1,2-diamine dinitrate.

4. The method of claim 1 wherein said amine salt is N,N,N′,N′ tetramethylpropane-1,2-diamine dinitrate.

5. The method of claim 1 wherein said amine salt is N,N,N′,N′ tetramethylpropane-1,3-diamine dinitrate.

6. The method of claim 1 wherein said amine salt is N,N,N′,N′ tetramethylbutane-1,3-diamine dinitrate.

7. The method of claim 1 wherein said amine salt is N,N,N′,N′ tetramethylhexane-1,6-diamine diperchlorate.

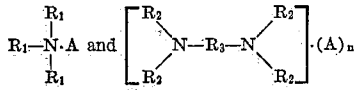
8. The method of claim 1 wherein said amine salt is triethylamine nitrate.

9. The method of claim 1 wherein said amine salt is triethylamine perchlorate.

10. The method of claim 1 wherein said amine salt is triethylamine picrate.

11. An oxidizer composition comprising between 99.9 and 90 weight percent of nitric acid and between 0.1 to 10 weight percent of an amine salt selected from the group consisting of piperidine picrate, pyridine picrate, 2-

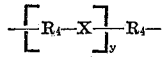
methylpyridine picrate, and amine salts characterized by a formula selected from the group consisting of



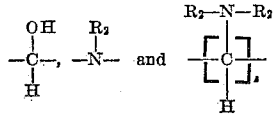
wherein: A is a picric acid molecule, and n is an integer of from 1 to 5; each R_1 and each R_2 is selected from the group consisting of acyclic, alicyclic, and aromatic hydrocarbon radicals containing from 1 to 8 carbon atoms, and hydrogen, at least one R_1 being one of said hydrocarbon radicals; and R_3 is selected from the group consisting of

(*a*) alkylene, alkenylene, and alkynylene hydrocarbon radicals containing from 2 to 8 carbon atoms wherein the carbon atoms attached to the nitrogen atoms are attached to adjoining carbon atoms by single valence bonds, and

(*b*)



radicals wherein each R_4 is an alkylene radical containing from 2 to 4 carbon atoms, and X is selected from the group consisting of oxygen, sulfur,
and



radicals wherein R_2 is as defined above, y is an integer of from 1 to 3, and z is an integer of from 1 to 3;

the total number of carbon atoms in the molecule does not exceed 40; and the total number of amino nitrogen atoms in the molecule does not exceed 5.

12. The composition of claim 11 wherein said amine salt is tri-n-butylamine picrate.

13. The composition of claim 11 wherein said amine salt is N,N,N'N' tetramethylethane-1,2-diamine dipicrate.

14. The composition of claim 11 wherein said amine salt is N,N,N',N' tetramethylpropane-1,2-diamine dipicrate.

15. The composition of claim 11 wherein said amine salt is N,N,N',N' tetramethylpropane-1,3-diamine dipicrate.

16. The composition of claim 11 wherein said amine salt is N,N,N',N' tetramethylbutane-1,3-diamine dipicrate.

17. The composition of claim 11 wherein said amine salt is N,N,N',N' tetramethylhexane-1,6-diamine dipicrate.

18. The composition of claim 11 wherein said amine salt is triethylamine picrate.

19. The composition of claim 11 wherein said amine salt is pyridine picrate.

20. The method of claim 1 wherein the amount of said amine salt incorporated in said nitric acid is an amount within the range of from 1 to 5 weight percent.

21. The oxidizer composition of claim 11 wherein said nitric acid is present in an amount within the range of from 99 to 95 weight percent and said amine salt is present in an amount within the range of from 1 to 5 weight percent.

No references cited.