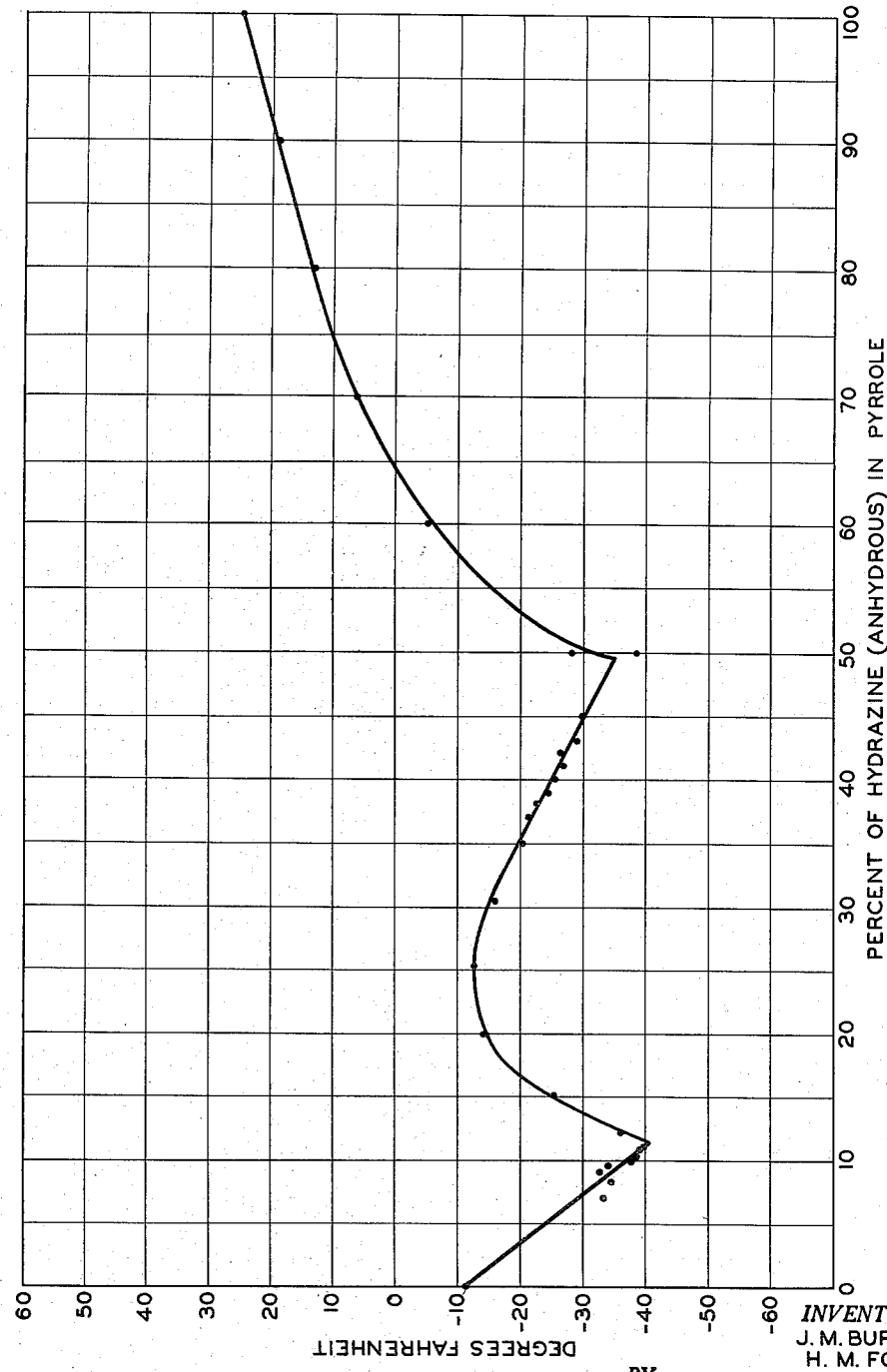
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REACTION MOTOR FUEL

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REACTION MOTOR FUEL

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This invention relates to reaction motor fuels. In one aspect this invention relates to rocket propellants. In another aspect this invention relates to hypergolic fuel. In another aspect, this invention relates to the application of hypergolic fuels to the propulsion of rockets. In another aspect this invention relates to fast-burning fuels.

This application is a continuation-in-part of our copending application, Serial No. 400,441, filed December 28, 1953, now abandoned.

Our invention is concerned with new and novel reaction motor fuels and their utilization. A rocket, or jet propulsion device, is defined herein as a rigid container for matter and energy, so arranged that a portion of the matter can absorb energy in kinetic form and subsequently be ejected in a specified direction. One type of reaction motor to which our invention is applied is that type of jet propulsion device designated as a "pure" rocket, i.e., a thrust producer which does not make use of the surrounding atmosphere. A rocket of this type is propelled by introduction of a propellant material into a combustion chamber therein, and burning it under conditions that will cause it to release energy at a high but controllable rate immediately after entering into the combustion chamber. Rocket propellants, as liquids, are advantageously utilized, inasmuch as the liquid propellant material can be carried in a light-weight, low-pressure vessel and pumped into the combustion chamber, the latter, though it must withstand high pressure and temperature, being only necessarily large enough to insure combustion. Also, the flow of liquid propellant into the combustion chamber can be regulated at will so that the thrust, continuous or an intermittent burst of power, can be sustained. The latter type of liquid propellant flow contributes to a longer life of the combustion chamber and thrust nozzle.

Various liquids and liquid combinations have been found useful as rocket propellants. Some propellants consist of a single material, and are termed "monopropellants." Those propellants involving two materials are termed "bipropellants" and normally consist of an oxidizer and a fuel. Hydrogen peroxide and nitromethane are each well known monopropellants. Well known bipropellants include hydrogen peroxide or liquid oxygen as the oxidant with a fuel component such as ethyl alcohol-water, ammonia, hydrazine, or hydrogen; and nitric acid as the oxidizer with aniline or a furfuryl alcohol as the hypergolic fuel component. Other materials which can be used in bipropellants include the heterocyclic nitrogen-containing compounds such as pyrrole, N-alkyl pyrrole, and alkyl derivatives of said heterocyclic nitrogen-containing compounds.

When employing 90 to 100 percent or more nitric acid, i.e., "white fuming nitric acid," as the oxidizer in a rocket propellant, it is often necessary, dependent on the specific fuel component, to make ignition more prompt by dissolving from 6 to 14 percent by weight of nitrogen dioxide in the white fuming nitric acid, forming thereby "red fuming" nitric acid. A fuel component of one type of bipropellant material described herein, is spontaneously ignited upon contacting the oxidizer, and for that reason, is referred to herein as being a "hypergolic" fuel. A ratio of oxidizer to hypergolic fuel, based on stoichiometric amounts, can be utilized within the

limits of 0.5:1 to 1.5:1, if desired, the efficiency of the combustion being less at ratios below 1:1 and the use of the oxidizer being less economical at ratios above 1:1. However, tactical consideration may necessitate the use of higher ranges, even as high as 6:1.

Other types of reaction motors in which the fuels of the invention can be utilized are the jet engines, i.e., ram jets, turbo-jets and pulse jets. The working cycle of the ram jet and the turbo-jet is essentially the same. One distinct difference in operation, however, is apparent in the compression step. Air is jammed into the combustion zone of the turbo-jet by a gas turbine. Compression in a ram jet engine is provided by the ramming effect of the oncoming air. Compression in the pulse jet engine is obtained by the ramming effect of the oncoming air and by the intermittent explosion of fuel which causes the closure of valves upstream of the combustion zone to prevent the escape of gases through the upstream end of the engine.

Fuel which is injected into the combustion zone of the above-designated jet engines may originally be ignited therein by a spark producing device, such as a conventional spark plug mounted in the wall of the combustion chamber. Additional fuel is thereafter ignited by the flame of burning fuel or by the heat from hot combustion gases remaining in the combustion zone or hot combustion chamber wall. The air and exhaust gases within the combustion zone are heated by the heat of combustion and are exhausted from the combustion zone through a rearwardly extending exhaust conduit at an exit velocity higher than the flying speed of the engine. The thrust produced thereby equals the gas mass flowing through the exhaust duct times its increase in speed, according to the law of momentum.

Various organic compounds, and especially certain non-hydrocarbons, are unstable in storage or in use, while being transferred, or during treatment, and form undesirable gums, undergo discoloration, become rancid or otherwise deteriorate due to oxidation, polymerization, or other undesired reactions. Included among the organic non-hydrocarbon compounds which undergo such deterioration are the heterocyclic nitrogen-containing compounds containing one nitrogen atom and four carbon atoms in the ring. Various inhibitors have been employed in the past to treat organic compounds in order to secure satisfactory stability. Although a large number of inhibitors have either been proposed or used, there is a constant search for new and improved inhibitors.

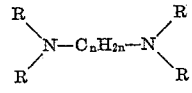
One important use of said heterocyclic nitrogen-containing compounds is as a reaction motor fuel. The problem of protecting such materials from deterioration during separation, manufacture, blending, storage, and use is important; and in many instances is essential for successful utilization of these compounds. In recent years the degradation of fuels for use in reaction motors has become prominent. The presence of gummy materials in the fuel interferes with the normal operation of the fuel system and injectors in reaction motors, thus lowering the efficiency of the motor. Heterocyclic nitrogen-containing compounds having one nitrogen atom and four carbon atoms in the ring utilized for purposes other than reaction motor fuels likewise require protection from deterioration during storage or use.

The following objects of this invention will be attained by at least one of the aspects of the invention.

An object of this invention is to provide new rocket propellants. Another object of the invention is to provide an improved hypergolic fuel. Another object of the invention is to provide a method for imparting immediate thrust to a rocket. Another object of the inven-

tion is to provide a rocket propellant having a freezing point suitable to make such propellant useful at low temperatures. Another object of this invention is to provide a method for stabilizing heterocyclic nitrogen-containing compounds having one nitrogen atom and four carbon atoms in the ring. Another object of this invention is to prevent formation of gum and undesirable color in said heterocyclic nitrogen-containing compounds during shipment or storage. Another object of this invention is to provide stabilizing agents for said heterocyclic nitrogen-containing compounds. Other aspects, objects and advantages of the invention will be apparent to those skilled in the art upon study of this disclosure and the drawing.

According to the invention, there is provided a fuel composition consisting essentially of a heterocyclic nitrogen-containing compound containing one nitrogen atom and four carbon atoms in the ring and from 0.1 to 54.6 percent by weight of a compound having the structural formula



wherein, each R is selected from the group consisting of hydrogen, alkyl, and aryl hydrocarbon radicals, and n is an integer from 0 to 6.

Further according to the invention, there is provided a method of stabilizing a heterocyclic nitrogen-containing compound containing one nitrogen atom and four carbon atoms in the ring which comprises admixing therewith a stabilizing amount of a compound having the above structural formula.

In the above formula, the various R's can be the same or different. It is preferred that n be an integer in the range of 0 to 6, more preferably in the range of 0 to 4, because such compounds are normally liquid; however, n can be larger and the compound still be effective. We have found that when R is hydrogen the stabilizing action of the compound is more effective than when R is a hydrocarbon radical; and further, that the smaller hydrocarbon radicals are preferred to the larger hydrocarbon radicals for the same reason. Therefore R preferably contains no more than 6 carbon atoms. It is preferred that at least one R be selected from the group consisting of hydrogen, methyl, ethyl, n-propyl, and isopropyl hydrocarbon groups, and the greater the number of such groups the more effective will be the stabilizing action of the compound.

Examples of compounds which can be used in the practice of the invention include, among others, hydrazine, N,N,N',N'-tetramethylhydrazine, N,N-diphenylhydrazine, ethylhydrazine, ethyl-phenylhydrazine, methyl hydrazine, isopropylhydrazine, N,N-diphenyl-N',N'-dimethylhydrazine, N,N,N',N'-tetrapropylhydrazine, N',N'-dihexyl-N,N-diethyl hydrazine, and the like; methylene diamine, ethane-1,2-diamine, propane-1,3-diamine, hexane-1,3-diamine, N,N-dimethyl ethane-1,2-diamine, N,N,N',N'-tetramethyl propane-1,3-diamine, N,N-dimethyl-N',N'-dihexyl pentane-1,5-diamine, N,N,N'-trihexyl hexane-1,6-diamine, N,N'-diphenyl butane-1,4-diamine, and the like. Other compounds which are effective as stabilizing agents include N,N,N',N'-tetrapentyl octane-1,8-diamine, N,N,N',N'-tetrahexyl octane-1,8-diamine, N,N,-dioctyl heptane-1,7-diamine, tetraheptyl hydrazine and the like. Hydrazine is the preferred stabilizing agent of the invention.

The heterocyclic nitrogen-containing compounds which can be stabilized in the practice of the invention are the unsaturated heterocyclic compounds containing four carbon atoms and one nitrogen atom, and the alkyl derivatives of these heterocyclic compounds. Examples of these preferred compounds include, among others, pyrrole; N-alkyl-pyrroles such as N-methyl pyrrole, N-ethyl pyrrole, N-propyl pyrrole, N-butyl pyrrole, N-amyl pyrrole, and the like; alkyl derivatives of pyrrole such as 2-methylpyrrole, 2,5-dimethylpyrrole, 2-methyl-3-ethylpyrrole, 2,4-diethylpyrrole, and the like.

The stabilizing agents of this invention are not necessarily equivalent in their effects and it should be understood that they cannot necessarily be used to replace one another with equal effect, either on a weight or chemically equivalent basis. The quantity of stabilizing agent employed will vary, but in general will range from about 0.1 to 5 weight percent, preferably from 0.1 to 3 weight percent. Amounts of stabilizing agent in excess of 3 weight percent are generally not desirable from the standpoint of economics. This is demonstrated by the specific examples given hereinafter. The exact quantity required is a function of the stabilizing agent used and of the heterocyclic nitrogen-containing compound as well as the desired stability of the organic compound treated.

Many of the above-mentioned heterocyclic nitrogen-containing compounds are useful as solvent materials, as reagents in chemical synthesis, or as reactants or other purposes in the chemical industry. In addition, pyrrole and N-methylpyrrole, for example, are all desirable reaction motor fuels, and when stabilized against discoloration and gum formation with hydrazine, for example, are particularly suitable as a fuel for a reaction motor such as a rocket, ram-jet, etc.; especially since the performance of the fuel, which includes such factors as ignition delay, specific thrust, and burning characteristics, will also be improved. The present invention provides a simple and economical method for the stabilization of said heterocyclic nitrogen-containing compounds so that the materials can be stored for relatively long periods or shipped long distances without gum formation or discoloration in appreciable amounts.

As pointed out hereinabove, hydrazine has been known as a fuel component in a bipropellant system. The use of this material at high altitude has been accompanied by attendant disadvantages, however, for hydrazine has a freezing point of —1.5° C. (+29° F.). Obviously, unless that freezing point is lowered, use of that fuel in a rocket would be impractical.

In one broad aspect our invention comprises a fuel utilizing up to 56 percent by volume (57.6 weight percent) of hydrazine, which does not have a freezing point sufficiently low to make its use generally practical in jet engines, in at least 44 percent by volume (42.4 weight percent) of pyrrole, which has too high a freezing point to make its use generally practical in an unmodified form. A minor amount, generally between 4 and 16 percent by volume (4.2 to 16.8 weight percent), preferably 8 to 13 percent by volume (8.4 to 13.7 weight per cent), of anhydrous hydrazine in pyrrole provides the low freezing point necessary to make the use of the fuel practical over a much wider range of operating conditions. Hydrazine in an amount of about 11.5 percent by volume (12.1 weight percent) results in lowering the freezing point of pyrrole to its lowest point. Slightly lower freezing points can be attained by incorporating water in an amount up to 4 percent by volume based on the hydrazine. Between 36 and 53 percent by volume (37.5 to 54.6 weight percent), preferably 44 to 51 percent by volume (45.6 to 52.7 weight percent), of hydrazine in pyrrole also results in a material lowering of the freezing point of the resulting mixture.

Better understanding of this aspect of the invention will be apparent upon study of the drawing which is a graphic representation of the result of lowering the freezing point of the total fuel to practical limits by the addition of minor amounts of anhydrous hydrazine to a major amount of pyrrole.

Thus, in accordance with our invention, we have provided a novel bipropellant fuel which comprises pyrrole and hydrazine. The pyrrole has good rocket fuel characteristics with the exception of a freezing point which is

too high for general practical use. The freezing point of pure pyrrole is −24° C. (−11° F.). However, for general practical use as a rocket fuel, the freezing point is preferably at least as low as −35° C. (−31° F.).

We have discovered that when a minor amount of hydrazine, for example 4 to 16 percent by volume (4.2 to 16.8 weight percent), either anhydrous or containing up to 5 percent by volume of water, is added to between 84 and 96 percent by volume (83.2 to 95.8 weight percent) of pyrrole as set forth herein, the freezing point of the composite fuel is lowered to such an extent that it is suitable for practical use as a rocket propellant. The amount of pyrrole is preferably in the range of 87 to 92 percent by volume (86.3 to 91.6 weight percent) of the fuel. We have discovered that a eutectic is formed when a minor amount of hydrazine is added to pyrrole. Although the freezing point of pure pyrrole is −24° C. (−11° F.) and the freezing point of hydrazine is −1.5° C. (+29° F.), the freezing point of the eutectic is considerably lower than the freezing point of either of the component materials when those component materials are combined within a certain critical range. An additional advantage of the use of hydrazine as the minor portion of the fuel is that the performance of the eutectic of hydrazine and pyrrole, which includes such factors as ignition delay, specific thrust and burning characteristics, is enhanced.

We have further found that a second eutectic is formed and that by combining from 36 to 53 percent by volume (37.5 to 54.6 weight percent), preferably 44 to 51 percent by volume (45.6 to 52.7 weight percent), of hydrazine (anhydrous or containing up to 5 percent by volume of water) in from 47 to 64 percent by volume (45.4 to 62.4 weight percent) of pyrrole, a second lowering of the freezing point is obtained. Reference to the drawing will disclose that the addition of any amount up to 57 percent by volume (59.2 weight percent) results in at least some lowering of the freezing point of the pyrrole. In making the conversions herein of volume percent to weight percent 0.948 was employed as the density of pyrrole and 1.011 was employed as the density of hydrazine.

salts such as the chlorides and naphthenates of iron, zinc, cobalt and similar heavy materials.

The advantages of this invention are illustrated in the following examples. The reactants and their proportions are presented as being typical and are not to be construed as unduly limiting of the invention.

EXAMPLE I

Ignition delay data have been obtained on a mixture of 90 percent pyrrole and 10 percent hydrazine (containing 5 percent water, based on the hydrazine) using white fuming nitric acid as the oxidizer. Using a drop test apparatus, ignition delays of 9 and 11 milliseconds were obtained at temperatures of 75° F. and −40° F., respectively. Using an impingement type apparatus, the ignition delay was 40 milliseconds at 75° F.

EXAMPLE II

A first series of test samples of pyrrole containing various amounts ranging from 0.0 to 5.0 weight percent of hydrazine admixed therewith as a stabilizing agent was prepared. Ignition delay, refractive index, color, and steam jet gum tests were run on a portion of each sample. Said gum tests were run in accordance with ASTM method D381–54T. The remainder of each sample was placed in a clear one-half pint glass bottle. Said bottles were filled approximately three-fourths full. Said bottles, open to the atmosphere, were then stored under essentially dark storage conditions by placing the bottles in an oven maintained at approximately 140° F. for a period of 60 days. At the end of the 60 days' storage period, the above named tests were again run on the stored samples.

A second series of test samples of N-methylpyrrole containing various amounts ranging from 0.0 to 5.0 weight percent of hydrazine admixed therewith as a stabilizing agent was prepared and tested as described above.

The results of the tests on both series of samples are given in the table below. It is evident from a comparison of the data in said table that hydrazine is an effective stabilizing agent.

Table

GUM AND COLOR STORAGE STABILITY, 140° F., 60 DAYS

Fuel	Start Test					End Test			
	Weight percent Hydrazine added	Ignition Delay	R.I.	NPA Color	Steam jet gum, mg./100 ml.	Ignition Delay	R.I.	NPA Color	Steam jet gum, mg./100 ml.
Pyrrole control	0.0	42.1	1.5079	Water White.	4.4	one shot	1.5082	7+	418.8
Pyrrole+	0.5	165.1	1.5079	---do	2.8	125.5			
Pyrrole+	1.0	39.8	1.5079	---do	3.0	73.3	1.5078	2	97.0
Pyrrole+	3.0	36.0	1.5082	---do	1.8	61.8	1.5077	1	28.6
Pyrrole+	5.0	46.3	1.5081	---do	1.2	28.6	1.5079	−1	10.0
						34.3	1.5069	slight tint	9.2
Pyrrole control+	1.0							0+	
N-Methyl Pyrrole control	0.0	16.6	1.4867	1½	14.2	111.8	1.5072	7+	532.0
N-Methyl Pyrrole+	0.5	18.4	1.4867	1	11.4	21.0	1.4871	Black	471.4
N-Methyl Pyrrole+	1.0	13.6	1.4867	−1	16.2	15.9	1.4862	−1	15.2
N-Methyl Pyrrole+	3.0	7.8	1.4859	−½	9.2	15.1	1.4862	1	12.8
N-Methyl Pyrrole control+	1.0					9.6	1.4861	1	17.8
						37.2	1.4862	8	288.8

Other oxidizers are suitable as oxidants for hypergolic fuels, in addition to white or red fuming nitric acid, and can be used in the practice of our invention. Suitable oxidants include materials such as hydrogen peroxide, ozone, nitrogen tetraoxide, liquid oxygen and mixed mineral acids, especially anhydrous mixtures of nitric and sulfuric acids, such as 80–90 percent by volume white or red fuming nitric acids and 10–20 percent by volume anhydrous or fuming sulfuric acid. It is within the scope of this invention to employ, preferably dissolved in the oxidizer, ignition catalysts or oxidation catalysts. These oxidation catalysts include certain metal

EXAMPLE III

Steam jet gum tests (ASTM D381–54T) were run on another control sample of N-methylpyrrole and a sample of N-methylpyrrole containing 5 weight percent of N,N,N',N'-tetramethylpropane-1,3-diamine, which samples had been stored under the conditions described in Example II. After storage as described, the gum content of the N-methylpyrrole containing no stabilizer was 321.4 milligrams per 100 milliliters, whereas the gum content for the sample of N-methylpyrrole containing said stabilizer was only 39.8 milligrams per 100 milliliters.

We claim:

1. In the method for developing thrust by the combustion of bipropellant components in a combustion chamber of a reaction motor, the steps comprising separately and simultaneously injecting a stream of an oxidant component and a stream of a fuel component into a combustion chamber of said motor in proportions, based on stoichiometric amounts, within the range of 0.5:1 to 1.5:1, said fuel component consisting essentially of a heterocyclic nitrogen containing compound selected from the group consisting of pyrrole and N-methyl pyrrole, and a second compound selected from the group consisting of hydrazine and N,N,N',N'-tetramethyl propane-1,3-diamine; wherein: when said hydrazine is present in said fuel component it is present in an amount within the ranges of about 0.5 to 16 percent inclusive and about 36 to 53 percent inclusive; and when said diamine is present in said fuel component it is present in an amount within the range of about 0.1 to about 5 percent.

2. The method of claim 1 wherein said fuel component consists essentially of pyrrole and about 4 to about 16 percent by volume hydrazine.

3. The method of claim 1 wherein said fuel component consists essentially of pyrrole and between 36 and 53 percent by volume of hydrazine.

4. The method of claim 1 wherein said nitrogen containing compound is N-methyl pyrrole and said second compound is N,N,N',N'-tetramethyl propane-1,3-diamine.

5. In the method for developing thrust by the combustion of bipropellant components in a combustion chamber of a reaction motor, the steps comprising separately and simultaneously injecting a stream of an oxidant component and a stream of a fuel component into a combustion chamber of said motor in proportions, based on stoichiometric amounts, within the range of 0.5:1 to 1.5:1, said fuel component consisting essentially of pyrrole and from about 0.1 to about 5 percent by weight of N,N,N',N'-tetramethyl propane-1,3-diamine.

6. The method of claim 5 wherein said diamine is present in an amount within the range of about 0.1 to about 3 percent by weight.

7. In the method for developing thrust by the combustion of bipropellant components in a combustion chamber of a reaction motor, the steps comprising separately and simultaneously injecting a stream of an oxidant component and a stream of a fuel component into a combustion chamber of said motor in proportions, based on stoichiometric amounts, within the range of 0.5:1 to 1.5:1, said fuel component consisting essentially of about 11.5 percent by volume of hydrazine and about 88.5 percent by volume of pyrrole.

8. In the method for developing thrust by the combustion of bipropellant components in a combustion chamber of a reaction motor, the steps comprising separately and simultaneously injecting a stream of an oxidant component and a stream of a fuel component into a combustion chamber of said motor in proportions, based on stoichiometric amounts, within the range of 0.5:1 to 1.5:1, said fuel component consisting essentially of about 49 percent by volume of hydrazine and about 51 percent by volume of pyrrole.

9. A fuel composition consisting essentially of a heterocyclic nitrogen containing compound selected from the group consisting of pyrrole and N-methyl pyrrole, and a second compound selected from the group consisting of hydrazine and N,N,N',N'-tetramethyl propane-1,3-diamine; wherein: when said hydrazine is present in said composition it is present in an amount within the ranges of about 0.5 to about 16 percent inclusive and about 36 to about 53 percent inclusive; and when said diamine is present in said composition it is present in an amount within the range of about 0.1 to about 5 percent.

10. A fuel composition according to claim 9 wherein said nitrogen containing compound is N-methyl pyrrole and said second compound is N,N,N',N'-tetramethyl propane-1,3-diamine.

11. A fuel composition consisting essentially of pyrrole and from about 0.1 to about 5 percent by weight of N,N,N',N'-tetramethyl propane-1,3-diamine.

12. A fuel composition consisting essentially of pyrrole and 4 to 16 percent by volume hydrazine.

13. A fuel composition consisting essentially of pyrrole and 8 to 13 percent by volume hydrazine.

14. The fuel of claim 12 wherein said hydrazine is anhydrous.

15. The fuel of claim 12 wherein said hydrazine contains up to 5 percent water.

16. A fuel composition consisting essentially of pyrrole and between 36 and 53 percent by volume of hydrazine.

17. A fuel composition consisting essentially of pyrrole and between 44 and 51 percent by volume of hydrazine.

18. A fuel composition consisting essentially of about 11.5 percent by volume of hydrazine and about 88.5 percent by volume of pyrrole.

19. A fuel composition consisting essentially of about 49 percent by volume of hydrazine and about 51 percent by volume of pyrrole.

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