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HIGH ENERGY FUELS CONTAINING ETHYLENE IMINE

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This invention relates to fuels, to methods of producing them, and to methods of utilizing them; and includes fuels capable of use in conventional internal combustion engines both of the spark-ignited and diesel types, but more particularly is concerned with fuels for jet propulsion, as for example in rockets.

The need for fuels of characteristics suitable for jet propulsion has been widely high-lighted in recent years. While many fuel compositions have been suggested for such purposes, the exacting requirements in this art emphasizes the fact that the demands have not been met. Some of the important characteristics in this connection are a high energy fuel that may be easily handled without undue hazard, of relatively high density, high boiling point, low freezing point, high heat of formation, and exhibiting spontaneous combustibility in the presence of a specified amount of a hypergolic oxidant. (The term hypergolic is used in its ordinary meaning of spontaneously combustible; so that a hypergolic oxidant is one which in contact with a given fuel in proper proportions produces spontaneous combustion.) The stated properties of fuels as given above are not all consistant with one another so that a balance or compromise must be made. This has led to fuels which because of such compromise are not as satisfactory as they should be.

Among the objects of the present invention is the production of fuels of well balanced properties for use in jet propulsion.

Further objects include conventional fuels with additives which convert them into super fuels for jet propulsion use.

Still further objects include conventional fuels with additives which materially improve their characteristics for conventional use.

Still further objects include methods of utilizing such fuels.

Still further objects and advantages of the present invention will appear from the more detailed description set forth below, it being understood that such more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accordance with the present invention, fuels of novel type having unique properties are produced by utilization of ethylene imine as a component of such fuels. Generally these fuels may be designated as compositions containing ethylene imine alone or an ignitible organic liquid with an amount of ethylene imine added thereto to give the properties desired. The formula of ethylene imine is



For example, the addition of ethylene imine to certain classes of ignitible liquids results in mixtures which have useful properties as fuels for jet propulsion purposes, and, in fact, for these purposes, they are superior

to the ignitible liquids alone. The liquids referred to include materials which are conventionally used at present as fuels, or are being developed experimentally for fuel purposes, or may be considered for future use as fuels. Fuels for jet propulsion purposes include use in rocket engines, turbo jets, and all types of ducted jets.

It has been discovered that ethylene imine itself has excellent fuel characteristics and imparts to many other chemicals improved fuel characteristics when added in certain amounts. Ethylene imine is a strongly endothermic compound having a heat of formation of 21.96 kcals./mole at 25° C. It is therefore capable of giving a higher theoretical specific impulse when used as a jet propulsion fuel, than do most of the commonly used fuels. The specific impulse is a measure of the energy deliverable by the fuel and a higher specific impulse makes possible an increased range or trajectory of a vehicle driven by jet propulsion, or an increased payload, or a decreased fuel consumption.

Consequently, the addition of ethylene imine to an ignitible liquid whose theoretical specific impulse is less than that of ethylene imine results in a mixture whose theoretical specific impulse lies between that of the ignitible liquid alone and that of ethylene imine, resulting thereby in an increase in the theoretical specific impulse of the ignitible liquid, the extent of the increase depending on, and in general, being in proportion to (not necessarily linear proportion) the amount of ethylene imine contained.

When employing these mixtures as fuels any oxidizing substance in use for the combustion of fuels for jet propulsion may be used. For example, air, gaseous oxygen, liquid oxygen, nitric acid, mixed acid, hydrogen peroxide, or nitrogen tetroxide.

Although a maximum increase in specific impulse is produced by using a maximum quantity of ethylene imine, other practical considerations connected with the particular applications of the fuels often lead to preferred mixtures containing less than the maximum quantity of ethylene imine. The most important considerations are customarily cost, availability and physical properties. These considerations are balanced one against the other, and the most desirable compromise of useful characteristics chosen. The requirements depend on the specific application: For example, in some cases a freezing point of the fuel of 0° C. or lower is satisfactory, but in other cases a freezing point of —40° C. or lower is necessary. Differences in physical properties of this type are attainable by varying the relative proportions of ethylene imine in the fuels. Sometimes, in order to achieve an ideal balance of desired properties, it is preferable to use combinations of more than one ignitible liquid in addition to the ethylene imine.

Furthermore, in order to achieve a desirable balance of excellent physical properties while maintaining a comparatively high theoretical specific impulse, it is often found advisable to add certain components to the ethylene imine, which added components may or may not be ignitible. For example, water in quantities of 0.1% to 25% by weight may be added to ethylene imine or any of the compositions containing ethylene imine, in order to lower the temperature of the combustion gases and in order to increase the heat capacity of the fuel. These properties are desirable in connection with preventing burn-out of the engine or any of its parts. The increased heat capacity imparted by the addition of water is very useful for regenerative cooling of rocket engines. Thus water may be included in ammonia-ethylene imine fuels. As much as 65–66% water may be added to ethylene imine while retaining hypergolic properties. In similar fashion, hydrazine or ammonia may be added to ethylene

imine in quantities ranging from 0.1% to 99% by weight, since they also lower the combustion temperature and increase the heat capacity of the fuel. These substances can be added in greater quantity than water, because they also have high theoretical specific impulses and will not lower that of ethylene imine appreciably.

It is notable that the superior properties imparted by ethylene imine when added to other ignitible liquids consist not only in an increase of the theoretical specific impulse, but also in improved ignition and combustion characteristics. Outstanding in this respect is its ability to render other ignitible liquids spontaneously inflammable when brought into contact with certain oxidizing agents, specifically, nitric acid, nitric acid containing nitrogen tetroxide (red fuming nitric acid) and mixed acid (nitric acid plus sulfuric acid). It also has the ability to improve this property in ignitible liquids which already possess the property to some degree.

This property of spontaneous inflammability on contact with an oxidizer may be termed "hypergolic ignitibility." It is a very desirable property for many applications in rocket propulsion, since it eliminates the requirement of an external source of ignition, resulting in reduced weight and greater simplicity in design and construction of the vehicle; furthermore, in many cases it produces safer starting characteristics and smoother combustion. The oxidizers, white fuming nitric acid, red fuming nitric acid and mixed acid, with which these ethylene imine-containing compositions are hypergolic, are commonly used as rocket propellants, and may be referred to as rocket propellant oxidizers.

If it is desired to impart hypergolic properties to a fuel, or to improve the already existing hypergolic properties of a fuel, an amount of ethylene imine may be added which accomplishes the desired objective with the particular oxidizer employed and under the conditions of actual use. The quantity required depends for example on the nature of the fuel, the nature and concentration of the oxidizer, and the conditions under which it is used. However, since the specific impulse can be improved by adding a maximum amount of ethylene imine, the amount used may be greater than necessary to produce hypergolic ignition, depending on balancing practical considerations against each other.

On the other hand, if practical considerations, as referred to above, permit addition of only less than the hypergolic amounts of ethylene imine, these smaller additions will improve, in addition to the theoretical specific impulse, the ignition characteristics of the fuel, when used with an external source of ignition (e.g.—glow plug, spark, powder squib); that is, ignition is more positive and ignition delay is decreased. Concomitantly, smoother combustion is also attained. The specific amounts preferred for this purpose depend on the fuel, the oxidizer, the strength of oxidizer, the type of igniter, and the conditions of use. However, since the specific impulse can be improved by adding a maximum amount of ethylene imine, the amount used may be greater, depending on all practical considerations balanced against each other.

It has been found that ethylene imine is miscible in all proportions with the ignitible liquids listed below, and we have also found that the solution resulting where ethylene imine is added to any one of these liquids has a higher theoretical specific impulse when burned with an oxidizer in any type of jet propulsion device than has the liquid to which no ethylene imine has been added. The extent of increase in specific impulse resulting from the addition of ethylene imine varies with the amount of the latter that is added, and is, in general, in proportion (not necessarily linear proportion) to the amount added.

The ignitible liquids referred to above are: hydrocarbons including gasoline, N-hexane, kerosene, petroleum ether (boiling range 30°–60° C.), benzene, toluene, xylene; alcohols such as methanol, ethanol, furfuryl alcohol; aliphatic, aromatic and heterocyclic amines such as isopropyl-amine, diethylamine, triethylamine, aniline, cyclohexylamine, pyridin; compounds of nitrogen and hydrogen including ammonia, hydrazine and hydrazines in which hydrogen has been replaced by organic substituents; methylal; diethylether; cyclic oxides such as ethylene oxide, propylene oxide, dioxane, furane, and tetrahydrofurane; mercaptans such as mixed butyl mercaptans, tertiary-butyl-mercaptan; etc.

Any or all of these liquids may therefore be used with ethylene imine as an additive to improve the theoretical specific impulse, and the range of concentrations of ethylene imine which may be used varies between 0.1% and 99% by weight ethylene imine.

However, the usefulness of ethylene imine as an additive is not limited to the materials listed above, since these materials represent classes of compounds, of which any individual member may be used effectively for the same purposes; and similar desirable fuel characteristics are imparted to them by the addition of ethylene imine. Therefore, ethylene imine is correspondingly effective with other aliphatic including saturated and olefinic, aromatic and hydroaromatic hydrocarbons, or mixtures thereof, such as JP–1 or JP–3; also with alcohols; alkyl, aromatic, hydroaromatic and heterocyclic amines; ethers and heterocyclic oxides; mercaptans; also combinations of these classes so that binary, ternary and higher mixtures may be used.

The following examples illustrate the invention, parts or ratios or percentages being by weight unless otherwise indicated.

I

Ethylene imine was found to be miscible in all proportions in gasoline and a solution containing 16.5% by weight of ethylene imine showed no separation of solid or liquid phase when cooled to −60° C. A solution of the same concentration ignited spontaneously when a few drops of it were added directly to 0.5 mls. of 96% nitric acid. Gasoline alone does not ignite spontaneously with nitric acid under these conditions.

Compositions containing higher amounts than the hypergolic amount referred to above may be used, for example

ethylene imine	gasoline
53.2	46.8
27.6	72.4
17.8	82.2

Compositions containing amounts of ethylene imine less than hypergolic are illustrated by:

ethylene imine	gasoline
15.0	85.0
14.8	85.2
11.2	88.8
5.7	94.3

II

A solution of n-hexane containing 23.9% by weight of ethylene imine ignited spontaneously when brought into contact with 96% nitric acid. N-hexane alone does not ignite spontaneously with nitric acid under these conditions.

Compositions containing lesser amounts of ethylene imine, are for example

ethylene imine	n-hexane
12.3	87.7
5.5	94.5

III

Ethylene imine was found to be miscible in all proportions in liquid ammonia. A solution containing 50% ethylene imine by weight ignited spontaneously when contacted with 85% nitric acid.

Compositions containing higher or lower amounts of ethylene imine may be used depending on the purposes in hand.

IV

A solution containing 49.7% (approximately 50/50) ethylene imine and 50.3% furfuryl alcohol by weight did not show separation of a liquid or solid phase when cooled to −60° C. Ethylene imine and furfuryl alcohol were found to be miscible in all proportions. A solution containing 9.9% ethylene imine ignited spontaneously when brought into contact with 85% nitric acid. Compositions containing higher or lower amounts of ethylene imine may be used depending on the purposes in hand.

V

Etheylene imine was found to be miscible in all proportions in aniline, and a solution containing 22% by weight of ethylene imine had a freezing point of approximately −40° C. This mixture showed hypergolic ignition with 95% nitric acid.

Other compositions include for example: 10% ethylene imine with 90% aniline; and 20.5% ethylene imine with 79.5% aniline. Illustrative ternary compositions are:

ethylene imine	aniline	hydrazine
7.1	76.8	16.1
8.7	78.5	12.8
14.5	75.3	10.2

VI

Ethylene imine is miscible in all proportions with ethyl alcohol. A solution containing 50% by weight of ethylene imine is hypergolic with 95% nitric acid. Other alcohol compositions may be:

ethylene imine	alcohol
10.5	89.5
20.8	79.2
28.0	72.0
41.2	58.8
51.2	48.8

VII

Ethylene imine was found to be miscible in all proportions with methylal. A solution containing 30% by weight of ethylene imine was ignited spontaneously on contact with 95% nitric acid. Compositions containing higher or lower amounts of ethylene imine may be used depending on the purposes in hand.

VIII

Etheylene imine was found to be miscible in all proportions with diethylamine, and a solution containing 20% by weight of ethylene imine ignited spontaneously on contact with 95% nitric acid. Compositions containing higher or lower amounts of ethylene imine may be used depending on the purposes in hand.

IX

Ethylene imine was found to be miscible in all proportions with isopropylamine, and a solution containing 30% by weight of ethylene imine ignited spontaneously on contact with 95% nitric acid. Compositions containing higher or lower amounts of ethylene imine may be used depending on the purposes in hand.

X

Ethylene imine was found to be miscible in all proportions with toluene, and a solution containing 40% by weight of ethylene imine ignited spontaneously on contact with 95% nitric acid. Compositions containing higher or lower amounts of ethylene imine may be used depending on the purposes in hand.

XI

A solution containing 30% by weight of ethylene imine in toluene ignited spontaneously on contact with "mixed acid." The "mixed acid" was composed of 82% nitric acid, 15% sulfuric acid and 3% water. Compositions containing higher or lower amounts of ethylene imine may be used depending on the purposes in hand.

XII

Ethylene imine was found to be miscible in all proportions with a solution of mixed butyl mercaptans. A mixture containing 30% ethylene imine ignited spontaneously on contact with 85% nitric acid. Compositions containing higher or lower amounts of ethylene imine may be used depending on the purposes in hand.

XIII

Ethylene imine was found to be miscible in all proportions with tetrahydrofuran. A solution containing 30% by weight of ethylene imine ignited spontaneously on contact with 95% nitric acid. Compositions containing higher or lower amounts of ethylene imine may be used depending on the purposes in hand.

In the ternary mixture of ethylene imine with hydrazine and aniline, the imine may be used advantageously for example, to lower the freezing point of the system to below −40° C. Thus 12.8% hydrazine, 78.6% aniline, and 8.6% ethylene imine (all by weight) has a freezing point of −43° C. Appreciable amounts of water may be present without raising the freezing point above −40° C. which may be taken as a generally desirable freezing point limitation on jet propulsion fuels. Thus a ternary composition freezing at −42° C. with 2% water added showed a freezing point of −41.0° C. 5% of water was required to raise the freezing point to −39.2° C. So that if a 95% grade hydrazine (containing 5% water) is used in preparing the ternary mixture, it would contain only 0.6% water. Consequently the solution will have a freezing point below −40° C. even if considerable contamination with water has occurred. Ethylene imine may be added to the eutectic of 17.3% hydrazine and 82.7% aniline or other mixtures thereof to improve the ignition characteristics very materially.

We claim:

1. A fuel composition of matter consisting essentially of an ignitible liquid component selected from the group consisting of a lower alkyl amine and hydrazine and ethylene imine in amount to increase the specific impulse of the composition.

2. A composition as in claim 1 in which the liquid component is a lower alkyl amine.

3. A composition as in claim 1 in which the liquid component is aniline in the ratio of weight of 10% to 22% of ethylene imine to 90% to 78% of aniline.

4. A composition as in claim 1 in which the liquid component is hydrazine.

5. A composition fuel consisting essentially of ethylene imine, aniline and hydrazine in the proportions respectively 7.1 to 14.5%, 78.5 to 75.3%, and 16.1 to 10.2%.

6. A composition as in claim 1 in which the liquid component is diethylamine in admixture with 20% ethylene imine.

7. A composition as in claim 1 in which the liquid component is isopropylamine in admixture with 30% ethylene imine.

8. A composition fuel consisting essentially of ethylene imine and the eutectic of 17.3% hydrazine and 82.7% aniline.

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