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THERMALLY STABILIZED FUEL

John A. Hannum, Detroit, Mich., assignor, by mesne assignments, to Borg-Warner Corporation, Chicago, Ill., a corporation of Illinois

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This invention relates to a thermally stable fuel or propellant of the type that comprises a wholly or partially self-sufficient mixture of fuel and oxidizing agent. In particular it relates to the addition of a substituted ammonia as a thermal stabilizing agent to a self-sufficient fuel to control its decomposition. The self-sufficient fuel of this invention includes a fuel component that is selected from the group of partially nitrated aliphatic hydrocarbons and an oxidizing component that is selected from the group of fully nitrated aliphatic hydrocarbons to supply the fuel with all or part of the additional oxygen required for combustion of the mixture.

Self-sufficient fuels combining both fuel and oxidant are to a degree subject to undesirable thermal decomposition in the presence of elevated temperatures, particularly when the fuel and oxidant are mixed and then stored for a considerable period of time. In the use of self-sufficient fuels where the fuel and oxidant are supplied in a ready mixed condition from a fuel tank to the combustion chamber where they are burned there is a tendency for the fuel to "flash back," particularly if the temperature of the mixture becomes too high; i. e., approaches the flash point of the mixture. This situation can arise because a mixture of fuel and oxygen sufficient for its combustion will be flowing as a stream from the fuel tank through the fuel system to the combustion chamber and no additional oxygen is required to burn such a mixture. Thus it is possible for the flame at the point of combustion to "flash back" through the system, particularly if the decomposition rate at the combustion chamber should become high enough to produce a detonating shock wave.

A further source of trouble that may arise in the use of such self-sufficient fuels is caused by heating the fuel at some place in the system other than the combustion chamber to a temperature exceeding its flash point creating what is known as a "hot spot" in the system. Such a condition can arise if a pump or like equipment in the fuel system becomes overheated due to lack of lubrication or for some other cause. The tendency of a self-sufficient fuel to "flash back" or decompose prematurely at any place in the fuel system other than in the combustion chamber can be reduced if its thermal stability is fortified

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so that it does not decompose at elevated temperatures such as may obtain due to accident or other cause. If its flash point is raised by addition of a thermal stabilizer a higher temperature must be reached before it will ignite prematurely.

A general object of the present invention is to provide a thermally stable self-sufficient fuel that comprises a nitro or polynitro aliphatic hydrocarbon fuel and a fully nitrated aliphatic oxidizing agent. Another object of the invention is to provide such a self-sufficient fuel that will remain stable at all desired times when the components are mixed and yet possess sufficient sensitivity to burn properly at the point of combustion. Still another object is to provide for a self-sufficient fuel a thermal stabilizer of the type indicated that is selected from the group of substituted ammonias, including both mono and poly-substituted ammonias. A still further object of the invention is to provide a self-sufficient fuel to which is added one or more materials from the group of substituted ammonias in an amount greater than a trace and substantially no greater than 10% by weight.

Amines in general have been used as stabilizers for explosives but in so far as I am aware have never been used as stabilizers for a self-sufficient fuel that has the characteristics described herein. Such fuels may be used for driving gas turbines, particularly to eliminate the compressors normally used therewith and to provide adequate oxygen for combustion at high altitudes. Other uses of such a fuel are as a source of power for reciprocating internal combustion engines. They may also be used in rockets in which both the fuel and oxygen are carried by the projectile.

In general the present invention comprises a self-sufficient fuel that includes three types of constituents. The first of these is the fuel component in the form of an organic chamical including in its composition carbon and hydrogen that are oxidized to end products in the form of carbon dioxide and water with the generation of gas and the giving off of heat in the process. The second constituent is the oxidant that supplies to the fuel oxygen necessary for its combustion. In most cases the fuel itself includes combined oxygen so the oxidant does not need to supply all of the total amount necessary to burn the hydrogen and carbon. Under certain

conditions these first and second constituents may be combined in one substance. The third constituent of the self-sufficient fuel is the thermal stabilizer that is added in the form of a substituted ammonia as hereafter described. This third constituent does not undesirably alter materially the combustion characteristics of the self-sufficient fuel at the combustion chamber but does act to prevent premature decomposition of the self-sufficient fuel in other parts of the system.

The invention is not to be construed as limited solely to a self-sufficient fuel consisting only of the above three ingredients. It is contemplated to be within the scope of this invention to add still other ingredients to the self-sufficient fuel to give to it other desired properties. For instance a coolant may be added to reduce the flame temperature at the point of combustion. Again, oxygen may be supplied to the self-sufficient fuel from an outside source such as the atmosphere if for some reason the self-sufficient fuel is not mixed in stoichiometric proportions. Again, a flash back preventer as described in copending application Serial No. 688,979, filed August 7, 1946, may be added within the scope of the present invention.

Conversely the present invention is not to be construed as limited to a fuel in which the herein described ingredients constitute the sole fuel source. As an example, percentages of the self-sufficient fuel that is the particular subject of this invention may be added in varying proportions to conventional liquid fuels that are not self-sufficient such as kerosene, gasoline and alcohol to improve their combustion characteristics for certain uses.

Various compounds such as the methyl and ethyl nitrates can be used in self-sufficient fuels although in the present invention I prefer to use a fuel selected from the group of nitro or polynitro aliphatic hydrocarbons. The fuel of the fuel-oxidant mixture embodied in the propellant will preferably be one such as nitromethane $CH_3(NO_2)$, that itself contains oxygen that may be used to support combustion. It is contemplated that other fuels from the class of nitro and polynitro aliphatic organic liquids may be used. Examples of such fuels in addition to nitromethane are:

Nitroethane, $CH_3.CH_2.NO_2$.
1-nitropropane, $CH_3.CH_2.CH_2.NO_2$
2-nitropropane, $(CH_3)_2CH.NO_2$
1,1-dinitropropane, $C_2H_5.CH(NO_2)_2$
2,2-dinitropropane, $(CH_3)_2C(NO_2)_2$
1,2-dinitropropane, $CH_2NO_2.CHNO_2.CH_3$
1,3-dinitropropane, $CH_2NO_2.CH_2.CH_2NO_2$
1,1-dinitroethane, $CH_3.CH(NO_2)_2$
1,1,1-trinitropropane, $C(NO_2).CH_2.CH_3$
1,2,3-trinitropropane, $CH_2NO_2.CHNO_2.CH_2NO_2$

Such nitro and polynitro aliphatics included as fuels, as distinguished from oxidants, within the scope of this invention include mononitromethane, dinitroethane and trinitropropane and those nitroethanes and nitropropanes below them in oxygen content but no nitroethanes or nitropropanes that are higher in oxygen content, as for instance dinitromethane. These are all to be distinguished from the unsuitable aromatic such as the nitrobenzols that are dangerous to handle even by skilled persons, to say nothing of persons who are not skilled in this art.

The fuel portion of the propellant mixture is limited to those nitro and polynitro aliphatics that contain not more than one nitro group for each carbon atom present. Under many conditions for most efficient use the fuel and oxidant will be combined in substantially stoichiometric proportions to burn to CO_2 and H_2O. This is the most economical use of the materials because after combustion there remains no appreciable amount of either unconsumed fuel or oxidant.

An advantage of using nitromethane or a similar oxygen containing fuel as listed above resides in the fact that it contains a considerable amount of oxygen that is available during combustion to burn part of the carbon or hydrogen in the fuel. This in turn does not require the inclusion in the propellant of as much oxidizing agent as would otherwise be necessary. These fuel components are non-brisant nitro and polynitro aliphatic compounds. When a fuel is said to be non-brisant within the terms of this disclosure it is meant that it may be burned in contact with chilled iron.

The oxidizing agent constituent of the present invention is selected from the group of fully nitrated aliphatic compounds and comprises tetranitromethane $C(NO_2)_4$ and hexanitroethane $C(NO_2)_3.C(NO_2)_3$. A preferred combination of fuel and oxidant comprises nitromethane as a fuel and tetranitromethane as an oxidant, mixed in stoichiometric proportions to burn to CO_2 and H_2O.

When tetranitromethane is the oxidant that is used, the following table indicates the percentages by weight of fuel that are to be used. In the first column the fuel is listed and in the second column the percentage by weight if a stoichiometric mixture of the fuel and tetranitromethane to burn to CO_2 and H_2O is desired. In the third column is listed the range of percentages by weight of fuel that, subject to the use intended, will provide a satisfactory product when combined with tetranitromethane. In the case of both columns 2 and 3 the amount of tetranitromethane to be used may be obtained by subtracting from 100% the percentage of the fuel indicated. This 100% does not refer to the entire self-sufficient fuel only to the fuel-oxidant proportion of the whole. As hereafter described the fuel-oxidant constituency of the whole self-sufficient fuel is something less than 100%.

This table is as follows:

Fuel	Fuel For Stoichiometric Mixture	Range of Percentages of Fuel
nitromethane	55.5	25–75
nitroethane	33.8	15–50
1-nitropropane	26.6	10–40
2-nitropropane	26.6	10–40
1,1-dinitropropane	45.8	20–65
2,2-dinitropropane	45.8	20–65
1,2-dinitropropane	45.8	20–65
1,3-dinitropropane	45.8	20–65
1,1-dinitroethane	65.5	35–90
1,1,1-trinitropropane	68.7	40–95
1,2,3-trinitropropane	68.7	40–95

If the oxidant to be used is hexanitroethane, the following table governs in which again the first column is the fuel and the second column is the percentage by weight of fuel required for a stoichiometric mixture with hexanitroethane to burn to CO_2 and H_2O, while the third column indicates the permissible range that may be used for a particular fuel. The amount of hexanitroethane to be added is obtained by subtracting from 100% the indicated percentage by weight of the fuel and this 100% refers to the

fuel-oxidant mixture and not to the whole of the self-sufficient fuel.

Fuel	Fuel For Stoichiometric Mixture	Range of Percentages of Fuel
nitromethane	52.2	20–70
nitroethane	30.8	10–45
1-nitropropane	24.2	10–40
2-nitropropane	24.2	10–40
1,1-dinitropropane	42.5	20–65
2,2-dinitropropane	42.5	20–65
1,2-dinitropropane	42.5	20–65
1,3-dinitropropane	42.5	20–65
1,1-dinitroethane	62.3	30–85
1,1,1-trinitropropane	65.6	35–90
1,2,3-trinitropropane	65.6	35–90

It should be pointed out that while it will generally be the case that the fuel component will consist of only one of the above ingredients it is contemplated to be within the scope of this invention to use a fuel that contains more than one compound, as one or more of these nitro or polynitro aliphatics. In such case the proportions for stoichiometric mixtures to burn to SO_2 and H_2O may be arrived at in accord with the molecular weights and the reaction formulae for the particular combinations that are contemplated. Since these calculations are within the ability of one skilled in the art they will not be given here.

Under certain conditions of use, fuels from the mono nitro aliphatics are preferred. It is to be noted that mono nitro aliphatics are referred to herein simply as nitro aliphatics and that the prefix "mono" is not used—as for example mono nitromethane is referred to simply as nitromethane. On the other hand in the case of poly nitro aliphatics the prefixes, as "di," "tri" and "tetra" are used. These mono nitro aliphatic compounds include the following:

Nitromethane, $CH_3(NO_2)$
Nitroethane, $CH_3.CH_2.NO_2$
1-nitropropane, $CH_3.CH_2.CH_2NO_2$
2-nitropropane, $(CH_3)_2\ CH.NO_2$

This group of fuels may be used individually or they may be used in admixture with each other. An example of the latter is the fortuitous mixture of these compounds that results from the reaction of propane and nitric acid in the vapor or gas phase. Such a mixture may be used with an oxidant in stoichiometric proportions, in which case the fuel of this fortuitous mixture is mixed with tetranitromethane in approximately the following proportions by weight to provide the fuel-oxidant proportion of the self-sufficient fuel:

	Per cent by weight
Tetranitromethane	65
Fortuitous fuel mixture	35

Again if the oxidant is hexanitroethane, the corresponding mixture will be approximately as follows:

	Per cent by weight
Hexanitroethane	70
Fortuitous fuel mixture	30

In each case the percentages of nitromethane, nitroethane, 1-nitropropane and 2-nitropropane are assumed to be present in proportions according to the reaction equation for propane and nitric acid. Considerable latitude in propellant composition is permissible within the scope of the invention, particularly when the fuel is such a fortuitous mixture as discussed above. Thus

if the oxidant is tetranitromethane the components of the fuel-oxidant part of the complete self-sufficient fuel that lie within the following percentages by weight are deemed to be within the present invention:

	Per cent by weight
Fortuitous fuel mixture	15–50
Tetranitromethane	85–50

Again the fuel-oxidant proportion of the self-sufficient fuel using hexanitroethane as the oxidant and a fortuitous fuel mixture, if mixed in approximately the following ranges of percentage by weight, fall within the scope of this invention:

	Per cent by weight
Hexanitroethane	90–55
Fortuitous fuel mixture	10–45

As indicated above the thermal stabilizer in the present invention is a substituted ammonia selected from the group that includes both mono and poly substituted ammonias. It will comprise a percentage of the total weight of the self-sufficient fuel that varies from a trace to substantially 10 per cent by weight. For example if the self-sufficient fuel includes (1) a fuel, (2) an oxidant, and (3) a thermal stabilizer and the thermal stabilizer makes up 10 per cent of the weight of the entire self-sufficient fuel the remaining 90 per cent of fuel and oxidant are themselves mixed in the proportions set out above when considering the fuel-oxidant mixture as 100 per cent. In most cases the amount of substituted ammonia will be approximately 1 to 2 per cent.

These substituted ammonias, when used as thermal stabilizers, must not in themselves react in a deleterious fashion with any of the fuel components under ordinary storage conditions. The substituted ammonias that now appear to be the most suitable are paraphenylene diamine and symmetrical diethyl diphenyl urea. Other substituted ammonias that are suitable are diphenyl nitrosamine, symmetrical dibutyl diphenyl urea, phenyl α naphthylamine, urea and diphenylamine.

The addition to the fuel-oxidant mixture of a substituted ammonia in the proportions indicated improves the thermal stability of the fuel. Thus it has a higher flash point and is less subject to thermal decomposition at elevated temperatures. This reduces the tendency to "flash back" through the fuel supply line or to decompose rapidly, in fact explosively, in the presence of a "hot-spot" in the fuel system such as might be created by an overheated pump. The substituted ammonia constituent of the self-sufficient fuel is added to the fuel-oxidant mixture to form a complete product.

In many cases this product comprises only fuel, oxidant and thermal stabilizer constituents and will be burned as such. On the other hand it is contemplated that in some cases a relatively small proportion of the complete self-sufficient fuel mixture may be added to other fuels to improve their combustion properties. As an example of this a mixture of approximately 90% gasoline and 10% self-sufficient fuel, the latter including fuel, oxidant and thermal stabilizer in proportions as described herein, may be mixed to form a propellant fuel. Again other constituents may be added to the self-sufficient fuel described herein to give it other properties.

Although a preferred use of the self-sufficient fuel of the present invention is in the form of a

single liquid entity that is stored, transported and fed to the point of combustion as such, this is not necessary. In certain cases it is desirable to maintain the constituents separate from each other until they are brought together at the point of combustion. Such a procedure would be desirable if the combustion characteristics of the self-sufficient fuel were to be altered during use by varying the percentages in which the constituents are mixed at the point of combustion.

The propellant that is the subject of this invention may be used for various purposes and in various ways. Its use in a gas turbine or other prime mover has been emphasized here but it is not to be limited to such use. It may be used either alone or in mixture with other materials in any apparatus and environment where combustion of a fuel is employed, as for instance as a source of gas under pressure by confined combustion and retention of the products of combustion.

I claim:

1. A liquid propellant comprising a mixture of a polynitro paraffin oxidant, a nitroparaffin fuel in which the number of nitro groups does not exceed the number of skeletal carbon atoms in the paraffin nucleus, and a thermal stabilizer selected from a group consisting of paraphenylene diamine, urea, diphenylamine, diphenyl nitrosamine, symmetrical diethyl diphenyl urea, symmetrical dibutyl diphenyl urea, and phenyl α naphthyl amine, such thermal stabilizer being present in an amount varying from a trace to substantially ten percent by weight of the total.

2. A propellant as in claim 1 in which the polynitro paraffin oxidant is selected from a group consisting of tetranitromethane and hexanitroethane.

3. A propellant as in claim 1 in which the nitro paraffin fuel is selected from a group consisting of nitromethane, nitroethane, dinitroethane, nitropropane, dinitropropane, trinitropropane, and mixtures thereof.

4. A propellant as in claim 1 including a conventional liquid fuel such as kerosene, gasoline, alcohol or the like.

JOHN A. HANNUM

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
914,624	Winand	Mar. 9, 1909
1,597,343	Chandler	Aug. 24, 1926
1,641,520	Bassett	Sept. 6, 1927
1,800,997	Greenstreet	Apr. 14, 1931
2,247,255	Senkus	June 24, 1941
2,298,255	Hopkins	Oct. 6, 1942
2,325,065	Lawrence	July 27, 1943

FOREIGN PATENTS

Number	Country	Date
24,839	Great Britain	1913

Certificate of Correction

Patent No. 2,542,193 February 20, 1951

JOHN A. HANNUM

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 40, for "chamical" read *chemical*; column 3, line 70, after "aromatic" insert *fuels*; column 4, line 46, after "fuel" insert *but*; column 5, line 24, for the formula "SO_2" read CO_2;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of April, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

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