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FUELS FOR REACTION MOTORS

John L. Van Winkle, San Lorenzo, and Francis G. Bollo and Rupert C. Morris, Berkeley, Calif., assignors to Shell Development Company, New York, N.Y., a corporation of Delaware

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10 Claims. (Cl. 60—35.4)

This invention relates to liquid propellants for reaction propulsion devices, particularly to self-sufficient liquid propellants for rocket motors. The invention provides a new class of fuels for use in rocket motors, these new fuels being characterized by their outstanding ignition and burning characteristics with standard oxidizing agents.

The provision of suitable propellants and/or ignition systems for reaction-type motors, that is, motors which directly apply Newton's third law of motion, such as rocket or jet motors, presents many interrelated problems. For example, it is usually necessary that the propellant be self-sufficient, in the sense that it must contain all of the materials necessary to its combustion and must operate without reliance on any material coming from without the propelled object. This problem has been solved to some extent by the use of so-called "monofuels," by which is meant fuels which contain in and of themselves all of the components essential to the combustion of the fuel. Such propellants can be ignited, and flame-outs prevented only through the use of a separate ignition system. Such ignition systems generally take one of two forms: a mechanical or electrical ignition system, or a hypergolic ignitor. A hypergolic igniter is a material which spontaneously ignites, and may be a single material which spontaneously ignited when introduced into the propellant composition, or it may comprise two or more materials which spontaneously ignite when mixed, normally in the combustion chamber. In either form of ignition system, the system represents dead weight which also must be propelled by the propellant.

As an alternative to the monofuel system, there has been used the multi-component propellant wherein one or more fuels are mixed with one or more oxidizers in the combustion chamber, the respective components of the propellant being so chosen that the mixture thereof is hypergolic—that is, the two materials ignite spontaneously when mixed. In such a system, ignition of the propellant is accomplished in a simple manner without any external means and flameouts are substantially precluded.

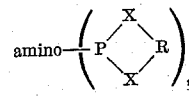
Also, in many applications, it is mandatory that the reaction-motor develop its maximum thrust in as short a time as possible after the motor is started. Highly hypergolic propellant mixtures are of substantial advantage in this type of application.

Consequently, there is much interest in the discovery and development of materials which are highly hypergolic with respect to materials commonly used as oxidizing agents, yet which are not explosive themselves, and which do not form explosive mixtures with the oxidizing agent employed. In addition, the fuel must meet the other requirements for satisfactory rocket motor fuels, such as: (*a*) low freezing point, and low viscosity near the freezing point; (*b*) high boiling point and low vapor pressure at ordinary or moderately elevated temperatures (150–175° F.); (*c*) low toxicity; (*d*) high energy content per unit weight—high density and heat of combustion; (*e*) yielding oxidation products of low molecular weight; (*f*) of low corrosivity and good compatibility with ordinary materials of construction; (*g*) stable chemically, inert with respect to ordinary materials of construction, and insensitive to thermal or mechanical shock; (*h*) easily and inexpensively derived from available raw materials and (*i*) having a high specific thrust.

At the present time, few compounds have been discovered which fulfil satisfactorily all of these requirements. Applicants, however, have found a class of materials which substantially comply with all of these requirements for a satisfactory liquid rocket fuel, said materials having excellent hypergolicity-stability characteristics with respect to ordinary oxidizing agents.

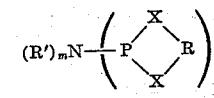
The terms "fuel" and "oxidizer" or "oxidizing agent," as used herein, have their ordinary meanings—i.e., a fuel is a material oxidized or burned; an oxidizer or oxidizing agent is the material which causes, effects and supports the oxidation or burning of the fuel.

The new class of rocket fuels discovered by applicants comprises at least one phospholane or phosphorinane in which the phosphorus atom is directly attached to the nitrogen atom of an amino group. These compounds may also be characterized as the cyclic amides of glycol diesters of phosphorous acid; they have the structural formula:



wherein X represents a chalcogen element and R represents the residue of a dihydric aliphatic alcohol, HO—R—OH, wherein the hydroxyl groups are substituted on different carbon atoms separated from each other by not more than one intervening carbon atom, and *n* represents 1, 2 or 3. In the preferred compounds of this class, X represents an oxygen or sulfur atom, and R is a divalent saturated hydrocarbon radical, even more preferably an alkylene radical, the atoms designated as X being linked to different carbon atoms of the said alkylene radical, the two carbon atoms so linked being separated by up to one intervening carbon atom. In phospholanes of this class, the carbon atoms of the group R linked to the atoms designated as X are adjacent carbon atoms; in the phosphorinanes of this class, the carbon atoms linked to the atoms designated as X are separated by one carbon atom. The valences of the carbon atoms of the group R not linked to other atoms of the phospholane and phosphorinane rings are satisfied by either hydrogen atoms, or by links to carbon atoms of hydrocarbon groups, preferably alkyl groups, and still more preferably lower alkyl groups, such as those containing not more than 4 carbon atoms in each group.

The novel compounds of this invention may also be characterized by the formula:



wherein X, R and *n* have the meanings hereinbefore set out, R' has the meaning set out hereinafter and $m=3-n$.

In the formula "amino" represents an amino radical, that is, the residue of ammonia or an organic amine, and can be represented by the general formula $-N(R')_2$ wherein R' is selected from the group consisting of the hydrogen atom and organic radicals, and wherein both groups R' together can represent a divalent radical which forms with the nitrogen atom a heterocyclic ring. The amino group preferably is the residue of an amine hav-

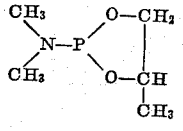
ing attached to the nitrogen atom from one to two hydrocarbon groups. Preferably the hydrocarbon groups are aliphatic groups such as alkyl groups, and preferably are lower alkyl, including cycloalkyl, groups containing not more than 6 carbon atoms each, or where both of R′ together represent a single group, they represent an alkylene group, preferably one containing not more than 10 carbon atoms.

Representative examples of this class of fuels include the following:

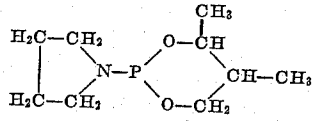
2-dimethylamino-1,3,2-dioxaphospholane,
2-methylamino-1,3,2-dioxaphospholane,
2-pyrrolidyl-1,3,2-dioxaphospholane,
2-pyrrolidyl-4-methyl-1,3,2-dioxaphospholane,
2-dimethylamino-4-methyl-1,3,2-dioxaphospholane,
N-methyl-bis(2-(1,3,2-dioxaphospholanyl))amine,
2-diisopropylamino-1,3,2-dioxaphospholane,
2-diisopropylamino-4-ethyl-1,3,2-dioxaphospholane,
2-(N-methyl-N-butylamino)-4-methyl-1,3,2-dioxaphospholane,
2-dimethylamino-5-methyl-1,3,2-dioxaphosphorinane,
2-(N-cyclohexyl-N-ethylamino)-1,3,2-dioxaphosphorinane,
2-dicyclohexylamino-1,3,2-dioxaphospholane,
2-dicyclopentylamino-4-methyl-5-ethyl-1,3,2-dioxaphosphorinane,
2-piperidino-1,3,2-dioxaphospholane,
2-methylpiperidino-1,3,2-dioxaphospholane,
2-pyrrolidyl-5-isopropyl-1,3,2-dioxaphospholane,
2-thiamorpholino-5-ethyl-1,3,2-dioxaphosphorinane,
2-dihexylamino-1,3,2-dithiaphospholane
2-dibutylamino-1,3,2-dithiaphosphorinane
2-octylamino-1,3,2-dithiaphospholane
2-pyrrolidyl-4-ethyl-1,3,2-dithiaphospholane
2-morpholino-4-methyl-5-ethyl-1,3,2-dithaphosphorinane
N-ethyl-bis(2-(1,3,2-dioxaphosphorinanyl))amine

The structure of these compounds is illustrated by the following examples:

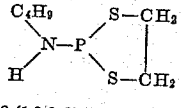
2-dimethylamino-4-methyl-1,3,2-dioxaphospholane



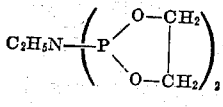
2-pyrrolidyl-4,5-dimethyl-1,3,2-dioxaphosphorinane



2-butylamino-1,3,2-dithiaphospholane



N-ethyl bis(2-(1,3,2-dioxaphospholanyl))amine



The new fuels are easily prepared by methods known in the art, the most convenient method being that set out by Lucas, Mitchell and Scully, Journal of the American Chemical Society, 72, 5491 (1950). This method employs readily available, inexpensive raw materials—i.e., glycols, phosphorus trichloride and primary or secondary amines. According to this method, the glycol is added to a solution of the phosphorus trichloride in an inert solvent, such as a liquid alkane or halogenated alkane, pentane, chloroform or methylene chloride being quite suitable, the temperature of the mixture being maintained so that gentle boiling of the mixture and evolution of hydrogen halide occur. When evolution of the hydrogen halide ceases, the mixture is reacted with an excess of the amine. In some cases, it is desirable to remove the solvent and any unreacted glycol after the reaction is complete, and then react the 2-chlorophospholane or phosphorinane with the amine, preferably in an inert solvent.

These new rocket fuels are highly hypergolic, but not explosive, with respect to materials commonly used as oxidizers for liquid rocket motor propellants, such as red fuming nitric acid, white fuming nitric acid, mixed acid (nitric acid with a small percentage of sulfurc acid), hydrogen peroxide or liquid oxygen. These new fuels may be used in any rocket, jet or other reaction motor, designed to operate on fuel-oxidizer propellants. This type of reaction motor, the method of handling the fuel and oxidizer and of conducting the combustion are well known in the art; for these purposes, the new fuels are substantially equivalent to other known fuels. Current practice with respect to the use of hypergolic fuel-oxidizer propellants is illustrated in some detail in U.S. Patent No. 2,573,471. It should be remembered, however, that the new fuels ignite spontaneously at an extremely high rate of speed when contacted with the oxidizing agent, ignition delays being of the order of 50 milliseconds or less. Maximum thrust is developed in an exceedingly short time. Accordingly, precautions should be taken to insure that premature contact of the fuel with the oxidizer does not occur.

The individual 2-amino-1,3,2-dioxaphospholanes and phosphorinanes may be used as the fuel, or mixtures of these compounds may be used. In many cases, mixtures have substantial advantages over the individual components thereof used each alone, for such mixtures often have more desirable physical characteristics than those of any of the individual components thereof. For example, mixtures of close homologs or analogs of this class of compounds normally have lower freezing points than do any of the component compounds of the mixture, the mixture thus being useful at temperature conditions where none of the component compounds thereof can be used. The most desirable of these mixtures are, of course, the eutectic mixtures. As an illustration of the use of mixtures, rather than the individual compounds of this invention, it has been found that the utility of 2-dimethyl-amino-4-methyl-1,3,2-dioxaphospholane, one of the most promising compounds of this invention, could be extended substantially by mixing it with its homolog, 2-dimethylamino-1,3,2-dioxaphospholane. The 4-methyl derivative alone has a freezing point of about −47° C.—the freezing point of the analog is about −30° C.; mixtures of these two compounds freeze at much lower temperatures, such mixtures containing from about 20% to about 60% by weight of the 4-methyl derivative freezing below about −54° C. (−65° F.). The eutectic mixture, about 55% by weight of the 4-methyl derivative, freezes at about −59° C., a temperature which represents a substantial extension in the utility of the two component compounds.

The utility of the 2-amino-1,3,2-dioxaphospholanes, -phosphorinanes and their thia analogs as highly hypergolic fuels when used with standard oxidizing agents is shown by the following tables, which summarize the results of ignition tests of representative members of these new compounds with several of the standard oxidizers. The method used for determining the ignition delay comprises injecting a measured amount of the oxidizer into a measured amount of the fuel under controlled temperature conditions. The time between injection of the oxidizer and combustion of the mixture is measured both photoelectrically and photographically. The ignition delay is reported in milliseconds.

Table I

[Oxidizer: 100% white fuming nitric acid.]

Fuel	Temperature (° C.)	Ignition Delay (milliseconds)
2-dimethylamino-4-methyl-1,3,2-dioxaphospholane.	20	13
	0	15
	−20	16
	−40	20
	−50	17
2-dimethylamino-1,3,2-dioxaphospholane	−40	11
2-methylamino-1,3,2-dioxaphospholane	−40	6
N-methyl-bis(2-(1,3,2-dioxaphospholanyl))amine	−40	10
Eutectic mixture (55 percent w. 2-dimethyl amino-4-methyl-1,3,2-dioxaphospholane, 45 percent w. 2-dimethyl-1,3,2-dioxaphospholane).	20	15
	−40	19
2-pyrrolidyl-4-methyl-1,3,2-dioxaphospholane	−40	18
2-pyrrolidyl-1,3,2-dioxaphospholane	−40	16

Table II

[Oxidizer: 90% white fuming nitric acid. Fuel: 2-dimethylamino-4-methyl-1,3,2-dioxaphospholane.]

Temperature, ° C.:	Ignition delay (milliseconds)
20	20
0	27
−20	22
−40	23
−60	28

Table III

[Oxidizer: 90% hydrogen peroxide. Fuel: 2-dimethylamino-4-methyl-1,3,2-dioxaphospholane.]

Temperature, ° C.:	Ignition delay (milliseconds)
20	16
−10	19

Table IV

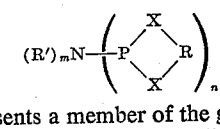
[Oxidizer: 100% red fuming nitric acid. Temperature: −40° C.]

Fuel:	Ignition delay (milliseconds)
2 - dimethylamino - 4 - methyl -1,3,2 - dioxaphospholane	20
Eutectic (for composition see Table I)	19

It should be noted that while the new amino-phospholanes and phosphorinanes are primarily useful as fuels for reaction motors, they also are useful as components for hypergolic igniter mixtures for other fuels, or as components for more complex fuel compositions for applications wherein it is desirable that high-speed, high-intensity combustion be attained and/or maintained.

We claim as our invention:

1. In the method for developing thrust in a jet motor having a combustion chamber and an exhaust nozzle wherein an oxidizer and a fuel are brought together in the said combustion chamber and the gaseous products produced by combustion of the oxidizer and fuel are ejected from the exhaust nozzle, the improvement comprising bringing together an oxidizer and at least one compound of the formula:



wherein X represents a member of the group consisting of oxygen and sulfur, R represents an alkylene group of up to 27 carbon atoms, the atoms designated as X each being linked to different carbon atoms of the said alkylene group, the two carbon atoms of the alkylene group so linked being separated by not more than one intervening carbon atom, R′ represents a member of the group consisting of the hydrogen atom and lower alkyl, including cycloalkyl, groups, with the proviso that both of the groups, R′, together can represent a lower alkylene group forming together with the indicated nitrogen atom a heterocyclic ring, *n* represents an integer from 1 to 3 and *m*=3−*n* the ratio of compound of said formula to oxidizer being in such proportions as to produce spontaneous ignition.

2. In the method for developing thrust in a jet motor having a combustion chamber and an exhaust nozzle wherein an oxidizer and a fuel are brought together in the said combustion chamber and the gaseous products produced by combustion of the oxidizer and fuel are ejected from the exhaust nozzle, the improvement comprising using as the fuel at least one 2-amino-1,3,2-dioxaphospholane the ratio of fuel to oxidizer being in such proportions as to produce spontaneous ignition.

3. In the method for developing thrust in a jet motor having a combustion chamber and an exhaust nozzle wherein an oxidizer and a fuel are brought together in the said combustion chamber and the gaseous products produced by combustion of the oxidizer and fuel are ejected from the exhaust nozzle, the improvement comprising using as the fuel at least one 2-amino-1,3,2-dioxaphosphorinane the ratio of fuel to oxidizer being in such proportions as to produce spontaneous ignition.

4. In the method for developing thrust in a jet motor having a combustion chamber and an exhaust nozzle wherein an oxidizer and a fuel are brought together in the said combustion chamber and the gaseous products produced by combustion of the oxidizer and fuel are ejected from the exhaust nozzle, the improvement comprising using as the fuel at least one amide of a primary amine and a 2-hydroxy-1,3,2-dioxaphospholane the ratio of fuel to oxidizer being in such proportions as to produce spontaneous ignition.

5. In the method for developing thrust in a jet motor having a combustion chamber and an exhaust nozzle wherein an oxidizer and a fuel are brought together in the said combustion chamber and the gaseous products produced by combustion of the oxidizer and fuel are ejected from the exhaust nozzle, the improvement comprising using as the fuel at least one amide of a secondary amine and a 2-hydroxy-1,3,2-dioxaphospholane the ratio of fuel to oxidizer being in such proportions as to produce spontaneous ignition.

6. In the method for developing thrust in a jet motor having a combustion chamber and an exhaust nozzle wherein an oxidizer and a fuel are brought together in the said combustion chamber and the gaseous products produced by combustion of the oxidizes and fuel are ejected from the exhaust nozzle, the improvement comprising using as the fuel 2-dimethylamino-4-methyl-1,3,2-dioxaphospholane the ratio of fuel to oxidizer being in such proportions as to produce spontaneous ignition.

7. In the method for developing thrust in a jet motor having a combustion chamber and an exhaust nozzle wherein an oxidizer and a fuel are brought together in the said combustion chamber and the gaseous products produced by combustion of the oxidizer and fuel are ejected from the exhaust nozzle, the improvement comprising using as the fuel a mixture comprising from about 20% by weight to about 60% by weight of 2-dimethylamino-4-methyl-1,3,2-dioxaphospholane, the remainder of said mixture being 2-dimethylamino-1,3,2-dioxaphospholane the ratio of fuel to oxidizer being in such proportions as to produce spontaneous ignition.

8. In the method for developing thrust in a jet motor having a combustion chamber and an exhaust nozzle wherein an oxidizer and a fuel are brought together in the said combustion chamber and the gaseous products produced by combustion of the oxidizer and fuel are ejected from the exhaust nozzle, the improvement comprising using as the fuel a mixture consisting of 55% by weight of 2-dimethylamino-4-methyl-1,3,2-dioxaphospholane and 45% by weight of 2-dimethylamino-1,3,2-dioxaphospholane the ratio of fuel to oxidizer being in such proportions as to produce spontaneous ignition.

9. A mixture comprising from about 20% by weight to about 60% by weight of 2-dimethylamino-4-methyl-

1,3,2-dioxaphospholane and from about 80% by weight to about 40% by weight of 2-dimethylamino-1,3,2-dioxaphospholane freezing below about —54° C.

10. The eutectic mixture consisting of about 55% by weight of 2-dimethylamino-4-methyl-1,3,2-dioxaphospholane and about 45% by weight of 2-dimethylamino-1,3,2-dioxaphospholane freezing at about —59° C.

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