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SOLID PROPELLANT COMPOSITION CONTAINING LIQUID ORGANOMETALLIC COMPOUND AND METHOD OF USE

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This application is a continuation-in-part of Ser. No. 113,084, filed May 29, 1961, now abandoned. This invention relates to solid propellants and to a new class of additives therefor. More specifically, this invention relates to organometallic additives to improve and modify the burning characteristics of solid propellant compositions.

Generally, vehicles propelled by solid propellants are of the free-flight type; that is, once the solid propellant grain is ignited, its burning characteristics are not externally controlled and the grain burns in accordance with its own specific properties. Thus, a given propellant grain finds application only in those situations wherein its inherent properties can meet operational specifications. Conversely, for a given application only those grains whose compositions inherently possess the requisite properties can be employed.

The thrust developed by a rocket motor is proportional to specific impulse and fuel mass flow rate. For solid propellants, mass flow rate is dependent upon burning surface area and linear burning rate. Thus, high thrust can be obtained by a large burning area, a fast burning rate, or both. Conversely, a low thrust for a correspondingly longer duration can be obtained if the burning area and/or burning rate is low.

Since a given combustion chamber will be able to hold only a limited amount of solid propellant, to further increase thrust, the exposed burning area is increased by altering the geometry of the propellant grain. Rather than being of the simple end burning type, the propellant grain may assume a multi-perforated configuration with internal burning thereby increasing the burning area. However, the physical strength of the propellant grain imposes a restriction as to the geometric form that the grain can assume.

Another method of increasing propellant flow rate and thereby increasing thrust is to increase propellant linear burning rate. The same amount of total energy will be generated by the grain, but at a faster rate. While the overall range of the propellant may not be altered, the objective is accomplished in a much shorter time. Thus, it is apparent that it becomes very desirable to modify propellant burning rate so as to increase the flexibility of any given propellant system.

Accordingly, it is an object of this invention to provide new compositions of matter. A further object is to provide novel propellant grain compositions. An additional object is to provide a new class of organometallic additives which impart to the propellant grain certain desirable properties. A further object of this invention is to provide a class of organometallic compounds which have the ability to modify the burning rate of solid propellants and to improve their overall combustion properties.

We have now made the discovery that certain organic compounds of certain metals have the property of modifying the combustion properties of solid propellants. The compounds which possess the property are those of the metals which have a significant effect on the combustion properties of liquid hydrocarbon fuels in internal combustion engines. Specifically, the compounds which we use as combustion modifiers for solid propellants are the liquid organometallic compounds of the metals of atomic numbers 24—28 and 81—83.

It is essential for the purposes of our invention that the organometallic rate control additive be liquid under ordinary conditions. We mean by this that the compound must be liquid at temperatures as low as substantially 40° C. This is a temperature which is ambient in many parts of the world, and when not ambient is achievable by very mild heating of the organometallic compound.

We have discovered that the effect of the above organometallic compounds on the combustion properties of solid propellants surprisingly parallels the effect of organometallic compounds on the combustion properties of liquid hydrocarbon fuels in an internal combustion engine. We have observed that organic compounds of those metals having the greatest effect on the combustion properties of fuels in an internal combustion engine show the greatest effect on the combustion characteristics of solid propellants in a rocket motor.

In considering combustion in an internal combustion engine, it is well known that in a given base fuel, different organic compounds of a given metal may have various degrees of effectiveness. Similarly, a given organometallic compound may have different effects in various fuel types. For example, tetraethyllead provides superior antiknock effectiveness when used in conventional gasoline, but it is actually a proknock when added to hydrocarbon materials such as styrene. Moreover, for a given base fuel various organic compounds of lead have varying degrees of effectiveness. For example, tetraphenyllead is much less effective than is tetraethyllead. Also, the concentration of the organometallic often has an effect on antiknock activity. Tetraethyllead, added to gasoline in very large concentrations, actually produces a proknock effect.

We have discovered that in a similar manner different organic compounds of the same metal show varying effects on the combustion properties of a given solid propellant grain. Also, a given organometallic compound exhibits different degrees of effectiveness when compounded in various solid propellant grains. Moreover, different effects can be achieved by significantly varying the concentration of the organometallic compound. However, the metals having the greatest effect on fuel combustion properties in an internal combustion engine will generally show the greatest effects on the combustion properties of solid propellant compositions. In other words, the effectiveness of a given metal in modifying the knocking tendency of liquid hydrocarbons is a measure of its potential ability to modify the combustion properties of solid propellant grains. Metals showing very great antiknock activity in hydrocarbon fuels in internal combustion engines are chromium, manganese, iron, cobalt, nickel, thallium, lead and bismuth.

The fact that our organometallic rate control additives are liquid possesses numerous advantages. For example, they are much easier to incorporate into the propellant mix than are solid additives, and in addition, behave better when the propellant is cured at elevated temperatures. Perhaps more importantly, use of our liquid organometallic additives results in better rate control throughout the propellant grain than does use of seemingly similar materials which are solid at normal temperatures. We do not know the reason for this; it may be due to the fact that the liquid state of our materials permits them to be dispersed more uniformly in the compounded solid propellant.

Accordingly, the objects of this invention are accomplished by providing solid propellant compositions containing from about 0.1 to 5 percent of a normally liquid organometallic compound, said organometallic compound being characterized by containing at least one metal atom which is normally effective in modifying the antiknock

tendency of liquid hydrocarbons in internal combustion engines. More specifically, the additives of this invention include liquid organic compounds of the metals of atomic numbers 24-28 and 81-83. These metals are chromium, manganese, iron, cobalt, nickel, thallium, lead and bismuth.

Although diverse liquid organic compounds of these metals are usable, we prefer to use those compounds which are relatively stable so as to permit long storage. Also, since propellant grains are cured at elevated temperatures, we prefer organometallic compounds of relatively low vapor pressure—boiling above about 200° C. A particularly effective concentration for our additives is from about 1 to 4 weight percent. Thus, a preferred embodiment of this invention comprises a solid propellant composition containing from about 1 to 4 weight percent of a liquid organic compound of a metal selected from the group consisting of the metals of atomic numbers 24-28 and 81-83, said liquid organometallic compound being characterized by being relatively stable and having a boiling point not less than 200° C.

The liquid organometallic compounds utilized in this invention may be further characterized as compounds in which there are carbon-to-metal bonds in the molecule. One group encompasses compounds in which there are monovalent carbon-to-metal bonds in the molecule. Typical examples are the metal alkyls and aryls such as tetraethyllead, tetrabutyllead, triethylbismuth, hexaethyldilead, triethyl thallium and dicumene chromium.

Another group of compounds usable in this invention are the liquid metal carbonyls wherein the metal is bonded to carbonyl groups. Typical examples are iron pentacarbonyl, and nickel tetracarbonyl.

The liquid metal carbonyl compounds may also contain various organic or organometallic radicals bonded to the metal atom. Typical examples are 1,3-butadiene iron tricarbonyl, cyclohexadiene iron tricarbonyl, ethyl phenylacetate chromium tricarbonyl, ethyl manganese pentacarbonyl, acetylene dicobalt hexacarbonyl, 2-butyne dicobalt hexacarbonyl, trimethyllead manganese pentacarbonyl and 1-pentyne dicobalt hexacarbonyl.

Other liquid organometallics usable as the additives of this invention are compounds wherein the metal is bonded to a cyclomatic radical such as cyclopentadienyl and indenyl radicals. The cyclomatic radical may be substituted with univalent aliphatic, aryl, aralkyl, alicyclic and alkaryl substituents. Typical examples of this group of liquid organometallic compounds are bis(methylcyclopentadienyl) iron, bis(tetrahydroindenyl)iron and bis(methylcyclopentadienyl)nickel.

The liquid cyclopentadienyl metal compounds stabilized by covalent bonding to electron-donating groups are also within the scope of this invention. These compounds include methylcyclopentadienyl manganese tricarbonyl, acetyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl iron dicarbonyl ethyl, cyclopentadienyl iron dicarbonyl phenyl, cyclopentadienyl cobalt dicarbonyl, methylcyclopentadienyl cobalt methylcyclopentadiene, cyclopentadienyl chromium dinitrosyl ethyl, (methylcyclopentadienyl) nickel nitrosyl and cyclopentadienyl nickel nitrosyl.

Compounds which are particularly useful and preferred as additives of this invention are tetraethyllead, methylcyclopentadienyl manganese tricarbonyl, bis methylcyclopentadienyl iron, cyclopentadienyl nickel nitrosyl, cyclopentadienyl cobalt dicarbonyl, bis-(methylcyclopentadienyl)nickel and pelargonyl methylcyclopentadienyl manganese tricarbonyl.

The additives of this invention act as burning rate modifiers thereby permitting greater flexibility in choosing a propellant grain to meet operational specifications. While it is generally desirable to increase burning rate, this invention also contemplates the use of certain organometallic additives to reduce burning rate. Thus,

when maximum flight time rather than maximum thrust is the objective, the use of certain organometallic compounds can be used to achieve the desired result.

In some cases the inherent combustion properties of the organometallic additive may improve the over-all combustion properties of the propellant grain. However, in general, the additives of this invention act as catalysts and benefits are obtained not because of the combustion of the organometallic itself, but due to its effect on the combustion properties of the propellant grain proper.

Other benefits that may be obtained by the use of the present liquid organometallic additives includes more even combustion of the propellant without surges or detonation. In many instances, improved combustion is manifested by a significant reduction in the smoke content of the exhaust gas. Also, many of the organometallic compounds act to reduce the temperature sensitivity of the propellant grain components.

In certain cases the use of these additives results in an increased burning rate without an attendant increase in specific impulse. In other words the inherent energy potential of the propellant is not increased, but only the rate of energy liberation is affected. In other situations the burning rate will not be affected but specific impulse will be increased. The increase in specific impulse may be due to more complete combustion of the grain composition effectuated by the organometallic compound. For example, in many cases the combustion of the propellant composition is incomplete and only a portion of the theoretical heat of the combustion is released. The organometallic additive serves to effect a more complete combustion thereby releasing more energy per pound of fuel than previously possible. In some cases the organometallic additive modifies both the burning rate and the specific impulse of the propellant.

Certain organometallic compounds of this invention can be used to reduce propellant burning rate. This is accomplished choosing the proper organometallic compound for the specific propellant grain. In some cases, an organometallic compound to reduce burning rate functions more effectively if incorporated into the grain in relatively large concentrations, say about 5 percent.

The effect of the organometallic additives on the propellant grain will vary dependent upon the concentration and type of organometallic compound and the propellant grain composition. Thus, a given organometallic compound will effectively increase the burning rate of a certain solid propellant grain, and have exactly the opposite effect with another type of propellant. In other words, the specific propellant grain compositions must be considered when choosing the organometallic additive.

Mixtures of two or more compounds of the same metal can be employed to achieve a desired result. Advantage can be taken of the fact that the different compounds will decompose at different rates and yield different combustion products. Similarly, it is sometimes desirable to use a mixture of compounds of different metals to impart superior properties to the propellant grain.

Organometallic compounds possess properties which make them superior to powders, dispersions, oxides and alloys of metals which have been previously suggested as solid propellant additives. The oxides formed during combustion by decomposition of the organometallic compounds are more widely dispersed and more energetic than metal oxides added as such to the grain. Moreover, a variety of organometallic compounds of the same metal are available with widely differing properties with respect to vapor pressure, solubility, decomposition temperature, etc. Thus, the organometallic will be superior by virtue of its ability to form a more effective decomposition product and because it can be chosen so as to decompose at the proper time. In some instances oxides of metals might be formed which are not ordinarily stable and thus cannot be incorporated into the grain as such. Additionally, the products formed from decomposition of the organo-

metallic compounds are oftentimes metastable or unstable and, therefore, extremely active. Another advantage is that the properties of the organometallic compound frequently allow it to be incorporated into a given propellant grain in a much more convenient manner than an insoluble metal oxide, alloy, or dispersion.

The organometallic compounds may be incorporated in all types of solid propellant grains. The grains may be of the composite or double base type, or a combination of these. The composite grains are composed of a mixture of a fuel and an oxidizer neither of which would burn satisfactorily without the presence of the other. With a double base type, a chemical compound capable of combustion in the absence of all other material makes up the majority of the grain. The latter type are generally composed of materials such as nitroglycerin and nitrocellulose but usually have minor amounts of other additives used to control the physical and chemical properties of the total grain.

In the composite type grains, perchlorates of sodium, potassium, magnesium or ammonium are often used as the oxidizer portion. Other oxidizers often used are inorganic nitrates of potassium, sodium and ammonium. The fuel portion, which may also serve as a binder, may be a petroleum derived hydrocarbon such as asphalt or a plastic such as phenol formaldehyde, phenol furfural resins, polystyrenes, polyurethanes, synthetic rubber, latex, polysulfides, urea aldehydes, vinyl polymers and the like. Also, finely divided metals or metal powders such as magnesium, beryllium, aluminum, boron, lithium, etc. may be included in solid propellant grains.

The organometallic additive can be incorporated into the grain at any convenient time during the manufacturing process. The time of introduction may vary greatly depending upon the specific manufacturing process in use. One particularly convenient time for introducing the organometallic is during that time when the oxidizer-fuel mixture is in a liquid state. This assures uniform blending of all the components. This expediency is possible with all solvent processes and also with most non-solvent processes wherein the mixing step includes a slurry formation. In any event the organometallic additive should be incorporated into the grain at the stage which facilitates maximum mixing and uniformity of the final grain composition.

The following solid propellant compositions wherein all percentages are in terms of weight illustrate typical compositions of this invention.

Example I

	Percent
Ammonium perchlorate	77
Asphalt	10
Cetylacetamid	3
Dibutyl sebacate	6
Dicumene chromium	4

The burning rate of this propellant is significantly increased as compared to the same propellant not containing the organochromium burning rate catalyst.

Example II

	Percent
Ammonium perchlorate	76
Asphalt	13
Cetylacetamid	3
Dibutyl sebacate	6
Bis(methylcyclopentadienyl)iron	2

The burning rate of this solid propellant is significantly increased by adding the organoiron compound.

Example III

	Percent
Ammonium perchlorate	73
Polyester	14
Styrene	12
Cyclopentadienyl chromium dinitrosyl ethyl	1

The burning rate of this solid propellant is increased by the inclusion of the organochromium compound.

Example IV

	Percent
Ammonium nitrate	82
Butadiene vinyl pyridine copolymer	10
Carbon black	2
Benzophenone	2
Cyclohexadiene iron tricarbonyl	3
Flexamine	1

The organoiron compound serves to significantly increase the burning rate of this solid propellant.

Example V

	Percent
Ammonium nitrate	76
Cellulose acetate	6
Dinitrodiphenyl ether	7
Ethylene glycol diglycolate	7
Carbon black	2
Cyclopentadienyl(diethylcyclopentadienyl)iron	2

Including the dicyclopentadienyl iron compound serves to significantly increase the burning rate of the solid propellant.

Example VI

	Percent
Ammonium nitrate	75
Sodium nitrate	8
Carbon black	3
Polyvinyl chloride	4
Dinitrotoluene	3
Dinitrodiphenyl ether	3
Acetylene dicobalt hexacarbonyl	4

This solid propellant has all the attributes contemplated by this invention.

Example VII

	Percent
Ammonium nitrate	83
Carbon black	2
Polyvinylacetate	6
Dinitrophenylpropyl ether	6
Hexaethyllead	3

Inclusion of the liquid organolead compound serves to significantly increase the burning rate of this solid propellant composition.

Example VIII

	Percent
Ammonium nitrate	78
Butadiene-vinyl pyridine copolymer	14
Carbon black	3
Dibutoxy ethoxyethyl formal	2
Tetraethyllead	3

The burning rate of this solid propellant is significantly higher as compared to the same propellant but excluding the tetraethyllead.

Example IX

	Percent
Potassium perchlorate	70
Phenol formaldehyde	10
Aluminum	18
Cyclopentadienyl cobalt dicarbonyl	2

The burning rate of this propellant is significantly improved by the inclusion of the organocobalt compound.

Example X

	Percent
Sodium perchlorate	68
Polyurethane	10
Magnesium	18
Tetramethyllead	4

The burning rate of this propellant is greater than that of the same propellant wherein the organolead compound is excluded.

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Example XI

	Percent
Lithium perchlorate -----	72
Polystyrene -----	8
Lithium -----	15
Acetylcyclopentadienyl manganese tricarbonyl -----	5

The organomanganese compound serves to increase the burning rate of this propellant.

Example XII

	Percent
Ammonium perchlorate -----	80
Asphalt -----	10
Cetylacetamid -----	2
Dibutyl sebacate -----	5
Pelargonyl methylcyclopentadienyl manganese tricarbonyl -----	3

The burning rates and combustion properties of solid propellant formulations of all types can be modified by the inclusion of our organometallic compounds therein. A tailor-made compound of a given metal can be included in the propellant grain to meet operational specifications. A large number of organometallic compounds are available with widely divergent properties. Thus, an additive can be chosen to be compatible with the propellant grain and yet have the requisite solubility, stability, temperature sensitivity, decomposition rate, etc.

The following examples further illustrate the compositions contemplated by this invention.

Example XIII

	Percent
Cellulose nitrate -----	56
Glycerol trinitrate -----	37
Carbon black -----	2
Methyl cyclopentadienyl manganese tricarbonyl -----	4
Diphenylamine -----	1

Example XIV

	Percent
Cellulose nitrate -----	63
Diethyleneglycol dinitrate -----	32
Cyclopentadienyl nickel nitrosyl -----	3.5
Diethyldiphenyl urea -----	1.5

Example XV

	Percent
Cellulose nitrate -----	88
Dibutyl phthalate -----	10
Diphenylamine -----	1
Triethyl bismuth -----	1

Example XVI

	Percent
Potassium perchlorate -----	53
Polyvinyl acetate -----	43
Triethyl thallium -----	4

References to methods for preparation of the liquid organometallic compounds which we use as additives can be found in standard texts such as Gilman "Organic Chemistry—An Advanced Treatise," John Wiley and Sons, New York, 1943; Emelius and Sharpe, "Advances in Inorganic Chemistry and Radiochemistry," Academic Press, New York, 1959; Bailar, "Chemistry of the Coordination Compounds," Reinhold Publishing Corporation, New York, 1956; Coates, "Organo-Metallic Compounds," John Wiley and Sons, New York, 2nd Edition, 1960; Krause and Von Grosse, "Chemie der Metallorganischen Verbindungen," Edward Brothers, Inc., Ann Arbor, 1943, and in many recent chemical journal articles.

We claim:

1. A solid propellant composition comprising from about 50 to 90 weight percent of an inorganic oxidizing salt, from about 10 to 50 weight percent of an organic binder, and from about 0.1 to 5 weight percent of an organometallic compound of chromium, said organo-

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metallic compound being liquid at substantially 40° C. and having at least one carbon-to-metal bond.

2. A solid propellant composition comprising from about 50 to 90 weight percent of an inorganic oxidizing salt, from about 10 to 50 weight percent of an organic binder, and from about 0.1 to 5 weight percent of an organometallic compound of manganese, said organometallic compound being liquid at substantially 40° C. and having at least one carbon-to-metal bond.

3. A solid propellant composition comprising from about 50 to 90 weight percent of an inorganic oxidizing salt, from about 10 to 50 weight percent of an organic binder, and from about 0.1 to 5 weight percent of an organometallic compound of cobalt, said organometallic compound being liquid at substantially 40° C. and having at least one carbon-to-metal bond.

4. A solid propellant composition comprising from about 50 to 90 weight percent of an inorganic oxidizing salt, from about 10 to 50 weight percent of an organic binder, and from about 0.1 to 5 weight percent of an organometallic compound of bismuth, said organometallic compound being liquid at substantially 40° C. and having at least one carbon-to-metal bond.

5. A solid propellant composition comprising from about 50 to 90 weight percent of an inorganic oxidizing salt, from about 10 to 50 weight percent of an organic binder, and from about 0.1 to 5 weight percent of an organometallic compound of lead, said organometallic compound being liquid at substantially 40° C. and having at least one carbon-to-metal bond.

6. A composition of claim 3 wherein said organometallic compound is a cyclopentadienyl cobalt dicarbonyl.

7. A composition of claim 2 wherein said organometallic compound is pelargonyl methylcyclopentadienyl manganese tricarbonyl.

8. A solid propellant composition comprising from about 50 to 90 weight percent of an inorganic oxidizing salt, from about 10 to 50 weight percent of an organic binder, and from about 0.1 to 5 weight percent of an organometallic compound of iron, said organometallic compound being liquid at substantially 40° C. and having at least one carbon-to-metal bond.

9. A composition of claim 8 wherein said organometallic compound is bis(methylcyclopentadienyl)iron.

10. A solid propellant composition comprising from about 50 to 90 weight percent of an inorganic oxidizing salt, and 10 to 50 weight percent of organic binder, and from about 0.1 to 5 weight percent of bis(methylcyclopentadienyl)nickel.

11. The composition of claim 2 wherein said liquid organometallic compound is methylcyclopentadienyl manganese tricarbonyl.

12. In the method of developing thrust comprising the combustion of a solid propellant composition in a rocket combustion chamber and the evolution of combustion gases which are exhausted from said combustion chamber, the improvement which comprises adding to said solid propellant composition from about 0.1 to 5 weight percent of an organometallic compound of iron, said organometallic compound being characterized by being liquid at substantially 40° C., and having at least one carbon-to-metal bond.

13. The improvement of claim 12 wherein said organometallic compound is bis(methylcyclopentadienyl)iron.

14. In the method of developing thrust comprising the combustion of a solid propellant composition in a rocket combustion chamber and the evolution of combustion gases which are exhausted from said combustion chamber, the improvement which comprises adding to said solid propellant composition from about 0.1 to 5 weight percent of bis(methylcyclopentadienyl)nickel.

15. In the method of developing thrust comprising the combustion of a solid propellant composition in a rocket combustion chamber and the evolution of combustion

gases which are exhausted from said combustion chamber, the improvement which comprises adding to said solid propellant composition from about 0.1 to 5 weight percent of an organometallic compound of chromium, said organometallic compound being characterized by being liquid at substantially 40° C., and having at least one carbon-to-metal bond.

16. In the method of developing thrust comprising the combustion of a solid propellant composition in a rocket combustion chamber and the evolution of combustion gases which are exhausted from said combustion chamber, the improvement which comprises adding to said solid propellant composition from about 0.1 to 5 weight percent of an organometallic compound of manganese, said organometallic compound being characterized by being liquid at substantially 40° C., and having at least one carbon-to-metal bond.

17. In the method of developing thrust comprising the combustion of a solid propellant composition in a rocket combustion chamber and the evolution of combustion gases which are exhausted from said combustion chamber, the improvement which comprises adding to said solid propellant composition from about 0.1 to 5 weight percent of an organometallic compound of cobalt, said organometallic compound being characterized by being liquid at substantially 40° C., and having at least one carbon-to-metal bond.

18. In the method of developing thrust comprising the combustion of a solid propellant composition in a rocket combustion chamber and the evolution of combustion

gases which are exhausted from said combustion chamber, the improvement which comprises adding to said solid propellant composition from about 0.1 to 5 weight percent of an organometallic compound of lead, said organometallic compound being characterized by being liquid at substantially 40° C., and having at least one carbon-to-metal bond.

19. In the method of developing thrust comprising the combustion of a solid propellant composition in a rocket combustion chamber and the evolution of combustion gases which are exhausted from said combustion chamber, the improvement which comprises adding to said solid propellant composition from about 0.1 to 5 weight percent of an organometallic compound of bismuth, said organometallic compound being characterized by being liquid at substantially 40° C., and having at least one carbon-to-metal bond.

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