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SOLID PROPELLANT CONTAINING ORGANIC OXIDIZERS AND POLYMERIC FUEL

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This invention relates to new propellants and more particularly to those propellants requiring specified physical and thermodynamic characteristics such as those suitable for small arms ammunition.

The term propellant as used herein refers to combustible materials which require no further oxygen from the atmosphere and which burn rapidly under controlled conditions to impart kinetic energy to a body.

Present day propellants, suitable for small arms ammunition for example, are primarily limited to the type having nitrocellulose as a base and containing small quantities of nitroglycerine, stabilizing agents and deterrents. Limiting the composition of the propellants to essentially nitrocellulose with small quantities of other materials such as nitroglycerin means that the performance of the propellant is confined to a narrow range with respect to flame temperature and impetus (sometimes called force). The simple expedient of increasing the nitroglycerin content to raise the flame temperature and impetus of a propellant is not workable because nitroglycerin exudes or migrates, thus causing the propellant to be unstable and unfit for extended storage.

Since the present so-called IMR propellants (consisting essentially of nitrocellulose with small quantities of deterrent, anti-flash salts, etc.) are illustrative of the nitrocellulose-base type of propellants now in use, this standard type propellant will be used as a basis for comparing the improved characteristics achieved by the propellants of this invention.

Any new type propellant should possess certain properties, namely high impetus, a flame temperature within the range which can be tolerated by the gun, thermal stability, and good storage qualities over extended periods and under a wide range of conditions. It is desirable, too, that a new type of propellant should give higher impetus (compared, for example, to that of IMR) and increased bullet velocity for an equal weight of propellant, or should give the same impetus for a lower weight of propellant, thus permitting lower charge to weight ratios. It is desirable that an increased impetus to weight ratio in an improved propellant be achieved at burning temperatures equal to or less than that reached by the present IMR propellants (about 3000° K.) to keep metal erosion to a minimum. Thus an additional improvement to be attained by a new type propellant is the development of the same impetus for the same or less weight at a lower burning temperature. However, a new type propellant should also be capable of sufficient flexibility in composition ratios so that materials can be made up having relatively high flame temperatures also. Such compositions could be conveniently used, for example, as core material in propellants formed of several layers or sections. In such an application where layers having well defined differences in flame temperatures, burning rates, etc., the various propellants making up the layers must be substantially free from components which tend to migrate or exude.

It is therefore an object of this invention to provide propellants which have greater impetus on an equal weight basis than those now known and used. It is another object to provide propellants which have greater impetus on an equal volume basis than those now known. A further object is to provide propellants, the composition ratios of which may be varied to obtain a wide range of such performance parameters as flame temperature, burning rate, etc. It is still a further object of this invention to provide propellants which possess good thermal stability over the accepted military range and which may be stored without any appreciable migration or exudation of the component materials taking place. Yet another object is to provide propellants which may be used to make up multi-layer grains. These and other objects will be seen to be accomplished by the propellants of this invention which are described in detail.

The impetus which is developed by the propellant and imparted to the bullet is a function of the quantity nRT where n is the number of moles of gas developed from the burning of the propellant, R is the gas constant expressed in appropriate units, and T is the adiabatic flame or burning temperature. The factor n is a function, in turn, of the propellant composition. T is dependent upon the composition of the final gas products and the heat of decomposition of the propellant, which in turn may be varied by varying the composition of the propellant.

If T is fixed within a fairly narrow range, for example at about 3000° K. for small arms, it must be maintained within its limiting composition and structure of the propellant. This composition and structure must, therefore, be such as to give a specified temperature while at the same time producing a maximum n, the only parameter in the quantity of nRT which may be raised to increase the impetus of the propellant. If, on the other hand, high flame temperatures are desired for a core-type propellant, for example, then T, as well as n, can be increased giving a marked increase in the nRT product. In a compound such as nitrocellulose, which generally serves as the primary component of a small arms propellant, both n and T are, of necessity, limited. On the other hand the single compounds which contain a favorable balance of carbon, hydrogen, and oxygen atoms and high heats of decomposition are generally highly explosive in character. The desired characteristics for a small arms propellant can therefore be more readily found in a suitable mixture of a high explosive, serving as an oxygen source and a means to increase n and T and a fuel providing material to burn. The use of a mixture containing a material with high available oxygen content makes possible adjustments in carbon, hydrogen and oxygen ratios, and thus the achieving of desired temperature and impetus over a wide range.

The fuel may contain oxygen but it is preferably one which is not capable of sustaining its own combustion without additional oxidants. In order to keep the number of components making up the propellant of this invention to a minimum, it is desirable that the fuel should also be capable of serving as a binder for the oxidant to make a final propellant which can be readily handled in such fabricating equipment as extruders, presses, etc.

I have found that, in accordance with the above discussion, a mixture comprising a high-energy organic material as an oxidant; a polymeric material, serving as fuel and binder; and, if necessary, a few percent of suitable plasticizers or stiffening agent and stabilizers, where required, can be so formulated to give a workable, extrudable, and stable propellant capable of achieving the objects of this invention. It is preferable that the oxygen of the organic material be present in such groups as a nitrate ester, aromatic nitro, aliphatic nitro, nitramine, azo, azide, nitroso, peroxide, ozonide, perchlorate, etc.

A propellant, for example, made up of the proper ratios of bis-(trinitroethyl)-nitramine as the high-energy oxidant, and a polyisobutylenepolyethylene mixture as the fuel and binder having a burning temperature of about 3000° K., equivalent to that for IMR, will develop an impetus equivalent to some 123% that of IMR on an

equal weight basis. If it is desired to produce a cool propellant with impetus equal to IMR, it is possible by increasing the amount of polymer to reduce the adiabatic flame temperature to about 2100° K. To illustrate the improvement of the new type propellant over the present propellants in yet another manner, it may be shown that an impetus equal to the present IMR may be attained by using only about 81% of the new propellant, density of 1.64 thus decreasing the cartridge volume.

It may be desirable to have propellants which burn at adiabatic flame temperatures considerably higher than 3000° K. to obtain short duration, high velocity firings or for one or more layers of a multilayer propellant. The compositions described in this invention make such high impetus, high temperature propellants possible, for by mixing a high-oxygen content material with an oxygen-deficient fuel binder, it is possible to adjust the composition ratio to achieve a maximum impetus. This maximum occurs at the point where just enough oxygen is present to burn all the carbon to CO_2 and the hydrogen to H_2O. For example, in the case of the bis-(trinitroethyl)-nitramine-polyisobutylene-polyethylene propellant, the molar ratio at this maximum impetus is 3 to 1 while the weight percents are 95.4% and 4.6% of bis-(trinitroethyl)-nitramine and polyisobutylene-polyethylene, respectively. Impetus developed by this mixture is equivalent to approximately 150% IMR.

The minimum amount of high-energy oxidant is that which will burn all but a predetermined amount of all of the carbon present to CO. It is not necessary to furnish oxygen for burning the hydrogen. The amount of permissible free carbon depends upon the application of the propellant, being less where flash must be kept to a minimum.

The maximum amount of high-energy oxidant which can be used depends upon the burning characteristics desired of the final propellant. That is, it is necessary to limit the quantity of the high-energy ingredient to achieve rapid burning, but not detonation. This means that there should not be more oxygen present than that required to burn all the carbon to CO_2 and the hydrogen to H_2O. The binding properties of the so-called fuel binder may also limit the proportions of the constituents. Control of the burning properties may also be achieved by adjusting the propellant geometry and by using suitable deterrents where desired.

In general, the range of the ratio of high-energy material to fuel in these new type propellants is between the ratios where the final gaseous products are CO, H_2, N_2 and where they are CO_2, H_2O, N_2; while the better range is between the ratios where the final gaseous products are CO, H_2O, N_2 and where they are CO_2, H_2O, N_2; and the preferred range is between the ratios where the final gaseous products are CO, H_2, N_2 and where they are CO, H_2O, N_2. Taking the bis(trinitroethyl)nitramine ($C_4H_4N_8O_{14}$)-polyisobutylene-polyethylene (C_4H_8, C_2H_4) propellant as an example, the general range of the ratio of the former (oxidant) to the latter (fuel) is between 73.5 to 26.5% by weight and 95.4 to 4.6%, while the better range is between 87.4 to 12.6% and 95.4 to 4.6%, and the preferred range in between 73.5 to 26.5% and 87.4 to 12.6%.

The oxidant for this new type propellant is not limited to bis(trinitroethyl)nitramine. Any high-oxygen content, reasonably stable compound, solid at normal temperatures and pressures, may be used with a compatible polymeric binder. It is preferable, although not necessary, that the oxygen in the oxidant be present in only high-energy groups. Among the other oxidants found to be suitable are cyclotetramethylenetetranitramine (HMX), cyclotrimethylenetrinitramine (RDX), methylenedinitramine, trinitroethyl trinitrobutyrate, bis(trinitroethyl) urea, and trinitroethyl nitrate.

Other polymeric fuels which may be used include any of the known hydrocarbon polymers, polymers containing nitrogen, such as polyacrylonitrile, natural rubber (polyisoprene), polyvinyl ethers, and combinations of two or more such polymers. Polymeric materials containing oxygen in non-plosophoric groups such as hydroxyl, ether, carboxyl, etc. where the oxygen has been partially reduced by being attached to the carbon atom are suitable fuel binders.

The point in the process at which polymerization of the fuel binder is achieved will depend upon the fuel binder chosen and the degree of compatibility existing between the oxidant and various degrees of polymerization of the fuel binder. Thus, the fuel binder may be completely polymerized before adding the high-energy oxidant; it may be partially polymerized before the oxidant is added and then polymerization completed; or the oxidant may be added to the unpolymerized fuel-binder and then polymerization accomplished.

Small quantities of suitable plasticizers or stiffening agents (in the order of a few percent) may be required to give the propellant suitable handling properties. Their use depends upon the polymer chosen. The necessity for such plasticizers or stiffening agents may be eliminated by blending two or more of the polymeric fuels to obtain the desired consistency for the final propellant. How this may be done is illustrated in Example 1 below. Also, small quantities of stabilizing agents may be added to prevent deterioration in storage. The plasticizer may be inert as diethylhexyl sebacate, or may be a high-energy material itself such as a polyglycol nitrate. Agents for controlling the burning rate of the propellant may also be added. For example, deterrents such as dinintrotoluene may be included to decrease burning rates while compounds such as described in my co-pending application Serial No. 516,374, filed June 20, 1955, now abandoned, may be added to increase burning rates.

Compounding of the oxidizing agent and fuel may be carried out in a suitable solvent, such as carbon tetrachloride, chloroform, xylene, or other suitable aromatic or aliphatic hydrocarbon solvents including the so-called rubber solvents, to make an easily workable propellant.

One method which I have found preferable is to cool rapidly a solution of the oxidant, fuel binder, and other additives such as stabilizers, in the solvent with vigorous agitation, and then mixing thoroughly in a multiple roll mill.

The compounding of the oxidizing agent and fuel may also be done under solventless conditions if the polymer serving as the fuel binder is in a suitable physical state for such solventless mixing. This method of mixing may be used when the fuel binder is added in an unpolymerized or partially polymerized state.

Propellants thus formulated may be extruded and cut or processed in any manner indicated by the use the propellant is to be put.

The following examples, which are considered as illustrative rather than limiting, will serve to explain the present invention in more detail.

EXAMPLE I

Twenty grams of bis(trinitroethyl)nitramine, 3.5 grams of polyethylene, and 22.5 grams of a 1/15 solution of polyisobutylene in carbon tetrachloride containing 1.5 grams of polyisobutylene of a molecular weight of approximately 100,000 were mixed in a glass flask. The mixture was heated to the point where incipient boiling of the carbon tetrachloride set in. Almost all of the bis(trinitroethyl)nitramine and polyethylene went into solution. The mixture was then poured into a small three-roll mill, the rolls having been precooled with tap water to a little above the ambient dew point. Milling was continued until sufficient carbon tetrachloride had evaporated to make the material extrudable and to reduce the particle size of the explosive which had recrystallized when cooled. This material was extruded and cut to proper length in the conventional manner for

smokeless powder manufacture. The final extruded and cut material was dried by a current of warm air.

EXAMPLE II

High-Impulse RDX Powder

Five grams of polyisobutylene having a molecular weight of about 120,000 was dissolved in a mixture of 50 ml. of a light petroleum solvent boiling range 83°–100° F., and 50 ml. benzene. This three-component mixture was put in a mixer and 45 grams of cyclotrimethylenetrinitramine (RDX) was added in the form of a very fine, dry powder (300 mesh or finer). The mixer was run until a uniform mixture was obtained, about 10 to 15 min. RDX is substantially insoluble in the solvents used but by this method is satisfactorily suspended in the binder. The soft mass was passed through a three-roll pigment mill until it became the proper consistency for extrusion. The extrusion, cutting, drying, etc. were conventional. This powder contained 90% RDX and 10% polyisobutylene.

EXAMPLE III

Cool RDX Powder

Five grams of polyisobutylene having a molecular weight of about 120,000 was dissolved in 50 ml. of a light petroleum solvent, boiling range 83°–100° F. Three grams of polyethylene was mixed with 50 ml. of benzene and heated to boiling to cause solution. This solution was poured into the polyisobutylene solution with vigorous stirring. Much of the polyethylene came out of solution but appeared to be in such finely divided form that it mixed satisfactorily with the other ingredients. This mixture was put in the mixer and 42 grams of RDX added in a finely powdered form (300 mesh). The milling, mixing, extruding and processing were the same as in Example II. This powder contained 84% RDX, 10% polyisobutylene and 6% polyethylene.

In deterring these propellants by the simple expedient of depositing a thin layer of slow burning material on the outside of the grain the technique of diffusion coating is not practical. This is because crystal faces of the organic high-energy material are exposed on the surface of the grains and the deterrent will not diffuse into such crystal faces. Deterrents may therefore be put on as a separate layer, usually on the outside if it is a grain of one composition only, or as one of the layers in a multilayer grain.

The powders formulated in the manner described in this invention provide propellants for such applications as small arms ammunition which are capable of producing higher bullet velocities than previously attained, or which require less powder for velocities comparable to those now achieved. These propellants also provide a flexibility in performance characteristics hitherto not achieved.

I claim:

1. A new-type propellant composition in the form of discrete solid pieces and consisting essentially of an intimate mixture of a solid high-energy, organic, oxygen-containing compound the oxygen of which is contained in a radical selected from the group consisting of nitrate, aromatic nitro, aliphatic nitro, nitramine, nitroso, peroxide, ozonide and perchlorate, the number of atoms of oxygen in said radical being greater than the number of atoms of carbon in said high-energy organic compound, and a hydrocarbon, polymeric fuel binder incapable of supporting its own combustion and selected from the group consisting of polyethylene, polyisobutylene, polyacrylonitrile, natural rubber, polyvinyl ether, and mixtures thereof; the weight ratio of said high-energy organic compound to said polymeric fuel binder being so adjusted as to provide at least one atom of oxygen for each atom of carbon in said high-energy compound and said fuel binder.

2. Propellant in accordance with claim 1 wherein said high-energy organic compound is cyclotrimethylenetrinitramine.

3. A new-type propellant composition in the form of discrete solid pieces and consisting essentially of an intimate mixture of a solid high-energy organic oxygen-containing compound selected from the group consisting of bis(trinitroethyl)nitramine, cyclotrimethylenetrinitramine, cyclotetramethylenetetranitramine, methylenedinitramine, trinitroethyl trinitrobutylrate, bis(trinitroethyl)-urea, and trinitroethyl nitrate, and a hydrocarbon polymeric fuel binder incapable of supporting its own combustion and selected from the group consisting of polyethylene, polyisobutylene, polyacrylonitrile, natural rubber, polyvinyl ether, and mixtures thereof; the weight ratio of said high-energy organic compound to said polymeric fuel binder being so adjusted as to provide at least one atom of oxygen for each atom of carbon in said high-energy compound and said fuel binder.

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