

1

3,725,154

MESA BURNING GAS GENERATOR PROPELLANT
Charles R. McCulloch and Bertram K. Moy, Shalimar,
Fla., and Thomas C. Randle, Oxon Hill, Md., assignors
to the United States of America as represented by the
Secretary of the Navy
No Drawing, Filed June 23, 1972, Ser. No. 265,938
Int. Cl. C06b 11/00

U.S. Cl. 149-21

10 Claims

ABSTRACT OF THE DISCLOSURE

A gas generating composite propellant having plateau and mesa burning characteristics, and containing a primary oxidizer which can vary in size from about 5 microns to about 20 microns and a coolant oxidizer which can vary in size from about 40 microns to about 600 microns.

BACKGROUND OF THE INVENTION

One principal type of solid gas generating propellant useful in rockets, torpedoes, inflation devices, etc., is the composite propellant type which comprises a binder and an oxidizer. The propellant can also contain a fuel and any other conventional additives such as plasticizers, curing agents, stabilizers, burning-rate additives, catalysts, etc.

One of the most important solid propellant parameters is the burning rate of the propellant. The basic solid propellant burning equation for restricted solid propellants, such as the type with which this invention is concerned, is expressed as:

$$r = cp^n$$

where r is the burning rate in inches per second, p , is the combustion pressure in pounds per square inch, c is a constant which varies with the ambient grain temperature and the particular propellant, and n is a constant known as the burning rate exponent and is characteristic of the particular propellant.

In many instances, a propellant will be chosen such that n is a positive value lying between 0 and 1. However, relatively recently, a great deal of interest has emerged in the development of plateau and mesa type propellants, wherein the value of n is 0 and negative, respectively. The value of n is determined by the slope of the straight line produced by the logarithmic graph of the burning rate of propellant plotted against pressure, since the burning rate equation can be reexpressed as $\log r = n \log p + \log c$. Thus, a plot of $\log r$ against $\log p$ for a conventional propellant gives a straight line which has a positive slope, representative of a progressive increase in burning rate for each increase in pressure. However, in the case of plateau type propellants, the pressure exponent n becomes zero in a certain region of pressure. Such propellants at a given temperature give a steady burning rate within the region and, consequently, a steady thrust. Since mesa propellants have a negative slope, the pressure stability of these propellants is even more favorable than for the plateau propellants and temperature dependency is also further improved.

There are a number of well known advantages to propellants exhibiting this "plateau" and "mesa" phenomena. For example, with many conventional propellants, pressures build up rapidly and a thick walled chamber is needed to contain the propellant tending to make rockets thus powered heavy and poor in ballistic performance. Pressure relief valves are commonly used in missile or guidance systems to prevent overpressurization of the unit and these valves are intricate in design, costly and easily clogged. If these valves are not included, too great a pressure could lead to too great a

2

burning rate, and it could either blow up the rocket or prevent proper guidance, therefore aborting the mission. The disadvantages of normal burning propellants are overcome by the plateau and mesa type propellants. Moreover, the mesa propellants exhibit advantages not possessed by plateau type propellants. For example, there is often an inherent tendency, in mesa type propellants, for overlapping of rate-pressure relationships at various temperatures as illustrated by logarithmic graphs of the relationships; that is, in certain regions of pressure, the burning rate of a propellant for firings at low temperature may be actually higher than the burning rate for firings at high temperature. Additionally, the variations in performance with change in temperature for mesa type propellants is negligible and in some cases, there is none at all. In light of the above enumerated advantages, it has now become desirable to formulate plateau and mesa burning propellants.

Furthermore, many presently available composite type gas generating propellants are currently based on ammonium nitrate as the oxidizer. However, these systems give too low and too limited a range of burning rates and in addition are hygroscopic and require stringent atmospheric controls. Systems based upon cyclotetramethylene tetranitramine as the oxidizer are also relatively slow burning and have high burning rate pressure exponents. Those systems based on perchlorate or dihydroxy glyoxime exotherm at 135° C. and are therefore not as stable as one would desire. In addition, the latter type propellants all burn to yield pressure exponents of 0.20 to 0.80.

SUMMARY OF THE INVENTION

It is an object of this invention to provide novel composite solid rocket propellants.

Another object of the instant invention is to provide a novel composition suitable in gas generators.

Another object of the present invention is to produce a propellant composition which has mesa or plateau burning characteristics.

It is still another object of this invention to produce a propellant which is non-hygroscopic.

It is yet another object of the instant invention to formulate a propellant having satisfactorily high burning rates.

It is even another object of the instant invention to produce a propellant which is stable.

These and other objects are accomplished by a composite propellant composition which comprises, as the oxidizer thereof, a mixture of a primary oxidizer with a coolant oxidizer wherein the particles of oxidizer have certain critical size limitations.

DESCRIPTION OF THE PREFERRED EMBODIMENT

It has been found that a mesa or plateau burning propellant can be obtained by utilizing a certain oxidizer combination in a conventional composite propellant comprising an oxidizer and binder.

The novel oxidizer combination of the instant composite propellant compositions comprises a mixture of a primary oxidizer and a coolant oxidizer wherein the primary oxidizer has a size which can range from about 5 to about 20 microns, preferably 10 to 20 microns, while the coolant oxidizer has a size which will vary from about 400 to about 600 microns. The primary oxidizer is selected from the group consisting of ammonium perchlorate, cyclotrimethylene trinitramine, cyclotetramethylene tetranitramine and pentaerythritol tetranitrate, while the coolant oxidizer is selected from the group consisting of ammonium sulfate, ammonium phosphate, ammonium sulfite, ammonium selenate, ferrous ammonium

3

sulfate, and sulfur. The amount of combined oxidizer present in the propellant composition can vary between about 70 and about 88 percent by weight of the total propellant composition. The amount of primary oxidizer can vary from about 50 weight percent to about 65 weight percent of the propellant composition while the amount of coolant oxidizer can vary between about 20 weight percent and about 30 weight percent by weight of the entire composition. A preferable propellant composition would contain ammonium perchlorate and ammonium sulfate, preferably in the amounts of 55 percent and 22 percent, respectively.

Any conventional binder may be utilized, such as polyurethanes, hydroxy and carboxy polybutadienes, poly 1,2-polybutadiene copolymerized with styrene or butyl acrylate oligomers, or any other well known binder. Any other conventional ingredient may be added which has been heretofore added to composite propellants. For example, the fabricator of solid propellants often seeks to control the burning rate of a solid propellant by utilizing small amounts of burning rate catalyst, such as carbon black, copper chromite, copper sulfate, ferrocene, ferrocene derivatives, cuprammonia sulfate, ferric sulfate, ferric sulfide, and, more preferably, iron oxide or milori blue. The amount of burning rate catalyst that is generally added to the propellant compositions can vary from about 0.05 percent to about 4 percent by weight of the propellant composition. The amount of binder present in the propellant composition is determined by the amount of oxidant, catalyst and any other conventional ingredient present, as the binder comprises the balance of the composition.

These propellants of the instant invention are non-hygroscopic and require minimal atmospheric control. Moreover, they are more stable than ammonium nitrate based propellants as they begin to exotherm at a higher temperature. For example, a propellant containing ammonium perchlorate and ammonium sulfate has an exotherm which does not begin until 170° C. The primary feature of the propellants of this invention is that they have either plateau or mesa burning characteristics. Thrust variations resulting from grain defects, inhibitor failure, nozzle erosion or nozzle buildup, are essentially self-compensating. Mechanical relief valves which are essential to gas generator systems with positive pressure exponents can be simplified or eliminated.

The particle sizes of the primary and coolant oxidizers are critical as only the indicated particle sizes will produce the unexpected results of the instant invention, namely, mesa or plateau burning characteristics. In addition, it has been found that the burning rates do not increase with decreasing particle size as one would expect, and a burning rate slower than would be expected enables better guidance of a rocket. In addition, it is noted that the larger the size of the coolant oxidizer, the deeper and more pronounced the mesa effect and the dip in the burning rate-pressure.

As exemplary of the invention and advantages to be obtained thereby, the following example is set forth. This example is not intended to limit the invention as the invention is susceptible to different modifications which will be recognized by one of ordinary skill in the art.

A propellant composition was made up of the following:

Ingredient:	Percent by weight of composition
Ammonium perchlorate—12 microns	55.0
Ammonium sulfate—525 microns	22.0
TP 4040 (a polyurethane) ¹	22.9
Milori blue	0.1

¹ TP 4040 is a 1,2-propylene oxide extended trimethylol propane having a molecular weight of about 4040 and containing about 1.6 percent by weight of HDI as a curative.

4

The following data was obtained for the above formulation:

Ballistics:

Impulse, sec. (shifting) 1000/14.7	183.2
T _c , ° F.	2022
T _b , ° F.	981
Density, lb./in. ³	0.057
Gas, mol, chamber	4.625
Gas, mol, exhaust	4.220
C ¹ , ft. sec. (shifting)	3670
Ht. of explosion, cal./grm.	780

Burning rate (1000 p.s.i.a.) (in./sec.):

Temp, ° F.:	
165	0.173
77	0.114
-65	0.077
π _k , percent/° F.	0.33
Pressure exponent (500-1500 p.s.i.)	0

DTA (° F.):

Onset of autoignition	338
Autoignition	403

Safety data:

Impact:

5 kg wt. (3 consec posit.)	mm-- 150
2 kg. wt. 20 til.	mm-- 262
Sliding friction, 8 ft./sec., 20 til.	lb-- 960
Electrostatic, 5K volts, 20 til.	joules-- 12.5

Exhaust gas composition (mol percent):¹

H ₂ O	25.62
CO ₂	19.57
H ₂	21.48
HCl	11.10
N ₂	9.5
CH ₄	4.90
CO	3.88
H ₂ S	3.87

¹ No particulate exhaust.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention; and it is to be understood that the foregoing discussion merely represents preferred embodiments which do not unduly limit this invention.

We claim:

1. A gas generating solid composite propellant composition comprising a conventional composite propellant binder and an oxidizer component; wherein said oxidizer component consists of a mixture of a primary oxidant selected from the group consisting of ammonium perchlorate, cyclotrimethylene trinitramine, cyclotetramethylene tetranitramine, and pentaerythritol tetranitrate, and a coolant oxidizer selected from the group consisting of ammonium sulfate, ammonium phosphate, ammonium sulfite, ammonium selenate, ferrous ammonium sulfate, and sulfur; and wherein the particles of said primary oxidizer can range in size from about 5 microns to about 20 microns while the particles of said coolant oxidizer can range in size from about 400 to about 600 microns.

2. The composition of claim 1 wherein said primary oxidizer ranges in size from 10 to 20 microns.

3. A composition according to claim 2 wherein said primary oxidizer is present in amounts that can vary from about 50 to about 65 percent by weight of the total propellant composition and said secondary oxidizer can vary from about 20 to about 30 weight percent of the total propellant composition.

5

4. The composition of claim 3 wherein said oxidizer component comprises from about 70 to about 88 percent by weight of the total composition.

5. The composition of claim 4 wherein said primary oxidizer is ammonium perchlorate and said coolant oxidizer is ammonium sulfate. 5

6. A composition according to claim 5, containing 55 weight percent of ammonium perchlorate and 22 weight percent of ammonium sulfate.

7. The composition of claim 1 wherein said primary oxidizer is ammonium perchlorate and said coolant oxidizer is ammonium sulfate. 10

8. The composition of claim 2 wherein said primary oxidizer is ammonium perchlorate and said coolant oxidizer is ammonium sulfate. 15

9. The composition of claim 7 wherein said ammonium perchlorate is present in amounts that can vary from about 50 to about 65 percent by weight of the total propellant composition and said ammonium sulfate can vary from about 20 to about 30 weight percent of the total propellant composition. 20

6

10. The composition of claim 8 wherein said ammonium perchlorate is present in amounts that can vary from about 50 to about 65 percent by weight of the total propellant composition and said ammonium sulfate can vary from about 20 to about 30 weight percent of the total propellant composition.

References Cited

UNITED STATES PATENTS

3,053,710	9/1962	Osborn et al.	149—76 X
3,149,009	9/1964	Ratliff	149—76 X
3,535,246	10/1970	Crowell	149—44 X

STEPHEN J. LECHERT, JR., Primary Examiner

U.S. Cl. X.R.

149—76, 92, 93, 110, 111, 113, 114