TEMPERATURE RESISTANT PROPELLANTS CONTAINING CYCLOTETRAMETHYLENETETRANITRAMINE

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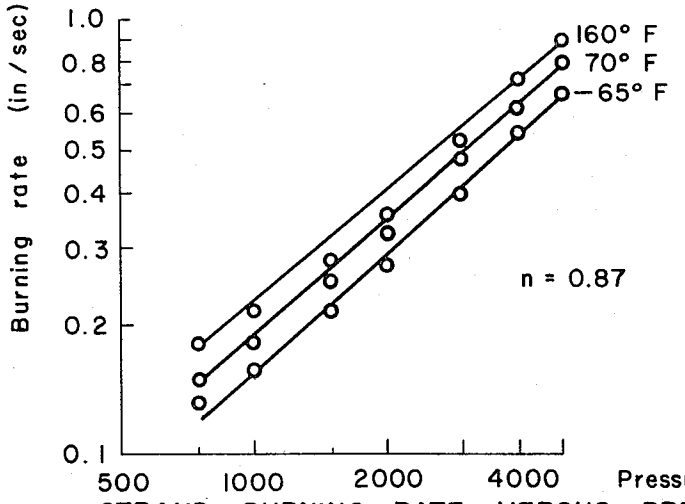


FIG. 1

STRAND BURNING RATE VERSUS PRESSURE

69 % HMX, 15 % potassium perchlorate, 16 % polyglycol adipate

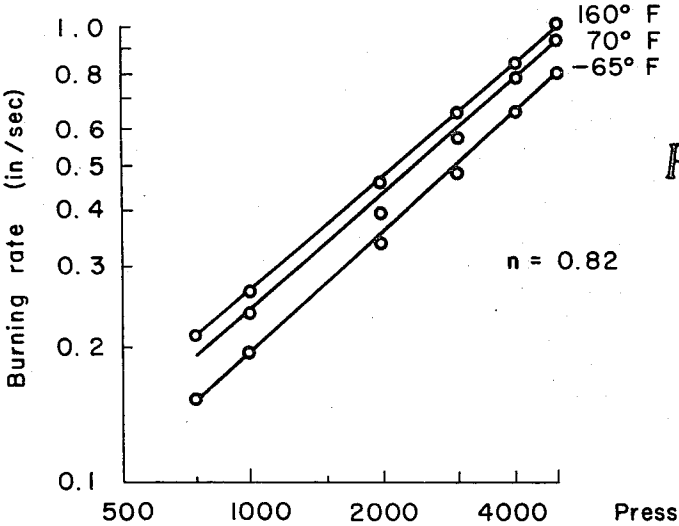


FIG. 2

STRAND BURNING RATE VERSUS PRESSURE

69 % HMX, 15 % potassium perchlorate, 14 % polyglycol adipate, 2 % copper chromite

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TEMPERATURE RESISTANT PROPELLANTS CONTAINING CYCLOTETRAMETHYLENETETRANITRAMINE

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Continuation-in-part of application Ser. No. 643,292, May 23, 1967. This application July 1, 1969, Ser. No. 839,802

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9 Claims

ABSTRACT OF THE DISCLOSURE

An oxidant for composite propellants comprising the admixture of HMX with potassium perchlorate.

A composite propellant wherein the above oxidant is incorporated with a fuel-matrix binder.

CROSS REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of application Ser. No. 643,292, filed May 23, 1967, now abandoned.

BACKGROUND OF INVENTION

This invention relates generally to composite type propellants and more specifically to a new oxidant mixture for composite type propellants and a novel composite propellant using the aforementioned oxidant.

Solid propellants are classified as either double base or composite depending upon their composition. The composite type is characterized by high thermal stability and burning rate and generally consists of a finely ground crystalline oxidant dispersed in a matrix of a plastic, resinous or elastomeric fuel. The double base compositions are characterized by high impetus and high burning rate and generally consist of an unstable self-combustible material such as the mixture of nitrocellulose with nitroglycerin.

Recent developments in the field of cartridge activated devices, specifically in the field of emergency personnel escape devices, have now generated a demand for a propellant characterized not only by high impetus and high burning rate, normally characteristic of double base propellant, but also by high temperature thermal stability (>300° F.) normally characteristic of the composite propellant. Neither the presently available composite nor the presently available double base propellants are capable of meeting these more stringent requirements; the double base type is insufficiently thermally stable and the composite type, while satisfying the high thermal stability, impetus and burning rate, tends to form corrosive and toxic gases and large quantities of carbon and carbon monoxide as by-products of combustion.

Since the oxidizer is the major constituent of composite propellants it contributes most to burning characteristics. The most common oxidizers presently available to the art have been potassium perchlorate, ammonium perchlorate, ammonium nitrate and sodium and potassium nitrate. While potassium or sodium perchlorate are characterized by relatively high burning rates and high flame temperatures, they tend to produce large quantities of corrosive and toxic hydrogen chloride gas which tends to destroy the cartridge and bomb ejector hardware. They also tend to produce a very dense smoke of the respective chloride salts and are subject to secondary flash characteristics. Sodium perchlorate is further unsuitable due to its high water solubility and high hydroscopicity.

Formulations containing ammonium perchlorate have a significantly lower burning rate and flame temperature and although not subject to formation of excessive smoke to tend to produce corrosive gases and are also undesirably hygroscopic. The nitrates are excessively slow burning and possess unduly low flame temperatures.

SUMMARY OF INVENTION

Accordingly it is an object of this invention to provide an improved composite propellant suitable for use in cartridge activated personnel escape devices.

Another object of this invention is to provide an oxidant for composite propellants, characterized by high impetus, high burning rate and high thermal stability (above about 300° F.) yet which is clean burning and does not form toxic and corrosive gases during combustion.

These and other objects are attained by providing a novel oxidant mixture in which a portion of the oxidant is a nitramine composition. Specifically these objects are attained by providing the mixed oxidant composition of from about 5–45 parts by weight of potassium perchlorate with from about 95–55 parts by weight of cyclotetramethylenetetranitramine (HMX). The oxidant mixture of this invention incorporates the thermal stability, nonhygroscopicity, high burning rate and high impulse characteristics of potassium perchlorate with the low corrosion and clean burning properties of the nitramines.

DESCRIPTION OF THE DRAWINGS

FIG. 1 and FIG. 2 are graphical representations of the burning rate performance characteristics of the preferred embodiments of this invention.

DETAILED DESCRIPTION

The composite propellants of this invention may use any elastomeric, plastic or resinous binder as the fuel matrix, such as the polyurethanes, polysulfide rubber, polyvinylchloride, epoxy resins, polyesters, hydrocarbon rubber, asphalt or acrylic polymers. Among those binders which are particularly applicable are the polymers of butadiene and acrylic acid such as Butarez CTL–II, the polymerization product of ethylenediamine and linoleic acid, the terpolymer of 2-methyl-5-vinyl-tetrazole/ethyl acrylate/acrylic acid, which is the subject of Navy Case 45,473 submitted by H. S. Haiss and J. U. Lowe, Jr., polyglycol adipate, and epoxy resins such as Epon 812, the diglycidyl ether of bisphenol A. The binder may additionally be cured with any of the common crosslinking agents such as DER–332 a diepoxide (MAPO) trismethylaziridinyl phosphine oxide and chromium naphthanate, and the like.

Preferably the nitramine component is mixed with potassium perchlorate in a ratio of 19:1 to 1.2:1. More preferably however is the admixture of from 80–60 parts by weight nitramine with 10–30 parts by weight potassium perchlorate.

The oxidant mixture is generally present in amounts of from about 50–95 parts per 100 parts of propellant, and more preferably in amounts of from almost 80–95 parts per 100 parts of propellant.

Other additives normally incorporated into solid oxidants and composite propellants may be added herein, such as any of the various accelerators, burning rate catalysts, extenders, reinforcing agents and fillers.

Burning characteristics may be improved for example by incorporating ammonium picrate, ferrocene, or aluminum powder, or the grains may be glazed with carbon black as a reinforcing agent. Burning rates can easily be obtained between 0.200–0.400 in./sec. at 1000 p.s.i.

The burning rate exponent (n) of Vieille's law, may be improved by incorporating a synergist such as those described in U.S. Pat. 3,138,499 filed by A. T. Camp which include copper chromite, lead salicylate, lead stearate and lead resorcylate. A preferred burning rate modifier is lead chromate ($PbCrO_4$).

To more clearly illustrate the present invention reference is made to the following examples which are pre-

sented for purposes of illustration and not to be restrictive in any manner. The following formulations were prepared in 2 pound quantities.

Example I

Composition: 69% HMX, 15% potassium perchlorate, 16% polyglycol adipate
Density: 1.618 g./cc.
Specific impulse, ideal: 229.61 lbf.-sec./lbm.
Flame temperature: Chamber, 4073°/F.; exhaust, 1483°/F.
Impact sensitivity: 3 til, 250 mm. (5-kg. wt.); 20 til, 262 mm. (2-kg. wt.) Allegany Ballistics Laboratory tools
Vacuum stability: 0.54 cc./g., 248° F./40 hr.
Autoignition temperature (DTA): 457° F.
Weight loss after storage of 28 days at 203° F.: 0.4%
(1) Burning rate: 0.223 in./sec. at 1000 p.s.i.
(2) Burning rate after storage: 0.279 in./sec. at 1000 p.s.i.
Weight loss after storage for 4 hours at 400° F.: 1.4%
Thermal stability at 302° F.:

Time (hr.):	Weight loss (percent)
24	0.3
48	1.0
96	1.4

Impetus: 369,800 lbf./lb.
Pressure exponent (n): 0.87

Example II

Composition: 69% HMX, 15% potassium perchlorate, 14% polyglycol adipate, 2% copper chromite
Density: 1.735 g./cc.
Specific impulse, ideal: 228.87 lbf.-sec./lbm.
Flame temperature: Chamber 4173° F.: exhaust 1558° F.
Impact sensitivity: 3 til, 200 mm. (5-kg. wt.): 20 til, 328 mm. (2-kg. wt.)
Vacuum stability: 0.45 cc./g., 248° F./40 hr.
Autoignition temperature (DTA): 441° F.
Weight loss after storage of 28 days at 203° F.: 0.4%
(1) Burning rate: 0.248 in./sec. at 1000 p.s.i.
(2) Burning rate after storage: 0.237 in./sec. at 1000 p.s.i.
Weight loss after storage of 4 hours at 400° F.: 5.8%
Thermal stability at 302° F.:

Time (hr.):	Weight loss (percent)
24	0.86
112	3.4
142	4.2
425	10

Burning rate after 445 hr. at 302° F.: 0.297 in./sec. at 1000 p.s.i.
Impetus: 365,000 lbf./lb.
Pressure exponent (n): 0.82

The variation of burning rate with temperature and pressure of these propellants is shown in FIGS. 1 and 2. n is the slope of the curve plotted on the log-log scale and represents the burning rate constant.

Example III

HMX	55.0
Potassium perchlorate	20.0
2-methyl-5-vinyl tetrazole/ethyl acrylate/acrylic acid (mol wt. 475)	23.0
Epon 812	2.0

Burning rate at 1000 p.s.i. (in./sec.): 0.272

Example IV

HMX	58.0
Potassium perchlorate	20.0
2-methyl-5-vinyltetrazole/ethyl acrylate/acrylic acid (mol wt. 475)	20.3
Epon 812	1.7

Burning rate at 1000 p.s.i. (in./sec.): 0.401

Example V

	Percent
HMX	64
Potassium nitrate	20
Lead carbonate	2
PGA	14

Burning rate at 1000 p.s.i. (in./sec.): 0.227

Example VI

	Percent
HMX	69
Potassium perchlorate	15
Butarez CTL–II	12
DER–332	0.5
MAPO	1.3
Chromium naphthenate	0.2
Copper chromite	2

Burning rate at 1000 p.s.i. (in./sec.): 0.235

Example VII

Composition: 69% HMX, 15% potassium perchlorate, 14% polyglycol adipate, 2% $PbCrO_4$
Density: 1.846 g./cc.
Impact sensitivity: 3 til, 125 mm. (5 kg. wt.) 20 til, Allegany Balistics Laboratory tools, 262 mm. (2 kg. wt.)
Vacuum stability: 0.35 and 0.27 cc./g. at 248° F./40 hr.
Autoignition temperature (DTA): 452° F. (18° F./min.)
Thermal stability at 302° F.: 500 hours with less than 10% weight loss
Thermal stability at 400° F. for 4 hours: Weight loss 2.4%
Burning rate exponent (n): 0.83 (750 to 3000 p.s.i.)
πk=0.49% ° F.
σ^p=0.10% ° F.
Mechanical properties: Sm 258 p.s.i., Em 6.15%
Impetus: 4.3×10^6 in. lb./lb.

In the foregoing examples impact sensitivity was determined by subjecting a small quantity of confined explosive to the transmitted shock from a falling weight (5 kg. and 2 kg.), and by determining the minimum height of fall that will cause at least one explosion in a given number of drops. In the Allegany Ballistics Laboratory test, 0.02 gm. of the material to be tested is spread evenly over an area of 1 cm. in diameter and confined by means of a plunger having a tip 1 cm. in diameter. A falling weight of 2 kg. strikes the upper end of the plunger. The results are recorded as minimum height to effect explosion in 20 drops.

To check the accuracy of this test, impact sensitivity was measured using a standard 5 kg. weight and the minimum height to effect explosion in 3 drops was recorded.

Vacuum stability measurements were made by placing a 1 gm. sample into an evacuated chamber situated in a hot water bath of 248° F. for 40 hours. The amount of gas formed was recorded in cc./gm.

Table I below contains comparative data illustrating the unexpected greater thermal stability of the HMX compositions of the present invention over similar RDX formulations.

TABLE I

Composition	Temperature, ° F.	Time (hours)	Percent weight loss
RDX (0.499 grams)	302	24	5
HMX (0.501 grams)	302	64	0.8
Example VII (1.364 grams)	302	24	0.63
Do		64	1.4
69% RDX, 15% potassium perchlorate, 14% polyglycol adipate, 2% $PbCrO_4$ (1.308)	302	24	7.1
Do	302	64	48

Other advantages of the propellants of this invention will be apparent to those skilled in the art in view of the above disclosure and various modifications can be made without departing from the scope of this invention.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A solid oxidizer for a composite type propellant comprising the admixture of from about 5–45 parts by weight of potassium perchlorate with from about 95–55 parts by weight of cyclotetramethylenetetranitramine.

2. A composite type, thermally stable, low corrosive propellant which comprises:

(a) an oxidizer comprising the admixture of from about 5–45 parts by weight of potassium perchlorate with 95–55 parts by weight of cyclotetramethylene-tetranitramine and

(b) a matrix of a fuel-binder composition selected from the group consisting of polysulfide rubber, polyurethane, polyvinylchloride, epoxy resins, polyesters, hydrocarbon rubber, asphalt and acrylic polymer.

3. The composite type propellant of claim 2 wherein the fuel-binder composition is selected from the group consisting of poly (butadiene-acrylic acid), the polymerization product of ethylenediamine and linoleic acid, the terpolymer of 2-methyl-5-vinyl-tetrazole, ethyl acrylate and acrylic acid, and the diglycidyl ether of bisphenol A.

4. The composite type propellant of claim 2 wherein the fuel-binder composition is the terpolymer of 2-methyl-5-vinyl-tetrazole, ethyl acrylate and acrylic acid.

5. The composite type propellant of claim 2 wherein the fuel-binder composition is polyglycol adipate.

6. The composite type propellant of claim 2 wherein the fuel-binder composition is the diglycidyl ether of bisphenol A.

7. The composite type propellant composition of claim 2 wherein a small quantity of a burning rate synergist is admixed with (a).

8. The composite type propellant composition of claim 7 wherein the burning rate synergist is selected from the group consisting of lead chromate, copper chromite, lead salicylate, lead stearate, and lead B-resorcylate.

9. The composite type propellant composition of claim 5 which comprises, on a weight percent basis, 69 percent of cyclotetramethylenetetranitramine, 15 percent potassium perchlorate, 14 percent polyglycol adipate and 2 percent lead chromate.

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