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[54] GAS GENERATOR COMPOSITIONS

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[73] Assignee: **The United States of America as represented by the Secretary of the Navy**

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[52] **U.S. Cl.** **149/18,** 149/20, 149/88, 149/92, 149/93, 149/96

[51] **Int. Cl.** **C06d 5/06**

[58] **Field of Search** 149/18, 19, 93, 97–99, 149/92, 96, 20

[56] **References Cited**

UNITED STATES PATENTS

2,942,964	6/1960	Birgwald et al.	149/19
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EXEMPLARY CLAIM

1. A gas generator composition consisting essentially of a fuel selected from

cellulose acetate, nitrocellulose and mixtures thereof;

an energetic plasticizer selected from the group consisting of trimethylolethane trinitrate, pentaerythritol trinitrate, diethylene glycol dinitrate and mixtures thereof;

a nonenergetic plasticizer selected from the group consisting of hydroxypropylglycerol, diethyl phthalate and dibutyl phthalate;

a stabilizer sedected from the group consisting of N-methyl-p-nitroaniline, ethyl centralite and resorcinol; and

a ballistic modifier selected from the group consisting of dibutyl tin maleate, lead salicylate, manganese dioxide, stannic oxide, zinc carbonate, monobasic cupric salicylate, monobasic lead beta resorcylate, monobasic lead salicylate and mixtures thereof.

8 Claims, No Drawings

GAS GENERATOR COMPOSITIONS

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to solid propellant compositions and in particular to an improved gas generator composition.

In recent years a considerable amount of research has been expended on improving the performance characteristics of solid propellants. Many compounds have been found which have the ability to change the burning properties of propellants, which are among their most important. Experiences gained from utilizing solid propellants have shown that the burning rate is influenced by the pressure of the gas in contact with the burning surface, by the temperature of the unburned propellant, by the velocity of the gas past the burning surface, and finally, by the composition of the propellant. The present invention provides a new propellant composition which is useful over a wide environmental range and which meets exacting requirements for auxiliary power sources in guided missiles.

It is therefore an object of the present invention to provide a propellant composition for modern missile systems.

Another object is to provide a propellant composition capable of being formed in a wide variety of grains and shapes, all with improved chemical and physical properties.

A further object is to provide a propellant composition which is relatively simple to manufacture and safe to handle.

Other objects, features and many of the attendant advantages of this invention will become readily appreciated as the same become better understood by reference to the following detailed description.

The present invention is for a gas generator composition comprising a fuel consisting of cellulose acetate, nitrocellulose, and mixtures thereof, either in commercial or plastisol form; an energetic plasticizer selected from the group consisting of trimethylolethane trinitrate (TMETN), pentaerythritol trinitrate (PETriN), diethylene glycol dinitrate (DEGN), and mixtures thereof; a nonenergetic plasticizer selected from the group consisting of hydroxypropylglycerol, diethyl phthalate, and dibutyl phthalate; a stabilizer for nitrate esters such as N-methyl-p-nitroloaniline and resorcinol and a ballistic modifier selected from the group consisting of dibutyl tin maleate, stannic oxide, zinc carbonate, lead salicylate, manganese dioxide, monobasic cupric salicylate, monobasic lead beta resorcylate, monobasic lead salicylate and mixtures thereof.

The solid grain utilizing the plastisol form of fuel ingredients is generally prepared by mixing the components together at room temperature in a sigma blade mixer for about 30 minutes until a homogeneous mixture results. The mixture is then cast in a rocket motor tube or casing and oven cured at temperatures between 120° and 180° F. for about 2 hours. The components, except the ballistic modifier, may also be mixed into a paste and rolled during which process the ballistic ingredient is added to the moist sheet of propellant. The ballistic modifier is worked in during the rolling mill action forming a rubbery sheet of modified propellant. The mixture may also be extruded into various grain forms.

The plastisol cellulose acetate was prepared by first dissolving pulverized cellulose acetate in a quantity nitromethane to form a lacquer. While this process is proceeding, a mixture of petroleum sulfonate emulsifying agent sold under the trade name Petromix, and water was poured into a colloid mill. The mill was put into operation and the lacquer made in the first step was slowly added. The mill was operated until an emulsion formed which was agitated for about 30 minutes in water at approximately 100° F. The wet plastisol material was then passed through a 200-mesh stainless steel screen and into a centrifuge. The material was vacuum dried at 180° F. for about 2 days. A dry, lump-free, plastisol cellulose acetate results which is free-flowing and has a reduced static charge.

Plastisol nitrocellulose into tiny, dense, spheres (of the order of 10 microns in diameter). The method is disclosed in

patent application, Ser. No. 761,448, filed Sept. 16, 1958, and is as follows: 90 grams of nitrocellulose (12.6% N), 1.2 grams of ethyl centralite and 1.4 liters of nitromethane placed in a flask and stirred vigorously until dissolution occurred. Stirring continued for an additional 10 minutes to insure homogeniety. To the resulting lacquer was added 19.2 grams of petroleum sulfonate emulsifying agent for nitrocellulose in about 900 ml. of water. This mixture was circulated through a colloid mill for about 10 minutes, then the resulting emulsion was drained from the mill into about 30 liters of water and stirred for about 15 minutes until a nitrocellulose precipitate formed which was filtered from the liquid, washed in hexane, dried for about 16 hours and sifted through a 200-mesh screen.

The following are representative examples of the preferred compositions prepared in accordance with this invention and should not be considered as limiting it.

EXAMPLE I

Ingredients	Percent by weight
Plastisol cellulose acetate	45.0
Metriol trinitrate (TMETN)	44.0
Dibutyl phthalate	5.0
Dibutyl tin maleate	5.0
N-methyl-p-nitroaniline	1.0
Following is data for the above composition:	
Measured heat of explosion	538 cal./g.
Temperature coefficient at 70° F. and 1000 p.s.i.a.	0.704
Pressure exponent, n, 70° F. Pressure interval: 400–2,000	0.66

EXAMPLE II

Ingredients	Percent by weight
Cellulose acetate	45.5
Trimethylolethane trinitrate	47.5
Resorcinol	1.0
Dibutyl tin maleate	3.0
Monobasic lead β-resorcylate	3.0

EXAMPLE III

Ingredients	Percent by weight
Plastisol cellulose acetate	35.0
Trimethylolethane trinitrate	46.0
Hydroxypropylglycerol	13.0
N-methyl-p-nitroaniline	1.0
Dibutyl tin maleate	5.0
Firing results:	
Heat of explosion	577 cal./g.
Pressure exponent, 70° F.	0.65
Burning rate in./sec.	
at 550 p.s.i. (70° F.)	0.034
at 820 p.s.i. (130° F.)	0.051

EXAMPLE IV

Ingredients	Percent by weight
Plastisol Nitrocellulose (12.6% N)	30.4
Cellulose acetate	7.6
Ethyl centralite	2.0
Pentaerythritol trinitrate	39.9
Dibutyl phthalate	16.6
N-methyl-p-nitroaniline	1.0
Zinc carbonate	2.5

The following data was obtained for the above composition:

Measured heat of explosion	660	cal./g.
Temperature coefficient at 70° F. and 500 p.s.i.	0.39	
Pressure exponent at 70° F. *n*		
Pressure interval: 400–950	0.43	
950–2,000	0.81	

EXAMPLE V

Ingredients	Percent by weight
Plastisol Nitrocellulose (12.6% N)	30.4
Cellulose acetate	7.6
Ethyl centralite	2.0
Pentaerythritol trinitrate	37.0
Dibutyl phthalate	17.0
N-methyl-p-nitroaniline	1.0
Stannic oxide	5.0

Data for the above composition is as follows:

Measured heat of explosion, cal./g.	627
Temperature Coefficient at 70° F. and 1500 psia	0.29
2000 psia	0.27
Pressure exponent at 70° F., *n*	0.45
Pressure interval: 850–4,000	
Burning rate at 1045 p.s.i. and 70° F., in./sec.	
Motor firing 0.10	
Strand burning 0.11	

EXAMPLE VI

Ingredients	Percent by weight
Plastisol nitrocellulose (12.6% N)	30.4
Cellulose acetate	7.6
Ethyl centralite	2.0
Pentaerythritol trinitrate	40.6
Dibutyl phthalate	13.4
N-methyl-p-nitroaniline	1.0
Dibutyl tin maleate	5.0

Data for the above composition is as follows:

Measured heat of explosion, cal./g.	644
Temperature Coefficient at 70° F. and 1000 psia	0.24
1500 psia	0,12
Pressure exponent at 70° F., *n*	
Pressure interval: 1250–1650	
1650–2100	0.22
Burning rate at 1,360 p.s.i. and 70° F., in./sec.	
Motor firing 0.14	
Strand burning 0.17	

EXAMPLE VII

Ingredients	Percent by weight
Plastisol nitrocellulose (12.6% N)	30.4
Cellulose acetate	7.6
Ethyl centralite	2.0
Pentaerythritol trinitrate	38.8
Dibutyl phthalate	15.2
N-methyl-p-nitroaniline	1.0
Dibutyl tin maleate	2.5
Stannic oxide	2.5

Data for the above composition is as follows:

Measured heat of explosion, cal./g.	637
Temperature Coefficient at 70° F. and 1000 psia	0.16
2000 psia	0.15
Pressure exponent at 70° F., *n*	
Pressure interval: 1,600–2,250	0.04

The ballistic modifier added to the gas generator compositions changed the burning rate by (1) lowering the pressure exponent, (2) lowering the temperature coefficient, (3) lowering both the pressure exponent and temperature coefficient. The use of more than one of the modifiers, namely, dibutyl tin maleate, zinc carbonate, stannic oxide, lead salicylate, manganese dioxide, monobasic cupric salicylate, monobasic lead beta resorcylate, monobasic lead salicylate usually has an additive effect. Table I below is a comparison of the burning data of an unmodified gas generator composition with those of the present invention.

TABLE I

Unmodified v. modified propellant

	Pressure exponent [1]	Temperature coefficient	Heat of explosion (cal./g.)
Sample 1* (unmodified)	0.91		426
Example I	0.66	0.704	538
Example III	0.65		577
Example IV	0.81	0.39	660
Example V	0.45	0.29–0.27	627
Example VI	0.22	0.24–0.12	644
Example VII	0.04	0.16 0.15	637

[1] At 70° F., 800–2,000 p.s.i.a.
*Plastisol cellulose acetate, 45.0; Metrial trinitrate, 44.0; Dibutyl phthalate, 5.0; Methyl methacrylate, 5.0; N-methyl-p-nitroaniline 1.0.

The use of metallic tin and organotin salts such as dibutyl tin maleate in the formulation generally aids in producing gas generator formulations with significantly lower pressure exponents and also modifies burning characteristics by producing compositions with less free carbon particles in the exhaust stream. The organotin compounds are reduced to molten metallic tin during the combustion process and apparently trap solids in the exhaust stream. One sample of the combustion residue analyzed was found to be 1 mole of tin to 11 moles of carbon with a small amount of unidentified organic compounds.

The use of copper and lead compounds generally lower the temperature coefficient but some decrease is noted in the pressure exponent.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A gas generator composition consisting essentially of a fuel selected from
   cellulose acetate, nitrocellulose and mixtures thereof;
   an energetic plasticizer selected from the group consisting of trimethylolethane trinitrate, pentaerythritol trinitrate, diethylene glycol dinitrate and mixtures thereof;
   a nonenergetic plasticizer selected from the group consisting of hydroxypropylglycerol, diethyl phthalate and dibutyl phthalate;
   a stabilizer selected from the group consisting of N-methyl-p-nitroaniline, ethyl centralite and resorcinol; and
   a ballistic modifier selected from the group consisting of dibutyl tin maleate, lead salicylate, manganese dioxide, stannic oxide, zinc carbonate, monobasic cupric salicylate, monobasic lead beta resorcylate, monobasic lead salicylate and mixtures thereof.

2. A gas generator composition consisting of the following

Ingredients	Percent by weight
Plastisol cellulose acetate	45.0
Trimethylolethane trinitrate	44.0
Dibutyl phthalate	5.0
Dibutyl tin maleate	5.0
N-methyl-p-nitroaniline	1.0.

3. A gas generator composition consisting of the following

Ingredients	Percent by weight

Cellulose acetate	45.5
Trimethylolethane trinitrate	47.5
Resorcinol	1.0
Dibutyl tin maleate	3.0
Monobasic lead β-resorcylate	3.0.

4. A gas generator composition consisting of the following

Ingredients	Percent by weight
Plastisol cellulose acetate	35.0
Trimethylolethane trinitrate	46.0
Hydroxypropylglycerol	13.0
N-methyl-p-nitroaniline	1.0
Dibutyl tin maleate	5.0.

5. A gas generator composition consisting of the following

Ingredients	Percent by weight
Plastisol nitrocellulose	30.4
Cellulose acetate	7.6
Ethyl centralite	2.0
Pentaerythritol trinitrate	39.9
Dibutyl phthalate	16.6
N-methyl-p-nitroaniline	1.0
Zinc carbonate	2.5.

6. A gas generator composition consisting of the following

Ingredients	Percent by weight
Plastisol nitrocellulose	30.4
Cellulose acetate	7.6
Ethyl centralite	2.0
Pentaerythritol trinitrate	37.0
Dibutyl phthalate	17.0
N-methyl-p-nitroaniline	1.0
Stannic oxide	5.0.

7. A gas generator composition consisting of the following

Ingredients	Percent by weight
Plastisol nitrocellulose	30.4
Cellulose acetate	7.6
Ethyl centralite	2.0
Pentaerythritol trinitrate	38.8
Dibutyl phthalate	15.2
N-methyl-p-nitroaniline	1.0
Dibutyl tin maleate	2.5
Stannic oxide	2.5

8. A gas generator composition consisting of the following

Ingredients	Percent by weight
Plastisol cellulose acetate	35.0
Trimethylolethane trinitrate	46.0
Dibutyl tin maleate	5.0
Hydroxypropylglycerol	13.0
N-methyl-p-nitroaniline	1.0.

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