

1

2

3,180,769

AMMONIUM NITRATE PROPELLANT CONTAINING A PARABANATE COMBUSTION CATALYST

Edwin F. Morello, Joliet, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana
No Drawing. Filed May 14, 1958, Ser. No. 736,440
4 Claims. (Cl. 149-19)

This invention relates to ammonium nitrate-type compositions and particularly a catalyst for promoting the combustion of ammonium nitrate containing compositions.

In gas generation and rocketry usages it is necessary that the gas affording composition develop gas at a uniform rate commonly spoken of as having a uniform burning rate. In compositions which consist essentially of ammonium nitrate particles and an oxidizable organic binder material, it is necessary to promote combustion thereof by the use of a catalyst. Well known combustion catalysts are: the inorganic chromium compounds particularly, ammonium dichromate; in the military field, the Prussian blues have attained eminence. These catalysts form oxides of such high melting points that they remain solids even at the elevated temperatures of grain burning; these solid oxide products in the combustion gases are believed to be a primary cause of nozzle erosion. Nozzle erosion is bad because it causes erratic changes in gas pressure within the combustion chamber.

An object of the invention is an ammonium nitrate gas generating composition. A particular object of the invention is an ammonium nitrate composition having low erosive characteristics. A further object is an ammonium nitrate composition whose burning rate is relatively insensitive to variations in burning chamber pressure. Other objects will become apparent in the course of the detailed description.

It has been found that an eminently suitable composition for gas generator and rocketry usage is obtained with ammonium nitrate as a predominant component, between about 10 and 40 weight percent of oxidizable organic binder material and between about 0.5 and 15 weight percent of alkali metal salt of parabanic acid as the combustion catalyst. This catalyst burns to form products which are in the gaseous state at the temperature existant in the burning chamber; these gaseous products have no appreciable erosive activity.

The alkali metal salts of parabanic acid may be prepared by reacting an oxalate, urea and alkali metal alkoxide in alcohol solution. The alkali metal parabanate is insoluble and separates as a fine white powder which is filtered from the reaction mixture. The sodium and potassium oxides have the lowest boiling points, therefore these are preferred alkali metal salts of the acid.

Sufficient catalyst must be used to promote the burning of the composition. The amount of catalyst used is also influenced by the desired rate of burning. To a point, the more catalyst present the faster the rate. (It is to be understood that the burning rate is also affected by the particular oxidizable organic material present.) In general, the composition will contain between about 0.5 and 15 weight percent of the catalyst. (Hereinafter all percentages are to be understood as weight percent.) With the thermoplastic matrix formers or binders obtained from cellulose esters and oxygenated hydrocarbon plasticizers therefor, between about 1 and 6% catalyst produces a satisfactory burning rate for typical military gas generation and rocketry usages.

The composition of the invention contains ammonium nitrate as the major component. The ammonium nitrate may be either ordinary commercial ammonium nitrate such as is used for fertilizer, which contains a small amount of impurities; also the particles are usually coated with moisture resisting material such as paraffin wax. Military

grade ammonium nitrate is particularly suitable because it is almost chemically pure. The ammonium nitrate is preferably in a finely divided particulate form; either prilled or ground material. Usually the composition contains between about 65% and 80% of ammonium nitrate; more or less may be present but always it is the predominant component.

In order to permit the shaping of the composition into definite configurations (shapes) a matrix former or binder material is present. Ammonium nitrate possesses oxidizing power in excess of that required for complete self-decomposition. Advantage of this excess oxygen is taken by using oxidizable materials as the binder. These oxidizable organic materials may contain only carbon and hydrogen, for example, high molecular weight hydrocarbons such as asphalts or residuums, and rubbers either natural or synthetic. Because more binder can be present without running into smoke production, oxygenated organic materials are preferred binder materials. The binder or matrix former may be a single compound such as a rubber or asphalt or it may be a mixture of compounds. The mixtures are particularly suitable when special characteristics are to be imparted to the grain.

The multi-component binder or matrix former commonly consists of a polymeric base material and a plasticizer therefor. Particularly suitable polymeric base materials are cellulose esters of alkanic acids containing from 2 to 4 carbon atoms such as cellulose acetate, cellulose acetate butyrate and cellulose propionate; the polyvinyl resins such as polyvinylchloride and polyvinyl acetate are also good bases; styrene-acrylonitrile is an example of a copolymer which forms a good base material. Polyacrylonitrile is another good polymeric base. In general the binder contains between about 15 and 45% of the particular polymeric base material.

The plasticizer may be broadly defined as an oxygenated hydrocarbon. The hydrocarbon base may be aliphatic, aromatic, or may contain, both forms. The oxygen may be present in one or more ether linkage(s) and/or hydroxyl group(s) and/or carboxyl group(s); also the oxygen may be present in inorganic substituents, particularly nitro groups. In general any plasticizer which is suitable for work with any one of the defined polymers may be used.

Exemplary classes of plasticizers which are suitable are set out below. It is to be understood that these classes are illustrative only and do not limit the types of oxygenated hydrocarbons which may be used to plasticize the polymer.

Di-lower alkyl-phthalates, e.g., dimethyl phthalate, dibutyl phthalate, dioctyl phthalate and dimethyl nitrophthalate. Nitrobenzene, e.g., nitrobenzene, dinitrobenzene, nitrotoluene, dinitrotoluene, nitroxyline, and nitrodiphenyl. Nitrodiphenyl ethers, e.g., nitrodiphenyl ether and 2,4-dinitrodiphenyl ether.

Tri-lower alkyl-citrate, e.g., triethyl citrate, tributyl citrate and triamyl citrate.

Acyl tri-lower alkyl-citrate where the acyl group contains 2-4 carbon atoms, e.g., acetyl triethyl citrate and acetyl tributyl citrate.

Glycerol-lower alkanoates, e.g., monoacetin, triacetin, glycerol, tripropionate and glycerol tributyrates.

Lower alkylene-glycol-lower alkanoates wherein the glycol portion has a molecular weight below about 200, e.g., ethylene glycol diacetate, triethylene glycol dihexoate, triethylene glycol dioctate, polyethylene glycol dioctate, dipropylene glycol diacetate, nitromethyl propanediol diacetate, hydroxyethyl acetate and hydroxy propyl acetate (propylene glycol monoacetate).

Dinitrophenyl-lower alkyl-lower alkanoates, e.g., dinitrophenyl ethyl-acetate, and dinitrophenyl amyloctate.

Lower alkylene-glycols wherein the molecular weight is below about 200, e.g., diethylene glycol, polyethylene glycol (200), and tetrapropylene glycol.

Lower alkylene-glycol oxalates, e.g., diethylene glycol oxalate and polyethylene glycol (200) oxalate.

Lower alkylene-glycol maleates, e.g., ethylene glycol maleate and bis-(diethylene glycol monoethyl ether) maleate.

Lower alkylene-glycol diglycolates, e.g., ethylene glycol diglycolate and diethylene glycol diglycolate.

Miscellaneous diglycolates, e.g., dibutyl diglycolate, dimethylalkyl diglycolate and methyl-Carbitol diglycolate.

Lower alkyl-phthalyl-lower alkyl-glycolate, e.g., methyl phthalyl ethyl glycolate, ethyl phthalyl ethyl glycolate and butyl phthalyl butyl glycolate.

Di-lower alkyloxy-tetraglycol, e.g., dimethoxy tetra glycol and dibutoxy tetra glycol.

Nitrophenyl ether of lower alkylene glycols, e.g., dinitrophenyl ether of triethylene glycol and nitrophenyl ether of polypropylene glycol.

Nitrophenoxy alkanols wherein the alkanol portion is derived from a glycol having a molecular weight of not more than about 200. These may be pure compounds or admixed with major component bis(nitrophenoxy) alkane.

A single plasticizer may be used or, more usually, two or more plasticizers may be used in conjunction. The particular requirements will determine not only the polymer but also the particular plasticizer or combination of plasticizers.

In addition to the basic components, i.e., ammonium nitrate, binder and catalyst, the gas-generator propellant composition may contain other materials. For example, materials may be introduced in order to improve low temperature ignitability, such as oximes or asphalt. Surfactants may be present in order to improve the coating of the nitrate with the binder and to improve the shaping characteristics.

Burning rate promoters, which are not catalysts per se, may be present. For example: Carbon may be used in the composition along with the catalyst. The carbon is preferably finely divided carbon which will pass through a #100 U.S. Standard sieve. Highly-adsorptive activated carbons, well-known in the art as activated carbon, made from residual organic material make up one class of effective burning rate promoters. A second general class of carbon useful for increasing the burning rate of the compositions are the carbon blacks, roughly classified as the channel blacks and the furnace combustion blacks. The carbon blacks are characterized by low ash content, that is, less than 0.5% and usually less than about 0.15%, and having extremely small particle size, that is, 50 to 5000 A. and contain adsorbed hydrogen and oxygen. However, to avoid dusting and to afford convenience in handling, some carbon blacks are formed to the so-called "bead" type carbon blacks. The "beads" are extremely soft and physically unstable and hence become disintegrated during the milling of the composition.

As an aid to ignition at low temperatures of the composition when shaped into grains, a small amount of asphalt may be added to the composition. Amounts of asphalt up to about 5% by weight of the composition are effective to promote low temperature ignition of the composition. The asphalt components require oxygen to obtain a stoichiometrically balanced composition and hence the amount used is kept to that minimum required to give satisfactory ignition and/or other physical characteristics of the grains with respect to shaping the propellant composition.

The aromatic hydrocarbon amines are stabilization additives. Examples of these aromatic amines are toluene diamine, diphenyl amine, naphthalene diamine, and toluene triamine. In general the aromatic hydrocarbon amines are used in amounts between about 0.5 and 5%.

For such uses as rocket propulsion, assist take-off service and gas generation for starting up the turbine of a jet engine, a gas-producing propellant is desired which has non-detonating characteristics. The burning characteristics of most explosives is dependent upon the temperature and pressure in the combustion chamber. Pressure exponent is a measure of this effect; this is equal to the slope of the curve of the burning rate in inches per second obtained by plotting the burning rate at various pressures, usually 600 p.s.i. to 1800 p.s.i., on log-log paper. The burning rates being plotted as ordinates and pressures are plotted as abscissas. The lower the value of the pressure exponent, the less detonating character possessed by the gas-producing composition, i.e., a more even and smooth burning of the propellant grain is obtained. A sustained thrust, rather than a detonation, is obtained by smooth burning in a rocket motor or a sustained flow of gas, from a gas generator, is obtained if the pressure exponent of the particular composition is low. The pressure exponent should be less than about 0.9 and is preferably below 0.7.

One method of preparing the compositions for use in grain form is as follows: The binder material is first prepared and the ammonium nitrate and catalyst are milled with plasticized binder. The binder is prepared by heating the plasticizer material to a temperature below about 150° C., usually within the range of from about 120° C. to about 140° C. The liquid or semi-liquid plasticizer material is stirred and the polymeric base material is added; heating and stirring being continued until a homogeneous mixture is obtained. The catalyst may be thoroughly mixed with the powdered ammonium nitrate before addition to the binder material. On the other hand, the catalyst may be added immediately preceding the addition of the ammonium nitrate. The ammonium nitrate and catalyst are then milled into the plasticized mass at a temperature not in excess of about 135° C. Milling is continued until a uniform texture is obtained; then the material is molded at temperatures not in excess of 135° C. into shaped configurations or burning rate test strips.

In preparing the burning rate test strips, the formulated composition is molded at 2000 pounds of pressure into rectangular strips of about one inch by three quarters inch cross-sectional dimension. These large strips are cut into twelve 1/4" by 1/2" test strips about 5 inches in length. The test strips have holes drilled 3" apart; fusible wires which are connected to a timing device for obtaining the burning rates, are passed through the holes.

The test strips are coated with lacquer grade cellulose acetate or other suitable plastic to inhibit surface burning and to force the strip to burn like a cigarette. The test strip is placed in a Crawford bomb under nitrogen pressure and electrical connection of the fuse wires is made to the timing device. The timing device is started by the fusing of one wire and as the test piece burns along its length the timing device is stopped by the fusing of the second wire. Thus, the time for burning of 3" of the test piece is obtained. Burning rates are determined at various pressures.

Gas-producing grains may be prepared by molding the compositions into cylindrical grains under a pressure of about 2000 to 6000 and at a temperature of about 105° C. The size and shape of the grains for commercial or military use will depend upon their intended use. For starting a jet engine the grains are usually cylindrical in shape and about 5" in diameter and 4" in length but may be about 3 to 6 inches in diameter and about 3 to 6 inches in length. The assist take-off grains may be about 2 to 3 feet in length. The grains are usually provided with a hole or opening extending lengthwise of the grain to provide an aperture which may be circular, starform, cruciform, etc., to afford increased burning surface. Such grains may be mounted in a conventional case and may be ignited or fired by electrical or other known means. The combustion of the grains is restricted with respect to burning

area by coating the annular ends with a material such as cellulose acetate or asphalt, thus causing the grain to burn only from the internal surface of the centrally located aperture and from the cylindrical surface of the grain.

Example 1

A commercial grade of ammonium nitrate was ground to a fine powder by a single pass through a pulverizer operated at 7500 r.p.m. The finely ground ammonium nitrate was intimately mixed with monosodium parabanate. All the components were carried out for a period of 1.5 hours at a mixture temperature of 120° C. to obtain a homogeneous plasticized product. The product was then molded at 110° C. and at a pressure of 2000 p.s.i. to obtain 1/4" x 1/4" x 5" strands. The composition of this particular grain was cellulose acetate, lacquer grade 65%, acetyl triethyl citrate 78%, dinitrophenoxy ethanol 6.8%, asphalt 1.7%, carbon black 3%, toluene diamine 1%, sodium salt 3%, and ammonium nitrate 70.2%. This composition had a burning rate at 1000 p.s.i. of 0.080 inch per second; the pressure exponent of this composition was 0.34.

A control composition was prepared identical to the above except that the sodium parabanate was replaced with ammonium nitrate. The control composition had a burning rate at 1000 p.s.i. of 0.068" per second and a pressure exponent of 0.86.

Example 2

Another composition was made up exactly like that of Example 1 except that monopotassium parabanate was the catalyst. This composition had a burning rate at 1000

p.s.i. of 0.096 inch per second and a pressure exponent of 0.43, an excellent burning rate for this low pressure exponent.

Thus having described the invention, what is claimed is:

1. A solid propellant composition consisting essentially of between about 0.5 and 15 weight percent of alkali-metal salt of parabanic acid combustion catalyst, between about 10 and 40 weight percent of oxidizable organic binder material consisting of a polymeric base selected from the class consisting of cellulose esters of alkanolic acids containing from 2 to 4 carbon atoms, polyvinyl resins, polyacrylonitriles, and styrene-acrylonitrile, and oxygenated hydrocarbon plasticizer therefor, and ammonium nitrate as the predominant component.
2. The composition of claim 1 wherein said catalyst is monosodium parabanate.
3. The composition of claim 1 wherein said catalyst is monopotassium parabanate.
4. A solid propellant composition essentially of ammonium nitrate as the predominant component, between about 1 and 6 weight percent of alkali-metal parabanate, between about 20 and 35 weight percent of a binder consisting of a cellulose ester of an alkanolic acid containing 2 to 4 carbon atoms and oxygenated hydrocarbon plasticizer therefor.

No references cited.

CARL D. QUARFORTH, *Primary Examiner.*

30 ROGER L. CAMPBELL, LEON D. ROSDOL,
Examiners.