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STABILIZED AMMONIUM NITRATE
PROPELLANT

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This invention relates to gas-generating compositions or propellants which are based upon ammonium nitrate as the oxidizer.

For use as a gas-generator material or a propellant for rockets ammonium nitrate must be formed into shapes which maintain their configuration. These shapes or grains are attained by admixing the ammonium nitrate with a matrix former or binder. Gas-generator compositions must produce gas at a uniform rate; therefore to the grain there is added a catalyst adapted for promoting the burning of the ammonium nitrate. When the binder contains a cellulose ester such as cellulose acetate as a major component the ammonium nitrate composition suffers the disability of instability at elevated temperatures. The Armed Forces of necessity must store gas-generators and propellants over the entire surface of the earth. It is common for storage buildings in the tropics to reach temperatures of 150° F. In order to meet these conditions the Armed Forces require ammonium nitrate propellants to be storage stable at temperatures on the order of 170° F. for a period of one year. After prolonged storage at these temperatures cellulose ester containing ammonium nitrate propellants tend to evolve gas; in extreme cases the gas evolution is sufficient to produce fissures in the grain and even to break the grain into several pieces.

An object of the invention is to produce cellulose ester containing ammonium nitrate gas-generator composition which has satisfactory storage stability at elevated atmospheric temperatures. Other objects will become apparent in the course of the detailed description.

It has been found that the presence of an N-phenylmorpholine has a very favorable effect on the storage stability of an ammonium nitrate composition using as a binder a combination of the cellulose ester of an alkanolic acid having from 2 to 4 carbon atoms and an oxygenated hydrocarbon plasticizer for said ester and a catalyst adapted for promoting the burning of said gas-generator composition.

The improved stabilizer composition of the invention contains ammonium nitrate as the major component. The ammonium nitrate may be ordinary commercial ammonium nitrate such as is used for fertilizers. This commercial grade material contains a small amount of impurities and the particles are usually coated with moisture resisting material such as paraffin wax. Military grade ammonium nitrate which is almost chemically pure is particularly suitable. The ammonium nitrate is preferably in a finely divided particulate form which may be either produced by prilling or by grinding. The ammonium nitrate is the major component of the gas-generator composition and usually the composition will contain between about 65 and 80 percent of ammonium nitrate. (It is to be understood that all percentages set out herein are percent by weight of the total composition.)

The binder or matrix which permits the forming of the ammonium nitrate particles into configurations or shapes consists essentially of a cellulose ester and a plasticizer therefor. The cellulose ester is a reaction product of cellulose and an alkanolic acid having from 2 to 4 carbon atoms. Examples of these esters are cellulose acetate, cellulose acetate butyrate, cellulose propionate and cellulose acetate propionate. The cellulose acetates

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are particularly suitable. In general the binder contains between about 15 and 45 percent of the defined ester.

The plasticizer component of the binder is broadly defined as an oxygenated hydrocarbon. The hydrocarbon base may be aliphatic or aromatic or may contain both forms. The oxygen may be present in the plasticizer in ether linkage and/or hydroxyl group and/or carboxyl groups; also the oxygen may be present in inorganic substituents particularly nitro groups. In general any plasticizer which is suitable for work with the defined cellulose esters may be used in the invention. 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 cellulose ester. Di-lower alkyl-phthalates, e.g., dimethyl phthalate; dibutyl phthalate dioctyl phthalate and dimethyl nitrophthalate. Nitrobenzenes, e.g. nitrobenzene, dinitrobenzene, nitrotoluene, dinitrotoluene, nitroxyethylene, 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 alkanates, e.g., monoacetin, triacetin, glycerol tripropionate and glycerol tributyrate. Lower alkylene-glycol-lower alkanates wherein the glycol portion has a molecular weight below about 200, e.g., ethylene glycol diacetate, triethylene glycol dihexoate, triethylene glycol dioctoate, polyethylene glycol dioctoate, dipropylene glycol diacetate, nitromethyl propanediol diacetate, hydroxyethyl acetate, hydroxyethyl acetate and hydroxy propyl acetate (propylene glycol monoacetate). Dinitrophenyl-lower alkyl-lower alkanates, e.g., dinitrophenyl ethylacetate, and dinitrophenyl amyloctoate. 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 methylcarbitol 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 bibutoxy 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 with respect to use will determine not only the cellulose ester but also the particular plasticizer or combination of plasticizers which are used.

The mixture of ammonium nitrate, cellulose ester and oxygenated hydrocarbon is essentially as insensitive to shock as is ammonium nitrate itself. It is extremely difficult to get this particular mixture to burn. Smooth burning is attained by the addition of a catalyst to the mixture. This catalyst is distinguished from the well known sensitizers. For example, nitro starch or nitroglycerine may be added to ammonium nitrate in order to

increase its sensitivity to shock and enable it to be more easily detonated for explosive use. Catalysts as a class do not promote sensitivity and are used to cause the ammonium nitrate composition to burn for example like a cigarette. The effectiveness of the catalyst is in general measured by its ability to impart a finite burning rate to a cylindrical strand of ammonium nitrate composition. The burning rate is specified as inches per second at a given pressure and temperature; usually these burning rates are obtained by a bomb procedure operating at 1000 p.s.i. and about 75° F. temperature.

Many catalysts which promote the burning of ammonium nitrate compositions are known. The inorganic chromium salts form the best known classes of catalysts. The better known members of this class are ammonium chromate, ammonium polychromate, the alkali metal chromates and polychromates, chromic oxide, chromic nitrate, and copper chromite. Ammonium dichromate is the most commonly used chromium salt. Various hydrocarbon amine chromates such as ethylene diamine chromate and piperidine chromate are also excellent chromium catalysts. Certain heavy metal cyanides particularly those of cobalt, copper, lead, nickel silver and zinc are effective catalysts. The cyanamides of barium, copper, lead mercury and silver are effective catalysts. The various Prussian blues are excellent catalysts.

In addition to the above primarily inorganic catalysts various organic catalysts are known. The organic catalysts are particularly useful when it is desired to have combustion products which are gases or vapors and thereby do not erode gas exit orifices. Two catalysts which do not contain any metal components are pyrogene blue (Color Index 956-961) and methylene blue. Particularly suitable catalysts are the alkali metal barbiturates. Finely divided carbon such as carbon black present in amounts of several percent is effective alone as a catalyst however, carbon is generally used in combination with another catalyst as a burning rate promoter.

The chromium salts and Prussian blue promote the rate of gas evolution of ammonium nitrate compositions containing cellulose esters and therefore the gas evolution prevention additive of the invention is particularly applicable to compositions containing these catalysts.

The catalysts are present in the gas-generator propellant composition in an amount determined by its use and also by the particular catalyst. In general between about 1 and 12 percent of catalyst is present and more usually between about 2 and 8 percent.

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 present to improve low temperature ignitability, for instance oximes may be present or, asphalt may be present. Surfactants may be present in order to improve the coating of the nitrate with the binder and to improve the shape characteristics of the composition. Various burning rate promoters, which are not catalyst per se, may also be present.

It has been found that a cellulose ester, oxygenated hydrocarbon, catalyst and ammonium nitrate containing composition may be effectively stabilized against gas evolution by the addition of N-phenylmorpholine itself or morpholine having an alkyl substituted phenyl group. For example, the additive may be N-tolylmorpholine or N-xylylmorpholine. The amount of the N-phenylmorpholine present is determined by the instability of the particular composition or by the specific requirements for a particular composition. In general the longer the specification storage time or the higher the temperature requirement the more of the N-phenylmorpholine additive is needed. The N-phenylmorpholines are plasticizers for cellulose esters. Thus the N-phenylmorpholines may serve a dual purpose between stabilizing composition and forming a physical part of the binder. Indeed it may be desirable in some cases to deliberately add N-phenylmor-

pholines to the binder to obtain better thermoplastic characteristics even though gas stabilization to that degree is not necessary. Thus the upper limit will vary with the particular use.

Various catalysts affect the gas evolution rate to different degrees. Lesser amounts of the N-phenylmorpholines may be necessary in such cases. When Prussian blue or one of the inorganic chromium salts is used as the catalyst or a mixture of these materials is used as the catalyst in the usual amount of about between 2 and 8 percent the N-phenylmorpholine may be present in the gas-generative composition in an amount between about 0.5 and 5 percent. In general the more catalyst the more N-phenylmorpholine present.

The aromatic hydrocarbon amines are known to be gas evolution 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 percent. While these aromatic hydrocarbon amines are effective, for severe duties they are frequently not sufficiently effective alone. It has been found that extremely good stabilization is obtained when the N-phenylmorpholine additive of this invention is used with an aromatic hydrocarbon amine. Because of the plasticizing power of the N-phenylmorpholine it is generally desirable to use the aromatic hydrocarbon amines as the primary stabilizing additive and the N-phenylmorpholine in an amount needed to obtain the specific stability. In general when aromatic hydrocarbon amines are present between about 0.1 and 1 percent of N-phenylmorpholine will be used.

Tests

Several grains were prepared by blending at a temperature of about 200° F. the cellulose acetate available commercially as lacquer grade CA: this cellulose acetate analyzed about 55 percent of acetic acid. The cellulose acetate and the plasticizers were blended together and the other additives introduced into the binder prior to the addition of the ammonium nitrate and the catalyst. The materials were thoroughly blended at this temperature until a very homogeneous pasty mass was formed. This pasty mass was extruded into small cylinders for burning rate tests. A portion of the mass was solidified and crushed for use in a gas stability test. The mass was also molded into cylindrical grains which were tested for large scale propellant use.

It has been found that a laboratory test is an excellent indicator of the long term high temperature storage stability of ammonium nitrate type compositions. Three grams of a finely divided ammonium nitrate base composition are placed in a vessel. The vessel is connected by tubing to a mercury manometer system which is so arranged that differential readings of the manometer are translatable into volume changes in the system. Since the volume change of the sample itself can be disregarded, the volume change in the system corresponds to the amount of gaseous decomposition products of the sample. The vessel is inserted to an opening in a metal block; this metal block is provided with electrical heating elements and controls which permit the block to be maintained at a temperature of 275° Fahrenheit. A period of 15 minutes is allowed for the sample to come to the temperature of 275° F. At this time the manometer is zeroed. Readings are taken at 15 minute intervals until sufficient readings have been taken to indicate that the gas product rate is substantially consistent i.e., has reached an equilibrium value or the gas product rate is so low that the sample obviously has more than satisfactory low gas-tendency. The manometer readings are converted directly to cc./g./hr. for each 15 minute interval.

Tests on numerous different ammonium nitrate compositions show that gas evolution may begin in detectable amounts immediately after the initial 15 minutes of

time needed to bring the apparatus to operating conditions. However, it is more normal for a finite period of time to pass before gas is evolved at a measurable rate. This period is generally referred to as "zero gassing time." The longer the zero gassing time the more stable the composition, obviously.

Test 1.—In this test the gas-generator composition contained ammonium nitrate 73.0 percent, lacquer grade cellulose acetate 4.8 percent, dinitrodiphenyl oxide 8 percent, acetyl acetone dioxime 2.3 percent, glycol diglycolate 8 percent, carbon black 1 percent, and Prussian blue 3 percent. In the 275° F. stability test this composition had a zero gassing time of 30 minutes and an equilibrium gas evolution rate of 5.8 cc./g./hr. with a maximum evolution rate of 21.0 cc./gm./hr.

The above composition was then adjusted so that it contained 2.0 percent of N-phenylmorpholine on the total composition. This composition in the 275° F. stability test had a zero period of 270 minutes with an equilibrium gas evolution rate of 2.0 and a maximum of only 3.8.

Test 2.—In this test the basic composition consisted of ammonium nitrate 74.0 percent, cellulose acetate lacquer grade 5.1 percent, dinitrodiphenyl oxide 8.7 percent, glycol diglycolate 8.7 percent, carbon black 0.5 percent, Prussian blue catalyst 1.0 percent, and ammonium dichromate 2.0 percent. In the 275° F. stability test the composition began to gas immediately at a substantial rate. The equilibrium gas evolution rate was 3.0 with a maximum rate of 6.0 cc./gm./hr.

The composition was then adjusted to contain 2.0 percent of N-phenylmorpholine. This composition had a zero gassing period of 360 minutes, with an equilibrium rate of 3.0 and a maximum rate of 4.0.

Test 3.—In this test the basic composition consisted of ammonium nitrate 70.2 percent, cellulose acetate lacquer grade 6.5 percent, acetyl triethyl citrate 7.8 percent, carbon black 3 percent, sodium barbiturate catalyst 3 percent, toluene diamine 1 percent, and 6.8 percent of a mixture containing about 2 parts of dinitrophenoxyethanol and 1 part of bis(dinitrophenoxy)ethane. This mixture was obtained naturally in the reaction of dinitrochlorobenzene and ethylene glycol in the presence of aqueous sodium hydroxide solution. In this test a full size gas-generator grain was molded. This grain was a tube having an outside diameter of 5 inches and an internal diameter of 1.5 inches and a length of 4 inches. Several grains were prepared of each composition and the grains were stored at 200° F. Each day the grains were inspected for surface

cracks; also grains were placed in a gas-generator and fired. The firing detects internal fissures which are not apparent to the eye.

The basic grain described above was fired successfully after 2 days of storage at 200° F. After 3 days surface cracks were observed in the grain.

The composition of the basic grain was adjusted to include 0.1 percent of N-phenylmorpholine. Observation of grains stored at 200° F. was concluded after 17 days of storage. At this time no surface cracks were observed in any of these N-phenylmorpholine containing grains and firings showed no internal fissures to be present.

In the 275° F. stability test the N-phenylmorpholine containing grain of this test had a zero gassing period of 37 hours and a very low gas evolution rate thereafter.

Thus having described the invention, what is claimed is:

1. An ammonium nitrate gas-generator composition consisting essentially of (a) ammonium nitrate as the major component, (b) a binder consisting essentially of (i) a cellulose ester of an alkanolic acid having from 2 to 4 carbon atoms and (ii) an oxygenated hydrocarbon plasticizer for said ester, (c) a catalyst adapted for promoting the burning of said ammonium nitrate and (d) N-phenylmorpholine in an amount at least sufficient to improve the stability of said composition with respect to gas evolution.

2. The composition of claim 1 wherein between about 0.5 and 5 weight percent of an aromatic hydrocarbon amine is present.

3. The composition of claim 2 wherein between about 0.1 and 1 weight percent of N-phenylmorpholine is present.

4. The composition of claim 1 wherein said catalyst is selected from the class consisting of Prussian blue, inorganic chromium salts, and mixtures thereof and is present in an amount between about 2 and 8 weight percent and said N-phenylmorpholine is present in an amount between about 0.5 and 5 weight percent.

5. An ammonium nitrate gas-generator composition consisting essentially of (a) cellulose acetate, about 6%, (b) acetyl triethyl citrate, about 8%, (c) about 7% of an about 2:1 mixture of dinitrophenoxyethanol and bis(dinitrophenoxy)ethane, (d) carbon, about 3%, (e) sodium barbiturate catalyst about 3%, (f) toluene diamine about 1%, (g) N-phenylmorpholine, about 0.1% and (h) the remainder essentially ammonium nitrate.

No references cited.