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AMMONIUM NITRATE PROPELLANT

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This invention relates to new and improved compositions for the generation of a gas and more particularly to compositions wherein ammonium nitrate is the oxidizer component. Still more particularly the invention relates to compositions comprising a predominant amount of ammonium nitrate, an oxidizable binder, at least one combustion catalyst and an amine N-oxide to promote the combustion of said compositions in adaptation of the compositions to rocket propulsion.

Ammonium nitrate is widely used as a component of high explosives. However, it is insensitive and cannot be detonated by the local application of heat. When ignited ammonium nitrate does not sustain flame propagation consistently. Normally it is mixed with oxidizable materials such as sulfur, carbon, hydrocarbons, cellulosic materials, etc. to utilize the excess oxygen available in the ammonium nitrate. These mixtures are either insensitive, or even when provided with a catalyst may not burn at a rate sufficient for the service desired.

When ammonium nitrate is mixed with oxidizable material such as plasticized synthetic resins to function as binder material, and a catalyst, the mixtures can be molded into grains which will burn uniformly. Such grains may be used in assist take-off service for aircraft, for rocket propulsion or missile applications provided the burning rate is adjusted to the desired rate for the particular service. The most commonly used method for increasing the burning rate of ammonium nitrate compositions is to add a combustion catalyst. Among the catalysts which have been used are chromates, iron oxides, dichromates and the iron cyanide types. While certain of these catalysts find use for combustion control of compositions used in propulsion of missiles and rockets and in assist take-off application, promoters are required to obtain high burning rates. In service where high temperature combustion gases contact metal parts erosion problems may arise and organic combustion catalysts are preferred. It is frequently desirable to increase the burning rate produced by such organic catalysts. The turbine and compressor in large engines require auxiliary starting. The gas produced under pressure by the combustion of the grains may be used to operate the turbine of an auxiliary starter. However, the gas so produced must be substantially non-erosive and non-corrosive to the blades and bearings of the auxiliary turbine.

An object of this invention is an improved ammonium nitrate gas-forming composition comprising ammonium nitrate, oxidizable material, a combustion catalyst and a promoter to increase the burning rate of said compositions. Another object is a gas-producing composition comprising a major amount of ammonium nitrate, a combustible binder, a combustion catalyst and a promoter for increasing the burning rate. Still another object of the invention is an improved catalyst-promoter combination for increasing the combustion rate of a gas-forming composition capable of being shaped into grains

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and comprising a predominant amount of ammonium nitrate, minor amounts of oxidizable organic components and said catalyst-promoter combination, the combustion of which will not cause erosion to metal surfaces at high temperatures and pressures. A still further object of the invention is to provide an organic combustion promoter which when present in a composition comprising ammonium nitrate, oxidizable binder and a combustion catalyst increases the combustion rate substantially. Other objects will appear from the description of the invention below.

The gas-producing composition of this invention comprises, on a weight basis, about 10% to about 25% of oxidizable binder material, about 0.5% to about 10% of at least one combustion catalyst selected from the class consisting of Prussian blue, ammonium dichromate, finely divided carbon, magnesium oxide and a sulfurized substituted diphenylamine blue dye having a color index of 956, about 0.5% to about 5% of an amine N-oxide promoter selected from the class consisting of pyridine N-oxide, 4-methyl pyridine N-oxide, N-methylmorpholine N-oxide, triisopropanolamine N-oxide, triethanolamine N-oxide, 2-diethylaminoethanol N-oxide, triethylamine N-oxide and tetrahydroxyethyl ethylene diamine N-oxide, the remainder of said composition consisting essentially of ammonium nitrate. Minor amounts of other oxidizable organic materials may be added to improve the properties of grains molded from the composition.

The amine N-oxides which are effective promoters are members of the class of N-oxides of pyridine and homologs of pyridine, N-oxides of aliphatic amines including aliphatic polyamines and N-oxides of heterocyclic amines which may have oxygen as well as nitrogen in the cyclic nucleus. When used alone as the sole means of promoting the combustion of ammonium nitrate based grains the amine N-oxides are ineffective. They are not true catalysts but are classed as promoters. Moreover, not all amine N-oxides are effective promoters. The combustion rate of a composition containing Prussian blue, carbon and magnesium oxide is essentially unimproved by the addition of 2,6-dimethyl pyridine N-oxide to the composition. Likewise the N-oxides of trimethylamine, tribenzylamine, dimethylaniline, dimethylaminoethanol, ethyldiethanolamine, dihydroxyethylaniline, and hydroxyethylmorpholine are ineffective.

The inorganic combustion catalysts are preferably selected from the class consisting of ammonium dichromate, Prussian blue and magnesium oxide. Certain iron catalysts, broadly defined as Prussian blue, are effective for the combustion of ammonium nitrate grains containing an oxidizable binder. Mixtures of ammonium dichromate and insoluble Prussian blue, or mixtures of either or both of these with magnesium oxide may be used. Magnesium oxide not only functions as a catalyst but is also an excellent stabilizer against chemical decomposition at elevated temperatures. When used alone the amount of these inorganic catalysts is in the range of 0.5 to 4.0% by weight, and these catalysts may be used with carbon. Finely divided carbon when used is included in the propellant composition in amounts within the range of about 0.5 to 4% by weight, preferably in amounts of 0.5 to about 3.0% by weight of the finished grain. Highly adsorptive activated carbon such as "Norit" and "Nuchar" make up one class of carbon catalysts. A second general type of carbon for use in gas-generation compositions are the carbon blacks roughly classified as channel blacks and furnace combustion blacks. These are characterized by low ash content and small particle size, 50-5000 A. Finely ground petroleum coke, obtained as residue in the pipestilling of Mid-Con-

tinant heavy residuum, which contains less than about 1% ash, may be used. The magnesium oxide in the compositions would be in the form of a very fine powder which would pass through a #200 U.S. Standard sieve.

The amine N-oxide promoter may also be used in conjunction with sulfurized substituted diphenylamine blue dyes which are catalysts for the combustion of the compositions of this invention. The blue dye has a color index of 956 and usually contains from 10 to 70% by weight of an alkali metal carbonate preferably from about 10 to about 35% by weight of sodium carbonate. The preferred blue dye which may be used as a catalyst component in the composition is known commercially as Pyrogene Direct Blue RL-CF. It may be prepared by heating 2,4-dinitro-4-hydroxy-diphenylamine or by heating 2-amino-4-nitro-4-hydroxy diphenylamine with sodium tetrasulfide in alcohol at a temperature of 135°-145° C. under a pressure of about 8 to 10 atmospheres for a period of 3 to 4 hours. Methods of preparing this dye are described in U.S. 665,726 and in "Color Index, Society of Dyers and Colorists," 1st edition, January 1924, under the specific color index. Examples of commercially available sulfurized substituted diphenylamine blue dyes which are effective catalysts are listed in the "Tech. Manual and Yearbook of American Textiles and Colorists," pages 240-1 under heading color index 956, specifically Pyrogene Direct Blue RL-CF and Sulfogene Direct Blue BN. The amount of these organic catalysts in the compositions is in the range of 0.5 to 4.0% by weight of the composition. Total amount of the catalyst components in the compositions of this invention is not more than 10% by weight and usually will not be more than 7% of the weight of the grain.

The binder of the gas-producing propellant composition is a thermoplastic material comprising at least one organic synthetic resin plasticized with at least one oxidizable organic plasticizer. Preferred synthetic resins are the cellulose acetates and cellulose acetate-butyrate and polyvinyl acetate. Cellulose acetate having an acetic acid content of 51 to 57% by weight of acetic acid may be used. Cellulose acetate-butyrate having a butyric acid content of 16 to 61% by weight and acetic acid content of 7 to 55% by weight is also a suitable synthetic resin for the binder of the composition. Polyvinyl acetate resins suitable for binders are solid homopolymers of relatively high molecular weight, the lowest molecular weight resin preferably having a softening point above about 190° C. Although these synthetic resins which contain relatively high oxygen content are preferred, other synthetic resins may be used as binder components. Mixtures of the resins may be used. Compatibility with the plasticizer and oxygen content are of primary importance in the choice of specific resins or mixtures thereof as base materials.

Plasticizer components for the binder of the ammonium nitrate gas-forming compositions consisting of highly oxygenated organic materials are preferred, other factors being equal. One or more of a group of nitro substituted compounds are preferred as a part of the plasticizer. This group includes dinitrobenzene, dinitrotoluene, and nitro-substituted aromatic ethers, these preferably containing on the average not more than 2.5 nitro groups per molecule and not more than 2 nitro groups per phenyl nucleus. The phenyl nucleus of the nitro-substituted aromatics may also contain in addition to nitro groups as substituent groups, methyl, alkoxy, phenoxy, nitrophenoxy and propenoxy groups. Examples are 2,4-dinitrodiphenyl ether, 2,4-dinitrophenylpropyl ether, 2,4-dinitrophenyl allyl ether, 2,4-dinitroanisole and di-(2,4-dinitrophenyl)-polyglycol ether.

It is desirable to use along with the nitro-aromatic compounds at least one non-nitro group containing plasticizer. These co-plasticizers are preferably high in oxygen content. Esters of polyhydric alcohols, polycarboxylic acids, aliphatic hydroxycarboxylic acids and polyglycols, are

suitable. Examples are diallylphthalate, trialkyl citrates (methyl, ethyl, propyl and butyl), diethyl and dibutyl tartrate, triethylene glycol di-2-ethylbutyrate, triglycol diacetate and polyglycol dioctanoate. These commercial products are described by Buttrey in "Plasticizers" (1950), pages 49-50. Asphalt may be added to the binder although such additives have a poor oxygen balance. Asphalt obtained by air blowing of a petroleum residuum, e.g. a Mid-Continent petroleum residuum, to obtain a product of flash point of at least 150° F. (Cleveland Open Cup) and a softening point of 215-235° F. is preferred. Generally the binder material contains from about 10 to about 60 parts by weight of the synthetic resin plasticized with 90 to 40 parts by weight of plasticizer. The relative amounts of different plasticizers in a given composition may be varied over a wide range. Thus, the plasticizer may consist entirely of 2,4-dinitrodiphenyl ether or mixtures of this ether with 2,4-dinitrotoluene, or the plasticizer may comprise di-(dinitrophenyl)-polyglycol ether as the sole nitro aromatic plasticizer or the plasticizer may be mixed with other nitro-substituted plasticizers. In general, the non-nitro group-containing plasticizers constitute not more than 70% by weight of the plasticizer components of the binder.

As indicated above the propellant composition comprises a major proportion of ammonium nitrate. The term "ammonium nitrate" as used in the specification and claims is indicated to mean either commercial grade ammonium nitrate such as conventionally grained ammonium nitrate containing a small amount of impurities which may be coated with a small amount of moisture-resisting material such as petrolatum or paraffin, or to mean military grade ammonium nitrate or a mixture of minor amounts (usually less than 10%) of other inorganic nitrates such as sodium nitrate or potassium nitrate with ammonium nitrate. A mixture of finely ground and coarsely ground ammonium nitrate is preferred, the major proportion of the nitrate being finely ground.

The burning characteristics of ammonium nitrate-oxidizable binder are dependent upon the temperature and pressure in the combustion chamber. The burning rate as affected by pressure is defined by the pressure exponent, the numerical value equal to the slope of the curve of the burning rate in inches per second obtained by plotting the burning rate at various pressures, the burning rates being plotted vertically and pressures plotted horizontally. The lower the value of the pressure exponent the less is the tendency to develop excessive pressures and safety disc rupture in firing the grains shaped from the compositions, and the more even and smooth is the burning of the propellant grain. Pressure exponents below about 0.8 are desirable and preferred exponents are below about 0.7. Thus a sustained thrust rather than a detonation is obtained by smooth burning of the grain and a sustained flow of gas from the gas generator is obtained if the pressure exponent of the composition is low.

One method of preparing the compositions is as follows. The binder is prepared by heating the plasticizer material to a temperature of 100-120° C. with stirring, and adding the resin, and milling until plasticization is complete. Not more than one hour is required for this operation. The ammonium nitrate, promoter and catalyst are then milled with the softened binder at a temperature not in excess of about 110° C. until a homogeneous product is obtained. The material is then molded into desired shapes.

In preparing burning rate strands the composition is molded at 2000 pounds pressure into slabs of about one inch by three-quarters inch cross-sectional dimension. These strips are cut into test strands about 5 inches in length, and the test strands are coated with lacquer grade cellulose acetate to inhibit surface burning. Strand burning rates are determined by burning in a Crawford bomb under varying pressures of nitrogen.

Gas-producing grains are fabricated by molding under

a pressure of about 2000 to 6000 p.s.i. and at a temperature of about 105° C. The size and shape of the grains will depend, of course, upon their intended use. The

taining pyridine N-oxide promoter and controls containing only catalysts components and not amine N-oxide promoter, are shown in Table I.

Table I

Test	Binder (Percent)	Catalyst			Pyridine N-oxide	Burning rate at 1,000 p.s.i.	Pressure Ex- ponent
		Prussian Blue	MgO	Carbon			
		Percent	Percent	Percent	Percent		
1 ¹ -----	13	3	1	2	2	0.126	0.68
2 ¹ -----	15	3	1	2	2	0.179	0.59
3-----	13	3	1	2	2	0.241	0.58
4-----	13	3	1	3	2	0.263	0.58
5 ¹ -----	13	3	2	3	2	0.081	0.79
6 ¹ -----	13	3	1	3	3	0.074	0.63
7-----	15	3	1	3	3	0.127	0.63
8-----	14.5	3	1	3	3.3	0.093	0.67
9 ¹ -----	18.0	3	3	3	3.0	0.071	0.76
10-----	15.0	3	3	3	3.0	0.094	0.76

¹ Control compositions.

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 may be restricted with respect to burning area by coating with a material such as cellulose acetate or asphalt, thus causing the grain to burn only from the unrestricted surfaces. The temperature of the combustion gases produced by burning of the grain may be of the order of 1500 to 2500° F. but preferably not above about 2100° F.

The following examples are illustrative of propellant compositions which may be used in the propelling of rockets and in assist take-off operations as described above.

TEST SERIES A

Binder material for a series of gas-producing propellant compositions was prepared by heating at a temperature of 120° C., 20 parts by weight of triethylene glycol di-2-ethylbutyrate with 30 parts by weight of 2,4-dinitrophenyl propyl ether and 10 parts by weight of 2,4-dinitrodiphenyl ether and stirring the mixture to homogeneity. To this stirred mixture was then added 40 parts by weight of polyvinyl acetate and stirring was continued until the plastic was homogeneous. The binder was tough and flexible. To the prepared binder was then added at a temperature of 105° C. finely ground ammonium nitrate containing intimately mixed therewith the combustion catalyst, and also intermixed therewith, amine oxide as indicated in Table I. The mixtures were stirred to homogeneity and during the mixing 1.0% based on the total weight of the composition, of a chemical stabilizer, m-phenylene diamine, was added to those mixtures which did not contain magnesium oxide catalyst. The compositions were molded into slabs and strands were burned in the bomb to determine burning rates and pressure exponents. The results obtained from compositions con-

Referring to Table I the maximum burning rate obtained by the use of catalyst alone without promoter was about 0.18" per second at 1000 pounds pressure. This rate was obtained using 3% Prussian blue, 1% magnesium oxide and 2% by weight of carbon as catalyst (see Test 2). When 2% of the ammonium nitrate was substituted by 2% of added pyridine N-oxide the burning rate was raised to 0.24" per second at 1000 pounds pressure and by increasing the amount of carbon from 2% to 3%, still holding the pyridine N-oxide at 2% by weight concentration in the composition, the burning rate was increased to 0.26" per second at 1000 p.s.i. (see Tests 3 and 4). In a test not shown in the table, increasing the carbon from 2% to 5% in a composition in other respects like the composition of Test 2 of Table I, the burning rate was increased only from 0.179 to 0.182. Compositions which do not contain conventional inorganic combustion catalysts such as Prussian blue or ammonium dichromate do not burn as rapidly as compositions which contain these catalysts. Thus compositions such as those used in Tests 5, 6 and 9 wherein the catalysts used were magnesium oxide, carbon or a mixture of these, the burning rates are relatively low. However, inclusion of pyridine N-oxide in such compositions produces marked improvement in the burning rates (Test 7 vs. Test 6) without changing the pressure exponent.

TEST SERIES B

The same binder components and same procedure as that described for the preparation of the compositions of Test Series A was used for the preparation of compositions of Test Series B. The amine oxides were prepared by oxidation of the amine with 30% aqueous hydrogen peroxide. Addition of the peroxide to the stirred amine induced evolution of heat. The reaction temperature was held under 100° C. by controlling the rate of peroxide addition and by external cooling when necessary. After stirring over night at room temperature unreacted amine and water were removed by vacuum topping. The

Table II

Test	Binder (Percent)	Catalyst Components			Amine N-oxide of (wt. percent)	Burning rate at 1,000 p.s.i.	Pressure Ex- ponent
		Prussian Blue	MgO	Carbon			
11-----	13	3	1	3	Pyridine (3)-----	0.263	0.58
12-----	13	3	1	2	4-methyl pyridine (2)-----	0.225	0.59
13-----	13	3	1	3	Triisopropanol (3)-----	0.251	0.60
14-----	13	3	1	3	2-diethylaminoethanol (2)-----	0.265	0.61
15-----	13	3	1	3	Triethanolamine (3)-----	0.271	0.66
16-----	13	3	1	3	N-methylmorpholine (2)-----	0.237	0.65
17-----	13	3	1	2	Triethylamine (2)-----	0.243	0.61
18-----	13	3	1	3	Tetrahydroxyethyl ethylenediamine (3)-----	0.240	0.65

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amine oxide product was not distilled. The pyridine N-oxide of Test Series A and B and 4-methylpyridine N-oxide were commercial products. The results of burning rate tests of compositions containing a wide range of amine N-oxide are given in Table II.

Referring to Table II the increase in burning rate of compositions containing the amine N-oxides over the burning rate of compositions containing non-promoted catalysts (see Table I, Test 2) varied from about 25% (Test 12) to about 51% (Test 15) and this increase in burning rate was accomplished without substantial change in the pressure exponent.

Percentage compositions are expressed herein as percentages by weight unless specified otherwise.

Having thus described the invention, we claim:

1. A solid ammonium nitrate-based propellant composition which consists essentially of about 10 to about 25% by weight of an oxidizable binder material consisting essentially of a resin selected from the class consisting of cellulose acetate, cellulose acetate butyrate, polyvinyl acetate and an oxygenated organic plasticizer therefor, about 0.5% to about 10% of at least one combustion catalyst selected from the class consisting of Prussian blue, ammonium dichromate, finely divided carbon, magnesium oxide and a sulfurized diphenylamide blue dye having a color index of 956, about 0.5% to about 5% of an amine N-oxide combustion promoter selected from the class consisting of pyridine N-oxide, 4-methylpyridine N-oxide, N-methylmorpholine N-oxide, triisopropanolamine N-oxide, triethanolamine N-oxide, 2-diethylaminoethanol N-oxide, triethylamine N-oxide, and tetrahydroxyethyl

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ethylenediamine N-oxide, and ammonium nitrate as the remainder of said composition.

2. The composition of claim 1 wherein the amine N-oxide combustion promoter is pyridine N-oxide.

5 3. The composition of claim 1 wherein the amine N-oxide combustion promoter is 2-diethylaminoethanol N-oxide.

4. The composition of claim 1 wherein the amine N-oxide combustion promoter is triethanolamine N-oxide.

10 5. The composition of claim 1 wherein the catalyst is finely divided carbon.

6. The composition of claim 1 wherein the catalyst is magnesium oxide.

15 7. The composition of claim 1 wherein the catalyst is Prussian blue.

8. A solid propellant composition consisting essentially of on a weight basis (1) from about 10 to about 25% of a combustible thermoplastic binder consisting essentially of about 10% to about 60% of polyvinyl acetate plasticized with about 40% to about 90% of a mixture of about 50% of 2,4-dinitrophenylpropyl ether, about 15% of 2,4-dinitrodiphenyl ether and about 35% of triethylene glycol di-2-ethylbutyrate, (2) from about 0.5% to about 4% of Prussian blue, from about 0.5 to about 4% of finely divided carbon, from about 0.5 to about 4% of magnesium oxide, (3) about 0.5% to about 5% of pyridine N-oxide and (4) ammonium nitrate as the remainder of said composition.

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No references cited.