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STABLE ROCKET PROPELLANT

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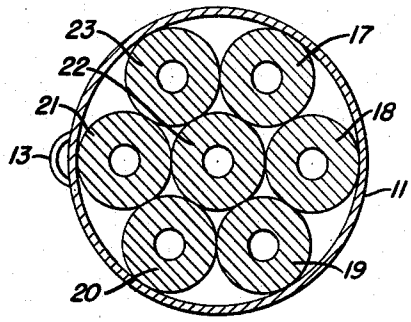


Fig. 2

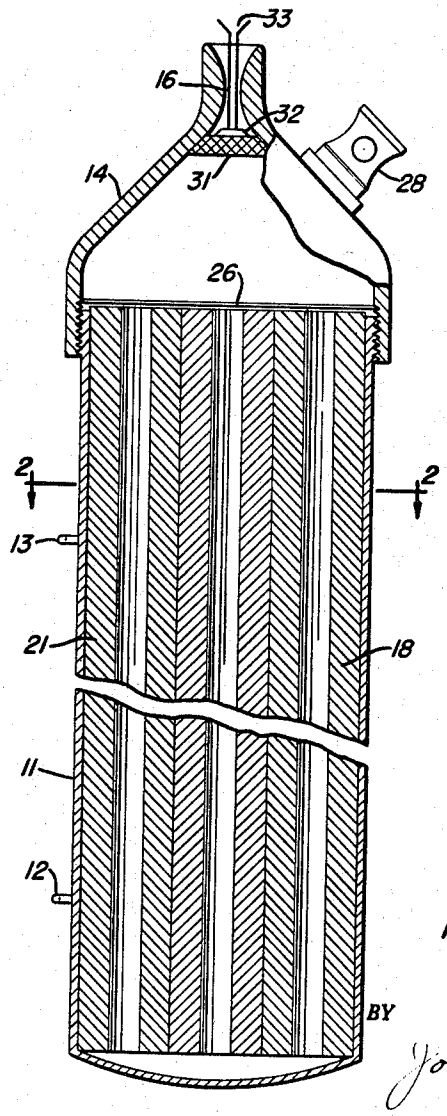


Fig. 1

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STABLE ROCKET PROPELLANT

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8 Claims. (Cl. 52—.5)

This invention relates to a composition for the generation of gas, said composition containing ammonium nitrate as the principal gas-producing agent. More specifically, the invention relates to a novel composition consisting essentially of ammonium nitrate, a defined binder material, a Prussian blue catalyst for the promotion of combustion in the composition, finely divided carbon, desirably an aliphatic oxime, and a defined aromatic amine gassing inhibitor.

Ammonium nitrate is widely used as a component of high explosives, particularly the so-called safe explosives. Even though classified as a high explosive, ammonium nitrate is extremely non-sensitive to ordinary heating and to shock and cannot be detonated readily by local application of heat or by a blasting cap. Furthermore, when ignited, ammonium nitrate does not burn uniformly and has a tendency to go out when used in the absence of combustible organic material. Thus, to improve the burning quality, to increase the sensitivity, and to utilize the excess free-oxygen made available by the decomposition of the ammonium nitrate, organic materials which also may function as binder material for the shaping of the ammonium nitrate into grains are admixed with ammonium nitrate. The choice of components of binder material must be such that satisfactory combustion of the propellant grain with respect to burning rate under conditions of use can be realized.

Modern warfare utilizes large quantities of rockets for ground-to-ground missiles, ship-to-shore missiles, air-to-ground missiles, and air-to-air missiles. These rockets are comprised essentially of thin wall casings, which contain a combustion chamber in which is incorporated a quantity of solid propellant, a nozzle through which the decomposition gases pass thereby to create the forward thrust of the missile, ignition means for igniting the propellant grain, stabilizing vanes and a war head which contains high explosive. Military rockets heretofore have utilized double-base powders such as ballastite as a solid propellant for use in such rockets. Rocket units have also been developed to assist in the take-off of heavy loaded airplanes and to make possible the use of short runways. Such units are commonly known as JATO (jet assisted take-off) or ATO (assisted take-off) units. A constant uniformly distributed assist impulse with respect to time is desirable for such take-off service and burning rates of the propellant material for use in such take-off service are usually within the range of from about 0.10 to 0.16 inch of propellant grain per second at about 1000 pounds per square inch pressure. The present invention is concerned primarily with propellant material for rockets, said propellant material having burning rates above about 0.16 inch per second at 1000 pounds pressure. Thus the burning rates desirable for rocket service are higher than for take-off service although the rate of burning is below that of detonation.

Economic considerations of cost and availability make

the use of ammonium nitrate as the base material in solid propellant for rockets and ATO units quite attractive. Moreover, the relative low flame temperature of the decomposition of ammonium nitrate (1730°–2150° C.) makes desirable the use of ammonium nitrate. The availability of free oxygen from the decomposition of the ammonium nitrate permits the use of oxidizable material in the binder material, the combustion of which enhances the energy available from the decomposition of the nitrate. Certain characteristics of ammonium nitrate require development of suitable associated material in the composition to make ammonium nitrate suitable as a gas-generation means for rocket service or for take-off service.

Solid ammonium nitrate exists in several different forms depending upon the temperature of the nitrate and in passing from one solid form to a different solid form, particularly at temperatures of about 32° C. and also −18° C. i.e., temperatures common to storage conditions, a considerable volume change takes place in the ammonium nitrate. Thus the binder material used with the ammonium nitrate to form physically stable grains must be flexible to compensate for changes in volume in order that such volume changes will produce a minimum amount of voids and cracks in the grain. Moreover, the solid propellant grain suitable for military use must be ballistically stable after prolonged storage at temperatures as high as 77° C. and as low as about −60° C. Production of fissures in the grain either internally or externally over the surface of the grain creates additional burning surface which results in unpredictability of the ballistic performance of the rocket or ATO unit. Thus it becomes necessary to provide a binder material which will provide a shaped grain of satisfactory physical stability. Furthermore, such grain must be capable of being ignited at extremely low or relatively high temperatures after being subjected to variable storage temperature conditions and to burn evenly and at such a rate as to distribute the impulse energy in accordance with the service required.

Finely powdered ammonium nitrate contains about 20% or more by volume of void space and this void space must be completely filled in order to obtain a shaped explosive grain of the desired physical characteristics. Moreover additional void space is produced when using an inorganic compound as the catalyst and the binder must not only fill the voids of the ammonium nitrate, but also the voids present in the finely powdered inorganic catalyst material. Another factor which contributes to the maintenance of uniform and smooth combustion of the propellant grain is that of stoichiometric oxygen balance for the production of water, carbon monoxide and carbon dioxide in the combustion of the propellant grain. Hence, binder material components capable of furnishing a part of the oxygen for combustion of the grain are used to supply any oxygen deficiency in the composition.

For such military uses as rocket propulsion and ATO service, an explosive is desired which has non-detonating characteristics rather than the detonating characteristics of ordinary ammonium nitrate explosives. The burning characteristics of non-detonating explosives are dependent upon the temperature and pressure in the combustion chamber. The relationship of burning rate and pressure at constant temperature is expressed by R. N. Wimpress in "Internal Ballistics of Solid Fuel Rockets" (1950), as

$$B=\beta\left(\frac{p}{1000}\right)^n$$

wherein B is the linear burning rate at pressure "p," β is the linear burning rate for the composition of 1000 p.s.i.,

"p" is the pressure in p.s.i. in the burning chamber and "n" is the pressure exponent showing dependence of burning rate on pressure and is the numerical value equal to the slope of the curve of burning rate in inches per second obtained by plotting the burning rate at various pressures on log-log paper. Ammonium nitrate compositions usually have a pressure exponent of about 0.7 or higher. Smokeless powders, such as ballistite and cordite have pressure exponents between about 0.6 and 0.7. The lower the value of "n" the less is the detonating character of the decomposition of a gas-producing composition and the more even and smooth is the burning rate of the propellant grain. Thus, a sustained thrust rather than a detonation is obtained by smooth burning of the grain. Propellant compositions having an exponent less than about 0.65 are preferred and these propellant compositions for use in rocket service should have burning rates of at least 0.16 inch per second at 1000 pounds pressure.

One of the more serious problems in the use of ammonium nitrate base explosives as propellants lies in the tendency of the composition to produce gaseous decomposition products in storage at extremely high atmospheric temperatures such as are prevalent in the tropic regions. This characteristic of ammonium nitrate base propellants is commonly known as gassing. Military specifications require that this gassing tendency be held to a minimum. Many materials added to the ammonium nitrate composition which increase the burning rate increase the gassing tendency of the composition. This is particularly true with compositions containing finely divided carbon. Gassing is a very serious problem because grain compositions which have "gassed" to an appreciable extent usually fail to give satisfactory firings. This is believed to be the result of increased porosity of the grain, which porosity causes uneven burning of the grain. Still more serious is the fact that grains which have "gassed" to a considerable extent tend to give erratic burning properties and even exhibit detonation properties.

An object of this invention is the preparation of a gas-generating composition for use in rockets, the principal gas-generating material of said composition being ammonium nitrate. Another object of the invention is the preparation of an explosive grain having a high burning rate which grain is dimensionally stable and non-fissuring over a wide range of storage temperatures. Still another object of the invention is the production of an explosive grain having a high burning rate and a moderately low pressure exponent, which explosive grain is suitable for use in military rockets. A still further object of the invention is to produce an ammonium nitrate-combustible binder material grain which will ignite at relatively low temperatures and pressures. An additional object of the invention is to produce a combustible ammonium nitrate propellant grain, the pressure exponent of the burning rate of which grain is desirably less than about 0.65 and the burning rate of which grain is desirable at least about 0.16 inch per second at 1000 pounds pressure. A particular object of the invention is an ammonium nitrate base composition containing finely divided carbon which composition has improved high temperature storage characteristics, that is, low gassing tendencies. A preferred object is a composition which has substantially no gassing tendency for a period of at least about one hour in storage at temperatures of about 135° C.

It has been discovered that an ammonium nitrate based propellant grain of suitably high burning rate, suitably low pressure exponent, and improved gassing tendency consists essentially of:

(1) An effective amount of a combustion catalyst comprising Prussian blue, generally from about 1% to about 8% by weight;

(2) From about 0.5% to about 7% by weight of finely divided carbon containing not more than about 5% ash, the particle size of said carbon being such that the finely divided carbon will pass through a #20 U.S. Standard sieve, preferably through a #200 U.S. Standard sieve and more preferably through a #325 U.S. Standard sieve;

(3) From about 10% to about 25% by weight of a plastic binder consisting essentially of:

(*a*) Between about 18% and 40% by weight of cellulose acetate which analyzes from about 51% to 57% by weight acetic acid; and

(*b*) From about 60% to about 82% by weight of plasticizer components consisting essentially of:

(i) The liquid polyesterification condensation product obtained by reacting one mol of an aliphatic oxydicarboxylic acid containing 4 to 6 carbon atoms per molecule with from about 1.08 mols to about 1.3 mols of at least one dihydric alcohol selected from the class consisting of ethylene glycol, propylene glycol, polyethylene glycol ether, polypropylene glycol ether and mixtures thereof which ethers and mixtures thereof have an average molecular weight not more than about 200 and which polyesterification condensation product is essentially anhydrous and has an average molecular weight of about 250 to about 1000; and

(ii) At least one nitrodiphenyl ether containing from one to three nitro groups per molecule and substantially not more than two nitro groups on any benzene nucleus, the ratio by weight of said polyesterification condensation product (i) to said nitrodiphenyl ether (ii) in said binder being in the range of 1:4 to 4:1.

(4) From about 0.5 to 4% of a gassing inhibitor selected from the class consisting of (*a*)

$$RZ(NR'R'')x$$

where R is selected from the class consisting of hydrogen and alkyl containing from 1 to 12 carbon atoms, Z is an aromatic nucleus selected from the class consisting of phenyl and naphthyl, R' and R'' are selected from the class consisting of hydrogen and alkyl containing from 1 to 4 carbon atoms and x is an integer from 1 to 3; and (*b*) diphenylamine, dinaphthylamine, and phenyl naphthylamine.

(5) The remainder essentially all ammonium nitrate, said composition containing at least about 70% by weight of ammonium nitrate.

To the above gas-producing propellant composition we prefer to add from about 1% to about 4% by weight of total composition an aliphatic oxime corresponding to the empirical formula

$$R-\overset{\overset{X}{\|}}{C}-(CH_2)_y-\overset{\overset{NOH}{\|}}{C}-R'$$

wherein R and R' are selected from the class consisting of methyl, ethyl and hydrogen, wherein X is selected from the class consisting of oxygen and NOH and wherein y is an integer from 0 to 2.

INHIBITOR COMPONENT

It has been discovered that certain aromatic amines when introduced into the ammonium nitrate based grain containing Prussian blue catalyst and finely divided carbon have the very desirable characteristic of decreasing the amount of gassing in high temperature storage and frequently even eliminating or essentially eliminating gassing for prolonged periods of time. In view of the extreme severity of the test conditions for hot storage stability, it is considered that the more effective aromatic amine, dinaphthylamine and phenyl naphthylamine. In any reasonable storage time at atmospheric temperature storage conditions.

The aromatic amine gassing inhibitors of this invention fall into two main classes. These classes are: diphenylamine, dinaphthylamine and phenyl naphthylamine. In the case of the naphthyl amines, the linkage between the naphthyl radical and the nitrogen may be either alpha or beta. The second group of aromatic amines which are

effective as gassing inhibitors are represented by the empirical formula:

$$RZ(NR'R'')x$$

In this empirical formula Z is an aromatic nucleus selected from the class consisting of phenyl and naphthyl; R is selected from the class consisting of hydrogen and alkyl containing from 1 to 12 carbon atoms; R' and R'' are selected from the class consisting of hydrogen, and alkyl containing from 1 to 4 carbon atoms; and x is an integer from 1 to 3.

Examples of monoamino-containing compounds are: aniline (monophenylamine, monoamino benzene), 1-naphthylamine, toluidine (methyl aniline) xylidine (dimethylaniline), dodecyl aniline, N-methyl aniline, N,N-dimethyl aniline, N-sec-butyl aniline.

Examples of the diamino compounds are: diamino benzene (phenylene diamine), diamino toluene (toluene diamine), diamino naphthylene, methyl diamino naphthylene, dodecyl diamino naphthylene, N-sec-butyl, diamino benzene, N,N'-di-sec-butyl diamino benzene, and N-methyl diamino naphthylene.

Examples of triamino compounds are: triamino benzene, triamino naphthylene, triamino toluene, and triamino methyl naphthylene.

A distinct improvement in the gassing tendency of the composition is obtained by the use of very small amounts on the order of 0.5% by weight of the total composition. In general, little additional benefit is obtained by the use of amounts of more than about 4% by weight of the gassing inhibitor. In general, it is preferred to use from about 1% to about 3% by weight based on the total weight of the propellant composition of the invention.

CARBON COMPONENT

The carbon component of the propellant grain when used in amounts of from about 0.5% to about 7% by weight of the grain increases the burning rate by about 0.01 to about 0.07 inch per second depending on the type and amount of carbon used. We prefer to use from about 1% to about 3% by weight of carbon in the composition. Carbon in excess of about 7% is undesirable because the slight increase in burning rate is more than counterbalanced by the "smokiness" imparted to the combustion gas stream.

The carbon component of the propellant composition which we add to increase the burning rate includes finely divided, highly adsorptive activated carbons. These are well known in the art of decolorizing sugar and adsorption of gases. Examples of these are "Norit" and "Nuchar," the former being a highly-adsorptive activated carbon used to adsorb odors, and to decolorize water, gases, chemical solutions, oils and greases. Nuchar is an activated carbon made from a residual organic material obtained in the manufacture of cellulose and is characterized by high porosity resulting in high adsorptive capacity. Like "Norit" it is used as a decolorizing and deodorizing agent.

A second general class of carbon useful for increasing the burning rate of the propellant composition are the carbon blacks. These are roughly classified as channel blacks prepared by the impingement of small natural gas flames, furnace combustion blacks produced by the partial combustion of essentially gaseous hydrocarbons in closed retorts and furnace thermal blacks produced by thermal decomposition of hydrocarbons such as acetylene in preheated furnaces. The carbon blacks are characterized by low ash content by having extremely small particle size, that is, 50 to 5000 A., and contain adsorbed hydrogen and oxygen. Other carbon blacks which may be used in the propellant grains are lamp blacks produced by burning liquid fuels such as petroleum oils, tars and aromatic residues in specially designed pans, combustion taking place under restricted air supply conditions. The carbon blacks as indicated above are generally characterized by exceedingly small particle size, that is, well below #325 U.S. Standard sieve particle size. However, to avoid dusting and convenience in handling, some carbon blacks are formed to the so-called "bead" type carbon blacks which "beads" are generally of such dimensions as to pass through a #20 U.S. Standard sieve and are retained on a #200 U.S. Standard sieve. The "beads" are very soft and are physically unstable as beads and become disintegrated to smaller than #325 U.S. Standard sieve during the mixing and milling of the composited propellant components as described hereinbelow. The carbon blacks are of low ash content, and usually contain less than 0.5% ash. Examples of "bead" type carbon blacks are Micronex Beads (channel blacks) and Statex Beads (furnace blacks).

A third type of carbon which is useful for improving the burning rate of our gas-producing propellant composition is graphite, flake and amorphous. If derived from a natural graphite, the ash content should be reduced below about 5% which can be accomplished by treating the natural product by air flotation or the ash content may be reduced by leaching with mineral acid or by other methods well known to the art. We prefer graphite of colloidal or semi-colloidal particle size.

Still another type of carbon which we have found effective for increasing the burning rate of the gas-forming composition is finely ground petroleum coke, particularly petroleum coke obtained as a residue in the pipe-stilling of Mid-Continent heavy residuums. Such coke usually contains less than about 1% ash and is preferably pulverized to pass through a #325 U.S. Standard sieve prior to incorporation in the gas-producing propellant composition. The coke may be activated by methods well known to the art to improve the efficiency thereof as a burning rate promoter in our propellant composition.

The "carbon" component of our composition contains not more than about 5% of ash and is in a finely divided state. Particularly suitable classes of carbons commercially available are activated carbon (active carbon or activated charcoal), carbon black, petroleum coke and graphite. In general, the finely divided carbon will pass through a #20 U.S. Standard sieve. Desirably more finely divided material is used, for example less than #200 U.S. Standard sieve size. It is preferred to use carbon having a particle size to pass through a #325 U.S. Standard sieve or which is readily reduced to such a size during the milling operation utilized in the preparation of the composition of the invention. Because of their uniformity in physical characteristics and their effectiveness in raising the burning rate, the commercially available carbon blacks are a preferred source of the carbon utilized herein. Activated carbons containing not more than about 3% ash are another preferred source of carbon for use herein.

AMMONIUM NITRATE

The term "ammonium nitrate" as used in this specification and in the claims is intended to mean either ordinary commercial grade ammonium nitrate, such as conventionally grained ammonium nitrate containing a small amount of impurities and which is then generally coated with a small amount of moisture-resisting material such as petrolatum or paraffin, or military grade ammonium nitrate, or a mixture of minor amounts of other inorganic nitrates such as sodium nitrate and/or potassium nitrate with the ammonium nitrate. Finely ground ammonium nitrate is preferred in order to reduce the voids to a minimum and hence avoid the use of excess binder material. The shaped grain usually contains at least about 70% by weight of ammonium nitrate. Although more ammonium nitrate may be used, it is preferred to limit the ammonium nitrate to not more than about 85%.

CATALYST

It has been discovered that certain iron compounds are effective catalysts for the combustion of ammonium nitrate and ammonium nitrate-oxidizable material mixtures. These catalysts are the subject matter of U.S. patent applications filed by Wayne A. Proell and William G. Stanley, Serial No. 273,564, filed February 26, 1952, and Serial No. 288,065, filed May 15, 1952. All of the combustion catalysts disclosed in these applications contain the iron cyanide radical, either ferrocyanide or ferricyanide. In addition to the iron cyanide radical, these catalysts contain a second iron ion which may be either ferric or ferro(us). In addition to the iron-iron cyanide complex, the catalyst may contain alkali metal and/or ammonium ions. It has been found that the generic classes of iron-iron cyanide compounds known as soluble Prussian blues and insoluble Prussian blues are effective catalysts for the purposes of this invention. It is known that the better soluble Prussian blues contain alkali metal(s) such as potassium and sodium and/or the ammonium radical. Some of the "compounds" which have been found to be effective area: ferro ferrocyanide, ferric ferrocyanide, ferro ferricyanide, ferric ferricyanide, potassium ferric ferrocyanide, sodium ferric ferrocyanide, ammonium ferric ferrocyanide, potassium soluble Prussian blue, sodium soluble Prussian blue and ammonium-sodium soluble Prussian blue.

These applications show that the so-called insoluble Prussian blues, either the chemical compound ferric ferrocyanide, or the commonly known insoluble Prussian blue, are more effective catalysts at high pressure operation than are the soluble Prussian blues. Thus when operating the combustion chamber containing the solid propellant at pressures between about 500 and 2000 p.s.i. a higher burning rate in inches per second is obtainable when using a given composition containing insoluble Prussian blue as the catalyst than is obtainable when using the same composition using soluble Prussian blue as the catalyst. The insoluble Prussian blue containing explosive compositions are difficult to ignite at atmospheric pressures when the amount of catalyst present is less than about 6 weight percent. However, these compositions ignite readily when an elevated pressure is imposed on the combustion chamber prior to the application of the igniting means.

The Prussian blue catalyst is an essential component of the grain composition of this invention. It is understood that sufficient Prussian blue is present in the grain to cause an undesirable amount of gassing in the high temperature test hereinafter described when the grain composition contains finely divided carbon in addition to the cellulose acetate, nitrodiphenyl ether and polyester condensation product binder. In general, the presence of about 0.5 weight percent, on the total composition, of Prussian blue causes increased gassing.

In addition to the Prussian blue, the grain composition of this invention may contain other inorganic combustion catalyst, for example, the composition may contain one or more of the conventional chromium salt catalysts used for promoting the combustion of ammonium nitrate. These chromium salts which are utilizable as combustion catalysts include ammonium chromate, ammonium polychromate, alkali- metal chromate, alkali-metal polychromate, chromic oxide, chromic nitrate and copper chromite. The dischromates are the more effective catalysts and it is preferred to use ammonium dichromate.

Copper oxide is another well-known catalyst for promoting the combustion of ammonium nitrate as is also ferric oxide.

It is preferred in the composition of the invention to use one of the Prussian blues alone. However, for special situations it may be desirable to use a mixture of Prussian blue and one of the chromium catalysts or cupric oxide or ferric oxide. In general, the mixed catalyst will have a weight ratio of Prussian blue to the other catalyst in the range of from about 1:1 to 1:3. More usually, the ratio is about 1:2. The prefered mixture consists of insoluble Prussian blue and ammonium dichromate.

In general, the compositions of the invention will contain between about 1% and 8% by weight, on the total composition, and preferably from about 2% to about 4%.

BINDER

The binder material of the gas-producing propellant composition consists essentially of cellulose acetate plasticized with:

(*a*) The liquid polyesterification condensation product obtained by reacting an aliphatic oxydicarboxylic acid containing 4 to 6 carbon atoms per molecule with a dihydric alcohol; and

(*b*) At least one nitrodiphenyl ether containing from one to three nitro groups per molecule and substantially not more than two nitro groups in any benzene nucleus.

The cellulose acetate used in this invention is known as a partially esterified cellulose acetate and is described as having an acetic acid content between about 51 and 57% by weight of acetic acid. The term "percent by weight of acetic acid" denotes the amount of acetic acid obtained on saponification of the cellulose acetate and is expressed as percent of the initial material. A particularly suitable cellulose acetate is lacquer grade, that is, a lacquer grade which analyzes between about 54 and 56% by weight of acetic acid. Lacquer grade cellulose acetate is described in addition to its acetic acid content by its viscosity, when dissolved in acetone, as between about 2 and 80 centipoises at 25° C. Hereinafter, the term "viscosity" as applied to cellulose acetate denotes the viscosity of an acetone solution containing 20% by weight of a cellulose acetate. The preferred cellulose acetate of this invention analyzes between about 54 and 56% by weight of acetic acid and has a viscosity within the range of about 2 to 10 centipoises. A binder having the proper characteristics for use in preparing the shaped explosive composition of this invention contains about 18 to 40% by weight of the defined cellulose acetate. Preferably, the binder contains between about 18 and about 25% of the defiled cellulose acetate.

The plasticizer utilized in the binder of this invention consists essentially of a combustion of two plasticizers, one of which is a liquid polyesterification condensation product obtained by reacting an aliphatic oxydicarboxylic acid containing 4 to 6 carbon atoms per molecule with an excess of at least one dihydric alcohol selected from the class consisting of ethylene glycol, propylene glycol, polyethylene glycol ether, polypropylene glycol ether and mixtures of ethylene glycol ether with propylene glycol ether, which ethers and mixtures thereof have an average molecular weight of not more than about 200. Polyethylene glycol–200, which is a mixture of tetraethylene glycol and pentaethylene glycol which may contain a minor amount of triethylene glycol, but which mixture is predominantly tetraethylene glycol, may also be used as the dihydric alcohol. A suitable aliphatic oxydicarboxylic acid for condensation with the polyhydric alcohol is diglycolic acid. Other oxydicarboxylic acids which may be used are oxyacetic-propanoic acid and oxydipropanoic acid. We prefer to esterify diglycolic acid with ethylene glycol and the polyesterification condensation product is essentially anhydrous and has an average molecular weight of about 250 to about 1000. The preferred polyesterification product obtained by reacting ethylene glycol with diglycolic acid will usually have a viscosity (S.U.S.) of from about 400 to about 600 seconds at 210° F. We prefer a polyesterification condensation product having an average molecular weight within the range of about 350 to about 600 as taught in the copending application of Norman J. Bowman and Wayne A. Proell, entitled "Polyester Plasticizers," filed November 30, 1954, Serial No. 471,992, now abandoned. Mol ratios of dihydric alcohol to the oxydicarboxylic acid

in the polyesterification reaction mixture are preferably within the range of from about 1.15–1.25 to 1.0. In preparing the polyesterification product the oxydicarboxylic acid is dissolved in the dihydric alcohol and the solution is heated, preferably in a 2-stage thermal treatment, the first stage being carried out at temperatures below about 150° C. and in the final heating stage temperatures within the range of from about 150° C. to about 200° C. are used. The extent of polyesterification is controlled by adjusting the factors of time, temperature and pressure at which the polyesterification is carried out and at least 70% of the water theoretically producible for complete esterification for the alcohol-acid charge is withdrawn. The amount of water withdrawn from the polyesterification mixture during the heating thereof is used as a measure of the progress of the polyesterification to completion. The heating of the reaction mixture is usually for a total time of at least six hours up to thirty hours or more. At least a part of the final heating stage may be carried out under reduced pressure conditions. Essentially anhydrous polyesterification products are produced, the average molecular weights of which products depend:

(1) On the mol ratio of dihydric alcohol to oxydicarboxylic acid in the solution introduced to the polyesterification reaction zone;

(2) On the extent of completion of the polyesterification reaction as indicated from the amount of water withdrawn from the reaction zone; and

(3) On the molecular weights of the dihydric alcohol and the oxydicarboxylic acid introduced to the polyesterification reaction zone. Preferably, the reaction is carried out to not less than 80% completion as based on the water theoretically producible. The term "water theoretically producible" as used herein is defined as two mols of water per mol of aliphatic oxydicarboxylic acid charged to the polyesterification reaction zone. In general, the greater the excess of dihydric alcohol used in the reaction mixture, the higher is the percent completion of the reaction. Thus, for a 20-mol percent excess dihydric alcohol in the reaction mixture, the reaction is carried out to 85–95% completion and when 30 mol percent excess dihydric alcohol is ued, the esterification should be carried out to 90–100% completion.

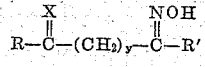
The other plasticizer component of the binder is a nitrodiphenyl ether, preferably nitrodiphenyl ether containing as an average about two nitro groups per molecule although nitrodiphenyl ethers containing from one to three nitro groups per molecule may be used. Substantially not more than two nitro groups are present on any benzene nucleus, and as an average less than about 2.5 nitro groups per molecule of nitrodiphenyl ether are present when a mixture of nitrodiphenyl ethers is used.

We prefer to use as the second plasticizer component 2,4-dinitrodiphenyl ether which may be prepared in high yields by reacting phenol with 2,4-dinitrochlorbenzene as described in copending application of Wayne A. Proell and Norman J. Bowman entitled "Thermoplastic Compositions," filed October 27, 1954, Serial No. 465,132. Mixtures of nitrodiphenyl ethers may be prepared from diphenyl ether by methods well-known in the art, using either fuming nitric acid or mixtures of concentrated nitric acid and concentrated sulfuric acid as nitrating agent. Commercial products consisting of a major proportion of diphenyl ether and a minor proportion of diphenyl may be used as the intermediate for nitration in the preparation of the nitrodiphenyl ether plasticizer component of this invention. "Dowtherm A" which is a eutectic mixture containing about 73.5% diphenyl ether and 26.5% diphenyl is such a commercial product and may be used for the production of mixtures comprising mononitrodiphenyl ethers with dinitrodiphenyl ethers and mixtures of trinitrodiphenyl ethers with these nitrodiphenyl ethers containing less nitro substituent groups than trinitrodiphenyl ethers. The term "mixtures of mononitrodiphenyl ether and dinitrodiphenyl ether and mixtures of the foregoing with trinitrodiphenyl ether" and in general, the term "nitrodiphenyl ether" is used in this specification and in the claims to include nitrodiphenyl ether and mixtures of nitrodiphenyl ethers produced from Dowtherm A. Such nitrodiphenyl ethers will contain minor amounts of nitrodiphenyls.

As indicated hereinabove, the proportion of binder material in the gas-producing propellant composition is within the range of from about 10 to about 25% by weight of the composition. The binder material consists of from about 18 to about 40% by weight of the cellulose acetate and from about 60% to about 82% by weight of the plasticizer components. The ratio (by weight) of the polyesterification condensation product plasticizer to nitrodiphenyl ether plasticizer in the binder is within the range of from about 1:4 to 4:1. We prefer about equal percents by weight of these two plasticizers in the binder material.

OXIME COMPONENT

As indicated hereinabove, we prefer a gas-forming propellant composition containing an aliphatic acyclic oxime which is added to the binder composition for the purpose of improving the combustion characteristics of the grain material with respect to the pressure exponent. The amount of oxime incorporated in the gas-producing composition is from about 1% to about 4% by weight of the composition and preferably between about 2% and 3%. Oximes corresponding to the formula



as defined above are preferred. Examples of such oximes are acetonylacetone dioxime, acetylacetone dioxime, acetonylacetone monoxime, and succinaldehyde dioxime. These oximes are particularly effective for depressing the pressure exponent of the defined explosive composition with which they are associated and are also effective in promoting ignitability of the compositions at extremely low temperatures. The oxime component is added to the molten binder material prior to the addition of the nitrate, catalyst and carbon or may be added during the milling operation to which the ammonium nitrate and binder are subjected in completing the fabrication of the grain composition.

Acetonylacetone monoxime and acetonylacetone dioxime may be prepared by reacting in stoichiometric proportions acetonylacetone with hydroxylammonium salts such as hydroxylammonium sulfate in the presence of an alkali metal hydroxide and water. Temperatures within the range of from 65° to 70° C. are used. After the reaction is complete, the mixture is cooled and stirred until the reaction mixture comes to room temperature. The oxime precipitate is filtered from the aqueous mixture and dried after washing with a small amount of water. Acetylacetone oximes may be prepared in similar manner using acetylacetone intermediate.

In preparing the compositions of this invention, the binder material is first prepared, the oxime being then thoroughly mixed with the binder after which the ammonium nitrate, carbon and catalyst are milled with the binder. The binder is prepared by heating the plasticizer material at a temperature not in excess of about 150° C., usually within the range of from about 120° C. to about 140° C. The heated plasticizer material, that is, the mixture of polyesterification condensation product, for example ethylene glycol diglycolate, and nitrodiphenyl ether, is stirred and the cellulose acetate is added, heating and stirring being continued until a homogeneous mixture is obtained. The oxime is then added to the mixture and is thoroughly mixed therewith before the addition of the thoroughly mixed ammonium nitrate, carbon and the catalyst components of the finished grain. The catalyst may be added, mixed with a part of the ammonium nitrate or it may be added immediately preced-

ing the addition of the ammonium nitrate. The ammonium nitrate, carbon and catalyst are then milled into the plasticized mass at a temperature below about 120° C. and preferably at a temperature of about 110° C. If desired, the carbon may be added and milled with the plasticized binder containing the oxime (where oxime is a component of the grain) before milling the ammonium nitrate and catalyst into the composition. Milling is continued until a product of uniform texture is obtained. Burning rate test strips are extruded or molded under pressure and the material is shaped into propellant grains as described hereinbelow.

The rate of burning of the grain material is determined at different pressures in an inert atmosphere. The test strands of materials for the determination of burning rates of compositions herein described were prepared by ram extrusion at about 110° C. The procedure outlined below describes the preparation of the gas-producing propellant compositions the results of burning tests of which are given in Tables 1 and 2 below.

PREPARATION OF PROPELLANT COMPOSITIONS

A mixture of 34.64 parts by weight of 2,4-dinitrodiphenyl ether and 34.64 parts by weight of ethylene glycol diglycolate, prepared according to the procedure described hereinabove, was added and stirred at a temperature within the range of 120°–140° C. to obtain a homogeneous mixture of the plasticizer material. To this mixture was added a total of 20.72 parts by weight of cellulose acetate (LL–1 lacquer grade) which analyzed between 54 and 56% by weight of acetic acid. The cellulose acetate was added in small portions during the stirring of the plasticizer and when all of the cellulose acetate had become plasticized as indicated by a homogeneous molten product, the molten product was colled to the range of 115–120° C. and 10 parts by weight of acetonylacetone dioxime was added. The oxime was incorporated in the plasticized mass by rapid stirring to form a homogeneous binder including the oxime. These 100 parts by weight constituted 23% by weight of the total grain composition and the binder components of these 100 parts, that is, 90 parts, constituted 20.7% of the total grain composition.

The ammonium nitrate used in fabricating the gas-forming propellant material, the performance of which is described in the tables, was a commercial grade. Samples of this ammonium nitrate (as received) were divided into 70% and 30% portions and the 70% portion was ground at 14,000 r.p.m., in a pulverizer to such a size that it would pass completely through a #325 U.S. Standard sieve. The ammonium nitrate (as received) was of such particle size as to pass substantially completely through a #325 U.S. Standard sieve. The ground material was recombined with the unground material and thoroughly mixed therewith to give ammonium nitrate of small particle size, at least 75% of which would pass through a #325 U.S. Standard sieve.

The ammonium nitrate was then divided into portions of one-third and two-thirds of the total of ammonium nitrate to be used in the grain. The finely divided carbon black in an amount of from 1 to 5% of the total grain composition and the insoluble Prussian blue catalyst were then thoroughly admixed with the one-third portion of the ammonium nitrate to be used. The binder material containing the oxime was stirred at 110° to 120° C. in a sigma blade mixer. The one-third portion of ammonium nitrate containing the carbon and Prussian blue catalyst were then added rapidly and the mixture was milled for from 15 to 20 minutes, the temperature of the mixture being maintained between about 110° and 120° C. At the end of this 15–20 minute period the remaining two-thirds portion of the ammonium nitrate was added and milling was continued for an additional 30 to 45 minutes. The last 15 minutes of this mixing period was completed under a vacuum of at least 15 inches of mercury. Homogenization was complete at the end of this milling period.

The amine inhibitor may be added to the liquid binder prior to the addition of the ammonium nitrate; this is desirable when the inhibitor is a liquid. Or, the inhibitor may be mixed into the ammonium nitrate prior to introduction into the binder; this method is more commonly used when the inhibitor is a friable solid.

Burning rate test strips of the above material were formed by subjecting the material contained in a 1" diameter cylinder to 2,000 pounds pressure and extruding therefrom through an aperture a strand of about 3/8" diameter. The composition of this invention flows fairly readily at temperatures above about 100° C. and becomes dimensionally stable at temperatures below about 90° C. This characteristic simplifies the problem of forming the test strips and also the grains since it eliminates the necessity for accelerated cooling of the mold or the extruded grain. The composition of the explosive of the invention has another distinct advantage over conventional solid propellant compositions. It was found that defective grains can be reworked alone or in admixture with fresh materials to produce satisfactory grains. The reworkability of rejects results in a substantial saving over conventional grains where rejects cannot be reworked. The material was maintained at a temperature of about 110° C. during the ram extrusion of the strand. After cooling, the strand was cut into test strips approximately 5" long and these were then coated with lacquer grade cellulose acetate to inhibit surface burning along the strand. The test strip was drilled at two points 3" apart along its length and fusible wires were inserted in the drilled holes. The test piece was then placed in a pressure bomb, electrical connection of the fuse wires being made to a timing device. The timing device was started by the fusing of one wire and as the test piece burned along its lentgh the timing device was stopped by the fusing of the second wire. Thus the time for the burning of the three inches of the test piece was obtained. The test piece was ignited by means of a Nichrome resistance wire placed in contact with one end of the test piece. Burning rates for the test pieces were determined at pressures of 600, 800, 1000, 1200, 1400, 1600, and 1800 pounds per square inch of nitrogen pressure. Burning rate in inches per second for the different pressures was plotted on log-log paper. The plot gave the straight-line relationship. The slope of this line is defined as the pressure exponent of the burning rate. Burning rates of the materials in this specification are defined as burning rates at 1000 pounds nitrogen pressure.

In the preparation of shaped propellant grains of the gas-forming material the hot mass was loaded into a 2¾" diameter mold, maintained at a temperature of about 110° C. Temperatures above about 120° C. are avoided in the milling and molding of the ammonium nitrate-containing grain in order to minimize the possibility of heat ignition of the composition under conditions of milling and molding. The mold in which the material is loaded is provided with an inset which may be of one or more different shapes. Thus the inset provides the grain with longitudinal aperture in the form of a cross, star, triangle or other shape to provide uniformly distributed internal burning surface. The grain may be tubular in form as illustrated in Figures 1 and 2.

Uniform internal burning surfaces may be provided by a multiplicity of insets in the mold. The propellant composition may also be molded into disc-shaped grains, preferably perforated for use in rockets and missiles. Discs of the material are suitably spaced in the rocket case to provide uniform combustion of the disc-shaped grains. In molding the material into grains the mold was subjected to 10,000 p.s.i. ram pressure for about five minutes after which the ram pressure was reduced to 5000 p.s.i. This pressure was maintained for an additional fifteen minutes. The mold was removed from the

press and allowed to cool to room temperature. The grain was removed from the mold and cut to 4" lengths. The exterior surface of the grains was inhibited to prevent surface burning by coating with Vistanex-asphalt mixtures. Other non-burning material such as cellulose acetate, ethyl cellulose acrylic plastics and so forth may be used.

Grains of the above composition containing activated carbon, that is, "Norite A" as the finely divided carbon component in the above composition were cycled through severe temperature changes in order to determine the resistance of the grain to fissuring. In this test, the grain was placed in a cabinet for a period of two hours, which cabinet was maintained at a temperature of 80° C. At the end of the two-hour period, the grain was removed and placed in a cold cabinet maintained at a temperature of —60° C. for a period of two hours. This complete cycle of extreme temperature change was followed immediately by a second cycle wherein the grain was again subjected to the temperature of 80° C. for two hours followed by a two-hour period in the —60° C. cabinet. Following this two-cycle temperature treatment, the grain was permitted to come to room temperature after which it was examined for external fissures and the condition of the internal structure of the grain, with respect to fissures, was determined by testing the grain in a miniature rocket motor. The grains so cycled showed no variation, with respect to burning properties, from similar grains which had not been subjected to the temperature cycling tests.

The grains prepared as described above were tested for burning properties in a miniature rocket motor. This motor consisted essentially of a cylinder closed at one end and threaded at the open end. The straight side of the cylinder was about 8 inches long and the cylinder had an internal diameter of about 3 inches. A funnel-shaped portion provided with an opening for the attachment of a nozzle and provided with threads at the larger end was threaded onto the cylindrical casing to complete the combustion chamber of the motor. Various sized orifices were provided in order to permit the operation of the motor at different combustion chamber pressures. These orifices varied from 0.17 to 0.24 inch in diameter. By varying the orifice size, the combustion chamber pressure could be varied from about 700 to about 2000 p.s.i.

In the combustion of a grain containing no internal fissures the pressure at the initial stage of the combustion rises rapidly to a level within the range of from about 700 p.s.i., to 1000 p.s.i., and remains at such level without appreciable variation during the combustion of the entire grain. Any irregularities such as fissures in the grain, internal or external, cause irregular fluctuation in the pressure developed by the combustion of the grain.

In order to reduce the amount of explosive material needed per motor test, a perforated cylindrical aluminum slug was used to take up about half the longitudinal volume of the motor. Thus in operation the motor contained the slug and a 2.5 inch diameter perforated grain 4 inches long.

The grain was ignited by a black powder mixture, which mixture was in turn ignited by means of an electrical squib. It was found that satisfactory ignition could be obtained by using 25 g. of the following mixture: sparkler powder, 10 g.; FFG gun powder, 7.5 g.; and FFFG powder, 7.5 g. This mixture was placed at the nozzle end of the funnel-shaped member and was held in place by means of a paper disc pressed firmly against the sloping sides of the member. The motor was assembled by inserting into the casing first the aluminum slug and then the grain to be tested. The test grain was inhibited on the exterior surface and the annular ends by coating with Vistanex-asphalt mixture. This inhibiting the total exterior of the grain results in the burning of the internal surfaces only. The nozzle end complete with powder igniter was then screwed to the casing. The electrical squib was then inserted through the nozzle opening until it contacted the powder mixture. This method of arming the motor is particularly desirable because the motor is essentially inert until a few seconds before the test run is fired. It has been found that this method of ignition gives ignition delays between about 100 and 500 milliseconds.

It is to be noted that the presence of ash in the carbon has little or no effect on the efficiency of the carbon for increasing the burning rate until the percentage reaches a figure above 5.0% ash. Thus graphite with an ash content of 3.52% increased the burning rate at 1% amount only about 14%. Nuchar which had an ash content of about 5% likewise was reduced in efficiency with respect to increasing the burning rate of the composition. The data with respect to channel blacks and furnace blacks indicate that samples of the latter which contained about 5.0% ash were of efficiency equal to the channel blacks, none of which contained more than about 0.15% ash. The compositions which contained 2.30% oxime exhibited low pressure exponents. Tests on various grain compositions consisting of the defined binder components, various types of finely divided carbon as defined herein, insoluble Prussian blue catalyst and mixtures of insoluble Prussian blue and ammonium dichromate were compared with the same compositions containing various of the defined amine inhibitors. It was found that the presence of the amine inhibitor had no deleterious effect on either the burning rate or the pressure exponent of the grain. In general, the burning rates ranged from 0.17 to 0.22 inch per second and the pressure exponents ranged from about 0.58 to 0.64. These burning rates and pressure exponents make these compositions suitable for use in rocket propelled missiles as well as in ATO units wherein high burning rates are desired.

HIGH TEMPERATURE STABILITY TESTS

The results obtainable by the addition of the defined amines to the composition consisting of the defined binder, insoluble Prussian blue catalyst or mixtures of catalyst and finely divided carbon are set out below. The gassing tendency was measured by an arbitrary test which has purposely been made more severe than anything that would be imposed on the composition at atmospheric temperatures. This test is commonly designated as "135° C. Gas Stability Test." This test is carried out as follows:

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 135° centigrade. A period of 15 minutes is allowed for the sample to come to the temperature of 135° C. 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 gassing tendency. The manometer readings are converted directly to cc./g./hr. for each 15 minute interval. The gas rate in cc./g./hr. for each 15 minute interval is then plotted against the time of heating of the sample. This rate is hereinafter written as cc./g./hr.

In the results reported hereinbelow, the rate of gassing

is set out at one hour, two hours and three hours, where the heating was continued for that length of time; and also the maximum rate of gassing and the time at which the maximum rate was reached. It has been found that some compositions have a hump in the curve and the maximum gas rate is higher than the long-term equilibrium rate.

In general, it is considered that a composition which has a zero gassing rate during the first hour of heating (essentially zero means within the limit of error of the test which is on the order of 0.3 cc./g./hr.) will be substantially free of gassing tendency in storage at atmospheric temperatures. It is considered that a composition which has a gassing tendency not in excess of about 2 cc./g./hr. at the first hour of heating at a temperature of 135° C. has a satisfactory gassing tendency with respect to hot storage, i.e., at temperatures as high as 77° C. for a period of 30 days. (Tests show that compositions consisting of the defined binder, Prussian blue catalyst and ammonium nitrate, while exhibiting appreciable gassing are of satisfactory gassing tendency. The presence of finely divided carbon in this composition markedly accelerates the gas product and renders such a composition unsatisfactory with respect to storage stability at atmospheric temperatures.)

Test Series A

A number of amines were tested for gas inhibition effectiveness in a control composition which had a rather high maximum gas rate. The control sample, that is, the sample containing no amine additive had the following composition:

Ingredient:	Percent
Ammonium nitrate	73.00
Insoluble Prussian blue	3.00
Norite A activated carbon	0.80
Carbon black	0.20
Binder:	
Cellulose acetate	4.76
Ethylene glycol diglycolate (polyester)	7.97
2,4-dinitrodiphenyl ether	7.97
Acetonylacetone dioxime	2.30

The ammonium nitrate of the composition was a commercial grade ammonium nitrate, of which 70% of the sample was ground in a micro-pulverizer at 14000 r.p.m., the remaining 30% being unground ammonium nitrate. At least 75% of the ammonium nitrate was of such particle size as to pass through a #325 U.S. Standard sieve. The carbon was of particle size to pass through a #325 U.S. Standard sieve and contained 3.27% ash. The carbon black contained no ash, was of particle size to pass through a #325 U.S. Standard sieve. The cellulose acetate of the binder was a lacquer grade analyzing between 54 and 56% by weight of acetic acid. The ethylene glycol diglycolate component of the binder was the polyesterification product obtained by reacting diglycolic acid with ethylene glycol prepared as described hereinabove. The product was liquid and had a molecular weight in the range of from about 350 to about 600. The 2,4-dinitrodiphenyl ether component was of high purity and was prepared by reacting 2,4-dinitrochlorbenzene with phenol as described hereinabove. The acetonylacetone dioxime component of the propellant material was prepared by reacting hydroxylammonium sulfate with acetonylacetone in the presence of sodium hydroxide and water as described hereinabove.

In preparing the samples for the tests the results of which are given in Table I, 100 parts by weight of the above composition were pulverized in the mortar and enough amine added to have 2% by weight present in the total inhibited composition. The amine was thoroughly mixed in the composition by grinding and stirring until a uniform mixture had been obtained.

The results of these tests are set out in Table I, the control sample containing no oxime indicated a maximum rate of gassing at the end of the first hour of heating and this maximum is particularly high at 21 cc. of gas per gram per hour. In general, it is desirable that the rate at anytime during the first hour does not exceed 10 cc. of gas per gram per hour. If on the other hand, the maximum rate is not more than about 10 or 11 cc. of gas per gram per hour, said maximum rate occurring in about three hours of heating, the damage to the burning qualities of the material, when fabricated in grain form, is not substantial. We have found that the high gassing rate maximum occurring in the early stages of the heating period, that is, the surge of gas from the material, is indicative of possible impaired burning properties of the composition. With the exception of triphenyl amine, the amines effectively reduced the gassing tendency of the compositions.

The more effective amines such as N,N-methylethyl aniline, phenyl beta-naphthylamine and N,N-dimethyl-p-toluidine gave substantially a zero gassing rate up to two hours of heating. The effectiveness of these amines is particularly noteworthy since the catalyst used was entirely Prussian blue.

Test Series B

In still another test, the propellant grain composition containing no carbon and no oxime was tested with respect to gassing properties, that is, a control sample and the same composition containing 2% of the diphenyl amine was examined. The control sample contained 74% of the ammonium nitrate, 8.05% cellulose acetate, 5.75% ethylene glycol diglycolate, 9.2% 2,4-dinitrodiphenyl ether, and 3.0% insoluble Prussian blue catalyst. This control sample containing no oxime, no carbon and no amine stabilizer established a gassing rate of 2 cc. of gas per gram per hour within a few minutes after heating of the sample was inaugurated, which rate was maintained for the three hour period of the test. This composition has a gassing tendency low enough to meet military requirements of high temperature storage stability. The addition of 2% by weight of diphenyl amine to this composition resulted in a material which showed a uniform maximum rate of 0.5 cc. gas per gram per hour after one hour of heating at 135° C.

Test Series C

In addition to the above tests, the effect of using a mixed catalyst was investigated. Thus, the 3% insoluble Prussian blue catalyst was substituted with a catalyst consisting of 1% insoluble Prussian blue and 2% of ammonium dichromate with and without the presence of amine stabilizer. The control sample and the amine stabilized sample had compositions tabulated below:

	Control	
Ammonium nitrate	73.00	71.50
Cellulose acetate	4.74	4.64
Ethylene glycol diglycolate	7.98	7.83
2,4-dinitrodiphenyl ether	7.98	7.83
Ammonium dichromate	2.00	1.96
Insoluble Prussian blue	1.00	.98
Acetonylacetone dioxime	2.30	2.26
Norite A	0.80	.80
Carbon black	0.20	.20
Diphenyl amine		2.00

Control sample showed no gassing at the end of one hour, a rate of 1 cc. per gram per hour at the two hour stage of the heating and a rate of 3.7 cc. of gas per gram per hour at the end of three hours. The sample which had been stabilized with diphenyl amine showed no gassing for a period of 6½ hours, with a maximum gassing rate of 1.90 cc. of gas per gram per hour at 7¾ hours. This test illustrates: (1) the reduced tendency with respect to gassing of the composition which contains the mixed catalyst, that is, reduced amount of insoluble Prussian blue catalyst; and (2) the favorable effect of diphenyl amine on stabilizing the composition even

though the tendency to gas in the absence of the amine is quite low.

Test Series D

In still another series of tests, the effect of omitting the oxime from the composition was examined. The composition of the control sample and of the sample containing diphenyl amine are tabulated below.

Components	Control	Diphenyl Amine Composition
Ammonium Nitrate	74.0	72.50
Celluslose acetate	5.1	5.00
Ethylene glycol diglycolate	8.7	8.53
2,4-dinitrodiphenyl ether	8.7	8.53
Ammonium dichromate	2.0	1.96
Prussian blue	1.0	.98
Carbon black	0.5	0.50
Diphenyl amine		2.00

An identical composition containing the N,N-diethyl aniline stabilizer instead of the diphenyl amine was also tested. Omission of the oxime from these compositions showed very little effect on the gassing properties. Thus the control sample containing no oxime and no amine stabilizer showed a uniform gassing rate of only 3 cc. of gas per gram per hour over the period of four hours heating. This rate was reached almost immediately after the sample was brought to equilibrium temperature, i.e., 135° C. The composition containing the 2% of diphenyl amine showed zero gassing for a period of 2¾ hours, with a rate of 4 cc. per gram per hour at the three hour heating time and the maximum rate of 5.6 cc. per gram per hour at the end of four hours. The sample containing the N,N-diethyl aniline did not gas until heated for a period of about 3 hours when the rate was 0.8 cc. per gram per hour. This sample reached a maximum rate of 4.3 cc. per gram per hour in about 5¼ hours. The gassing rates of compositions containing no amine, even though low, are greatly reduced when the amine was added.

The drawings, Figures 1 and 2, show a particular application of this invention to an assisted take-off unit. The ATO unit illustrated is designed to be hung under the wing of an aircraft; normally at least two units, i.e., one under each wing, will be used. In Figure 1, the body of the unit is made up of a tubular member **11** which is closed at one end and which is provided with threads at the open end. Member **11** is provided with two loops, **12** and **13**. These loops are used to hang the unit from a carrier, not shown, which is attached to the wing of the aircraft. This carrier makes it possible to jettison the unit after take-off. A somewhat funnel shaped member **14** is attached to member **11** by engagement of the threads at the large open end of member **14** with the threads on member **11**. Member **14** is provided with a nozzle **16** through which the decomposition products pass. The size of nozzle **16** determines in part the pressure maintained inside of the chamber formed by members **12** and **14**.

The solid propellant fills the cylindrical portion of member **11**. The solid propellant in this illustration consists of seven tubular grains, **17**, **18**, **19**, **20**, **21**, **22** and **23**; each having an O.D. of about 3 inches and having a centrally located cylindrical opening 1 inch in diameter, the full length of the grain; the grains are approximately 30 inches long. The grains used herein consist essentially of Prussin blue catalyst, which may be insoluble Prussian blue catalyst, diaminotoluene binder, oxime, carbon and ammonium nitrate as described for grain compositions described above.

Each grain has the annular area at each end inhibited against burning by a coating of asphalt in order that the burning may take place on the cylindrical surfaces only. For some uses it is desirable to have a grain which burns cigarette fashion in which case the outer surface and one end of the grain will be inhibited to prevent combustion.

Although a tubular grain is illustrated herein, the invention is not limited to such a grain. Any particular shape may be utilized. Examples of other shapes are cylinder, cruciform, triform, hexaform, octaform and slab as described above. In the case of perforated grains, the perforation may be circular or star-shaped with various numbers of points in the star. Furthermore, a singly cylindrical grain having one or more longitudinal perforations may be utilized in some cases, instead of the multi-grain unit shown.

The grains are held in longitudinal position and prevented by sliding back and forth in the combustion chamber by means of a wire grid **26**. Wire grid **26** consists of a ring cut to fit the threads of member **14** and provided with a grid work of metal wires that will resist the high temperature existing in the combustion chamber.

On one side of the conical portion of member **14** there is provided for the combustion chamber a safety venting means **28**. Venting means **28** comprises a tubular member fastened to member **14**, which tubular member has full access to the combustion chamber and is provided with a rupture disc, not shown. The rupture disc is of such construction that excess pressure in the combustion chamber will blow out the disc, whereby the pressure in the combustion chamber will be held below the point of serious damage to the unit.

An igniter means is positioned within member **14** so as to close off the nozzle **16**. The igniter means consists of a container **31** filled with black powder, or some other easily ignited material, which can produce a large volume of gases at elevated pressure. A squib **32** for igniting the powder, is attached to the container **31** in communication with the powder contained therein. Electrical wires **33** connnect a wire in the squib to the electrical system of the aircraft and a switch therein (the connections to the aircraft are not shown).

The ATO unit is assembled as follows: The grains are inserted into member **11**. Venting means **28** are fastened to member **14**. Igniter **31** is inserted through the large open end and fitted so as to close the nozzle, the wires **33** having first been passed through the nozzle **16**. The wire grid **26** is screwed into the large open end of member **14**. The assembled nozzle portion is then securely screwed onto member **11**.

The assembled unit is then attached to the wing of the aircraft by loops **12** and **13**; wires **33** are connected to the electrical operating assembly in the aircraft. When the pilot desires to obtain the assisted take-off, he throws the switch which causes the current to pass through wire **33** and to heat up the firing wire in squib **32**, which in turn ignites the powder in the container **31**.

The container is of sufficient strength to withstand the initial pressure generated by the gases from the powder. The hot gases raise the pressure in the combustion chamber high enough to permit the grain to ignite. The combustion of the grain causes the pressure in the chamber to rise to a point which cannot be resisted by container **31**. The container disintegrates and the pieces are discharged through nozzle **16**. The total time from throwing the switch to full operation of the unit is on the order of less than 0.5 second.

As the gases pass out of the nozzle the reaction acts on the aircraft and adds its thrust to assist the aircraft's propeller; a marked increase in forward speed results and permits the aircraft to take off in a shorter space of time or it permits lifting a load heavier than could be airborne by the use of the propellers alone.

When using about 4% or more of the iron-type catalyst, the grain will ignite at relatively low pressures and no special precautions are necessary to maintain elevated pressure in the chamber until ignition occurs, as shown above. In this case, the igniter may be introduced into the combustion chamber by a means attached to the coni-

cal portion of member 14 (this procedure is conventionally used and is illustrated in U.S. 2,479,828) and no closure is placed on nozzle 16.

The conventional placement of the igniter may be used with the lower catalyst content grains. However, it is necessary to use a much heavier powder charge in the igniter or, preferably, the nozzle is provided with a rupture disc, which is set to blow out at about 500 p.s.i. Other methods of igniting the grain can be readily devised.

While the invention has been illustrated by an assisted take-off operation it is probable that the preferred use will be in air-to-air missiles.

TABLE

Inhibitor	Gassing Rate, cc./g./hr.				
	1 hr.	2 hrs.	3 hrs.	Maximum	
				hrs.	Rate
None	21.0	6.4	5.8	1	21.0
Diphenyl amine (i)	8.8	4.2	------	1	8.8
Diphenyl amine	0.5	1.8	4.0	3½	8.4
Phenyl beta naphthylamine	0.0	1.0	1.7	4	4.4
Triphenyl amine	------	------	------	¼	13.8
N,N-methylethyl aniline	0.0	0.0	1.1	4½	7.2
Aniline	0.6	0.0	5.8	3¼	8.6
N-methyl aniline	0.6	0.3	0.3	4¾	12.4
N,N-dimethyl aniline	0.0	0.0	1.5	5¾	11.0
2,4-diaminotoluene	0.0	0.0	0.6	6½	8.0
N,N-dimethyl-p-toluidine	0.0	0.0	7.0	3¾	22.0
p-phenylene diamine	1.3	0.4	2.5	3¾	11.4
o-phenylene diamine	1.3	0.4	3.5	3¾	11.4
p-dodecyl aniline	4.0	------	------	1¾	13.3

We claim:

1. A composition of matter suitable for use as a propellant consisting of an effective amount of a combustion catalyst comprising Prussian blue; from about 0.5% to about 7% by weight of finely divided carbon containing not more than about 5% ash, the particle size of said carbon being such that the finely divided carbon will pass through a #20 U.S. Standard sieve, from about 10% to about 25% by weight of a plastic binder consisting essentially of between about 18% and 40% by weight of cellulose acetate which analyzes from about 51% to 57% by weight acetic acid; and from about 60% to about 82% by weight of plasticizer components consisting essentially of the liquid polyesterification condensation product obtained by reacting one mol of an aliphatic oxydicarboxylic acid containing 4 to 6 carbon atoms per molecule with from about 1.08 mols to about 1.3 mols of at least one dihydric alcohol selected from the class consisting of ethylene glycol, propylene glycol, polyethylene glycol ether, polypropylene glycol ether and mixtures thereof which ethers and mixtures thereof have an average molecular weight not more than about 200 and which polyesterification condensation product is essentially anhydrous and has an average molecular weight of about 250 to about 1000; and at least one nitrodiphenyl ether containing from one to three nitro groups per molecule and substantially not more than two nitro groups on any benzene nucleus, the ratio by weight of said polyesterification condensation product to said nitrodiphenyl ether in said binder being in the range of 1:4 to 4:1; from about 0.5 to 4% of a gassing inhibitor selected from the class consisting of (*a*) $RZ(NR'R'')x$ where R is selected from the class consisting of hydrogen and alkyl containing from 1 to 12 carbon atoms, Z is an aromatic nucleus selected from the class consisting of phenyl and naphthyl, R' and R'' are selected from the class consisting of hydrogen and alkyl containing from 1 to 4 carbon atoms and *x* is an integer from 1 to 3; and (*b*) diphenylamine, dinaphthylamine, and phenyl naphthylamine; the remainder essentially all ammonium nitrate, said composition containing at least about 70% by weight of ammonium nitrate.

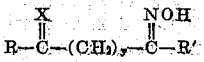
2. The composition of claim 1 wherein said combustion catalyst is present in an amount between about 1% and about 8% by weight.

3. The composition of claim 1 wherein said combustion catalyst is insoluble Prussian blue.

4. The composition of claim 1 wherein said inhibitor is diaminotoluene.

5. The composition of claim 1 wherein said inhibitor is diphenylamine.

6. The composition as described in claim 1 containing from about 1% to about 4% by weight of said composition, an aliphatic oxime corresponding to the empirical formula:



wherein R and R' are selected from the class consisting of methyl, ethyl and hydrogen, X is selected from the class consisting of oxygen and NOH, and *y* is an integer from 0 to 2.

7. The composition of claim 6 wherein the oxime is acetonylacetone dioxime.

8. A shaped gas-producing propellant grain composition consisting of (*a*) about 4.75% by weight of cellulose acetate which analyzes 54% to 56% by weight of acetic acid, (*b*) about 8% by weight of 2,4-dinitrodiphenyl-ether, (*c*) about 8% by weight of the anhydrous, liquid polyesterification condensation product of ethylene glycol with diglycolic acid, said condensation product having an average molecular weight within the range of about 350 to about 600, (*d*) about 3% by weight of insoluble Prussian blue catalyst, (*e*) about 2.3% by weight of acetonyl-acetone dioxime, (*f*) about 1% to about 5% by weight of activated carbon of particle size to pass through a #325 U.S. Standard sieve and containing not more than about 5% ash, (*g*) about 2% by weight of diaminotoluene, (*h*) the remainder essentially all ammonium nitrate.

No references cited.