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ROCKET PROPELLANT

Filed Dec. 23, 1954

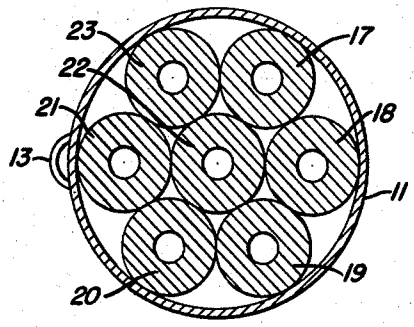


Fig. 2

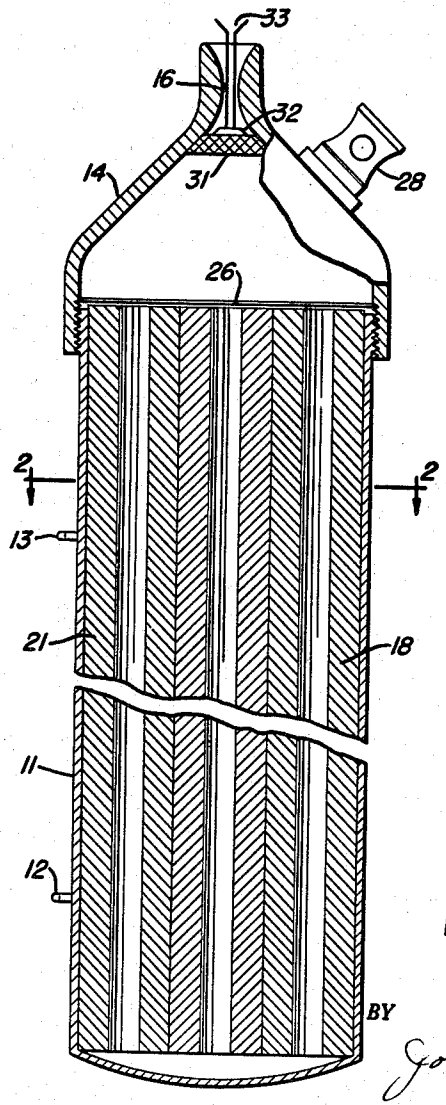


Fig. 1

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ROCKET PROPELLANT

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12 Claims. (Cl. 52—.5)

This invention relates to a composition for the generation of gas, said composition containing ammonium nitrate as a principal gas-producing agent. More particularly, the invention relates to a novel composition usable with a binder material as a shaped explosive. Specifically, the invention relates to a novel composition consisting essentially of ammonium nitrate gas-producing agent, a binder material, a catalyst for the promotion of combustion of the composition, and finely divided carbon to improve the combustion characteristics of the composition, particularly to increase the burning rate thereof, to which composition may be added an aliphatic acyclic oxime. More specifically, the invention relates to a shaped explosive grain consisting essentially of the above components.

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 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 Fuels in 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 at 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 ballastite and cordite have pressure exponents between about 0.6 and 0.7. A composition having a pressure exponent of the order of 1 readily passes into detonation with only a small amount of shock. 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.

An object of this invention is the preparation of a gas-generating composition for use in rockets, the principle 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 desirably at least about 0.16 inch per second at 1000 pounds' pressure. Other objects will become apparent from the description of the invention hereinbelow.

We have discovered that a gas-producing propellant grain composition consisting essentially of a hereinafter defined mixture containing a major proportion of ammonium nitrate, a Prussian blue combustion catalyst, finely divided carbon and a plastic binder consisting essentially of cellulose acetate plasticized with a 2-component plasticizer consisting of a nitrodiphenyl ether and a liqid polyester condensation product of a dihydric alcohol and an aliphatic oxydicarboxylic acid has a relatively high burning rate and is physically stable with respect to non-development of fissures when subjected to wide ranges of storage temperatures. To this composition may also be added an aliphatic ketoxime or ketodioxime to improve the burning characteristics of the grain with respect to ignitability at low temperatures and with respect to improving the pressure exponent of the propellant grain as described above. We have found that the incorporation of finely divided carbon in the grain composition imparts greatly increased burning rate thereof without adversely affecting the improvement in pressure exponent accomplished by incorporation of the oxime in the grain composition.

Briefly, our gas-producing propellant composition consists essentially of:

(1) At least 70% by weight of ammonium nitrate, usually from about 70% to about 85% by weight;

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

(3) 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; and

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

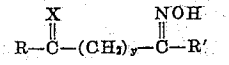
(*a*) Between about 18% and 40% by weight of cellulose acetate which analyzes from about 51% to 57% by weight acetic acid; and

(*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 everage 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.

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



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.

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 hydro-

gen 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 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.

PRUSSIAN BLUE 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 are: 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 Prussion 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.

An application, Serial Number 288,549, filed May 17, 1952, by Wayne A. Proell, discloses that ammoniated insoluble Prussian blue is an effective catalyst for the combustion of ammonium nitrate or ammonium nitrate-oxidizable material mixtures. The ammoniated insoluble Prussian blue catalyst possesses the ignition characteristics of the soluble Prussian blue catalyst and the burning rate characteristics of the insoluble Prussian blue catalyst. When used in the mixture in amounts of about 3 to 4%, the ammoniated insoluble Prussian blue catalyzed mixture is hard to ignite and does not sustain combustion in an inert atmosphere. The ammoniated insoluble Prussian blue catalyst is produced by exposing an insoluble Prussian blue to the action of ammonia gas. The temperature of the reaction zone containing the insoluble Prussian blue and ammonia gas increases rapidly until a temperature of about 60° C. is reached; as the temperature increases, the rate of increase decreases until at about 60° C. a plateau is reached. As measured by temperature increase, the interaction of ammonia and the insoluble Prussian blue is believed to substantially stop when the temperature of the reaction zone reaches the plateau of about 60° C. The ammoniated insoluble Prussian blue has a strong odor of ammonia after being cooled to room temperature. An ammoniated insoluble Prussian blue of catalytic activity about equal to the odorous material which does not possess any appreciable ammonia odor can be obtained by maintaining the odorous material at a temperature of about 70° C. for several hours. The

ammoniation of the insoluble Prussian blue does not change the physical appearance of the material and is noticeable principally in that the catalytic activity of the insoluble Prussian blue, particularly at low operating pressures, is markedly improved. By this treatment various catalytically active grades of insoluble Prussian blue can be converted to materials having about equal catalytic activity, i.e., the normal variation in catalytic activity of Prussian blue obtained from different manufacturers can be eliminated by this ammoniation procedure. The term "ammoniated insoluble Prussian blue" is intended to include both the ammonia-odorous material and the substantially odor-free material.

An application, Serial Number 287,623, filed May 13, 1952, by Wayne A. Proell, discloses that alkali metal-iron cyanide and ammonium-iron cyanide are effective catalysts for sensitizing the ignition and combustion of ammonium nitrate-base explosives. Particularly effective are potassium ferricyanide and ammonium ferricyanide. These "iron cyanide" catalysts are not as effective when used in compositions containing oxygenated oxidizable materials as are the iron-iron cyanide complexes, the soluble Prussian blues, the insoluble Prussian blues and the ammoniated insoluble Prussian blues.

When using any one or a mixture of iron-type catalysts defined above, between about 1% and 8% by weight, preferably about 2% to about 4% by weight of catalyst based on the total weight of the grain is used.

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 exposive 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 defined cellulose acetate.

The plasticizer utilized in the binder of this invention consists essentially of a combination 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 Plasticizer," 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 depends:

(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 used, 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.

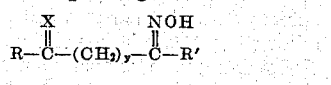
We prefer to use as the second plasticizer component

2,4-dinitrodiphenyl ether which may be prepared in high yields by reacting phenol with 2,4-dinitrochlorobenzene 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 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 monooxime, 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 nitrate and binder are subjected in completing the fabrica- of the nitrate, catalyst and carbon or may be added during the milling operation to which the ammonium tion of the grain composition.

Acetonylacetone monooxime 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 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 preceding 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 as 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 cooled 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 product. Samples of the 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 Micropulverizer 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 #35 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 grains and burning test strips produced from this material fabricated as described below had the following approximate composition:

	Percent
Cellulose acetate	4.75
2,4-dinitrodiphenyl ether	8.00
Ethylene glycol diglycolate	8.00
Insoluble Prussian blue catalyst	3.00
Acetonylacetone dioxime	2.30
Finely divided carbon	1 to 5

The remainder essentially all ammonium nitrate.[1]

[1] Where the amount of carbon added to the composition amounted to 1% by weight, the ammonium nitrate content of the grain was about 73%. When 5% of carbon was included in the binder, the percent ammonium nitrate in the finished grain was about 69%.

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 length 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.

The results of burning tests of strand materials having compositions indicated above and fabricated as described above are shown in Tables 1 and 2. Burning rates for the compositions are expressed in inches per second at 1000 pounds' pressure of inert gas, that is, nitrogen. The catalyst used in these compositions was insoluble Prussian blue. The ammonium nitrate used in the compositions was finely ground to particle size such that the major portion, that is, at least 75% would pass through a #325 U.S. Standard sieve. We have found that this grade of ammonium nitrate when finely ground exhibits relatively high burning rate even in the absence of finely divided carbon with which it is associated in the composition.

Table 1

Experiment	Carbon (Percent)	Oxime (Percent)	Burning Rate (Inches/Sec.)	Pressure Exponent
1	None	None	0.14	ca 0.8
2	None	Acetonylacetone Dioxime (2.3%).	0.14	0.58
3	Norit A [1] (1%)	do	0.19	0.60
4	Norit A [1] (5%)	do	0.22	0.60
5	Carbon Black [2] (1%)	do	0.19	0.65
6	{Petroleum Coke [3] (0.8%) {Carbon Black [2] (0.2%)	do	0.17	0.60

[1] Commercial grade Norit activated carbon. Particle size less than #325 sieve. Ash content 3.27%.
[2] Particle size less than #325 U.S. Standard sieve. Ash—zero.
[3] Obtained by coking Mid-Continent residuum, ground to particle size to pass through a #325 U.S. Standard sieve. Ash 0.42%.

The above data in Table 1 indicate a relatively high burning rate for the strand containing no carbon and no oxime. The addition of oxime to the composition had substantially no effect on the burning rate of this strand but drastically reduced the value of the pressure exponent. The compositions containing the activated carbon showed greatly increased burning rates over the compositions containing no carbon, and this increase in burning rate (about 35% for 1% carbon and approximately 60% for 5% activated carbon in the composition) was accomplished without materially affecting the value of the pressure exponent. Likewise, the burning rate of the composition containing 1% of carbon black showed a burning rate increase of about 35% resulting from the presence of carbon black. The mixture of petroleum coke with the carbon black incorporated in the composition increased the burning rate about 20%.

The burning rate of gas-forming propellant compositions containing cellulose acetate, 2,4-dinitrodiphenyl ether, ethylene glycol diglycolate, insoluble Prussian blue catalyst, acetonylacetone dioxime, ammonium nitrate and different types of finely divided carbon in equal amounts in the different examples, that is, 1% on the total weight of the strand material, and in proportion shown above with respect to the components, is shown in Table 2. The ash content of these finely divided carbons is also included in the table. Included in the general types of carbon are channel blacks, furnace blacks, graphite and Nuchar (activated carbon).

Table 2

Experiment	Carbon		Burning Rate (Inches/Sec.)	Pressure Exponent
	Type	Ash, Percent		
7	None		0.14	0.58
8	Micronex Beads (W-6) (Channel).	0.13	0.20	0.60
9	Peerless Mark II (Channel).	0.09	0.19	0.61
10	Statex Beads (125) (Furnace).	0.53	0.20	0.58
11	Continex Furnace Black (HAF).	0.50	0.19	0.54
12	Continex Furnace Black (HMF).	0.35	0.18	0.67
13	Continental Channel Black (E.P.C.).	0.15	0.18	0.61
14	Witco Channel Black (MPR).	0.15	0.17	0.64
15	Graphite (Flake)	3.52	0.16	0.65
16	Nuchar (C-190-N)	5.25	0.16	0.55

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 0.5% 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 0.5% 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.

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 Prussian blue catalyst, which may be insoluble Prussian blue catalyst, 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 gasses 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** connect 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 conical 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.

We claim:

1. A composition of matter suitable for use as a gas-producing propellant consisting essentially of from about 70% to about 85% by weight of ammonium nitrate, from about 1% to about 8% by weight of Prussian blue combustion catalyst, from about 0.5% to about 7% of finely divided carbon containing not more than about 5% by weight of ash and a plastic binder material in an amount within the range of from about 10% to about 25% by weight of said composition which binder material consists essentially of (*a*) from about 18% to about 40% by weight of cellulose acetate which analyzes from about 51% to about 57% 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 oxydi-

carboxylic acid containing 4 to 6 carbon atoms per molecule with about 1.08 mols to about 1.30 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,

wherein the ratio by weight of said polyesterification condensation product (i) to said nitrodiphenyl ether (ii) in said binder is from about 1:4 to about 4:1.

2. The composition of claim 1 wherein the cellulose acetate analyzes from 54% to 56% by weight of acetic acid.

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

4. The composition of claim 1 wherein the carbon is of particle size to pass substantially completely through a #325 U.S. Standard sieve.

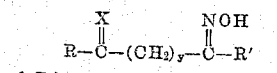
5. The composition of claim 1 wherein the carbon is carbon black.

6. The composition of claim 1 wherein the carbon is activated carbon.

7. The composition of claim 1 wherein the carbon is petroleum coke.

8. The composition of claim 1 wherein the carbon is graphite.

9. 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.

10. The composition of claim 9 wherein the oxime is acetonylacetone dioxime.

11. The composition of claim 9 wherein the oxime is acetylacetone dioxime.

12. 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 acetonylacetone 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 and (*g*) the remainder essentially all ammonium nitrate.

No references cited.