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GAS-GENERATING COMPOSITION

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This invention relates to a composition for the generation of a gas; and pertains, more particularly, to an improved gas-generating composition comprising ammonium nitrate as the primary gas-producing component of the composition, intimately mixed with a combustible binder material comprising plasticized styrene-acrylonitrile copolymer resin. Such composition is useful for the propulsion of rockets for ground-to-ground missiles, ship-to-shore missiles, air-to-ground missiles and air-to-air missiles and the compositions may also be used as propulsion means in "assist take-off" of military and commercial aircraft.

Ammonium nitrate is widely used as a component of high explosives, particularly the so called safe explosives. Even though ammonium nitrate is classified as a high explosive, it is extremely insensitive to ordinary heating and to shock and cannot readily be detonated by the local application of heat or by a blasting cap. Further, when ignited, ammonium nitrate alone does not burn uniformly and has a tendency to go out. In order to improve the burning quality, to utilize the excess free oxygen available from the decomposition of the ammonium nitrate, and to provide shaped grains suitable for use in rocket motors and assist take-off motors, combustible binder material is used in the ammonium nitrate composition.

The use of ammonium nitrate base compositions as solid propellants for rockets and assist take-off units is attractive because of the cheapness and availability of ammonium nitrate, because of the relatively low flame temperature of decomposition of ammonium nitrate, that is, between about 3150° and 2900° F. and because of the availability of the excess free oxygen. The physical characteristics of ammonium nitrate and grain material produced therefrom introduce problems with respect to choice of binder components. Thus solid ammonium nitrate exists in different crystalline forms at different temperatures, the transition from one form to a different form involving a volume change of the ammonium nitrate. Volume changes which occur at about 90° F. and also at about 0° F. involve 3.5% and about 3%, respectively. It would therefore appear that an ammonium nitrate-base composition could be seriously affected by storage under the variable temperatures encountered in many parts of the world.

One requirement for a solid propellant grain suitable for military use is that it be ballistically stable after prolonged storage at temperatures as high as 170° F. or as low as —75° F. Another requirement is that the grain not shatter, crack or malperform ballistically after being subjected to temperature extremes; that is, 170° F. followed immediately by transfer to a cold box held at —75° F. in a series of at least two repeated cycles. Another severe requirement imposed on solid propellant grains is ignition at temperatures down to —75° F. with the same igniter charge which is suitable at ambient temperatures. Grains must also be able to withstand shattering at low temperatures and distortion at high temperatures when subjected to shock.

An object of this invention is the preparation of a gas-generating composition using ammonium nitrate as the principal gas-generating material. Another object of the invention is the preparation of a shaped propellant composition (grain), consisting essentially of ammonium nitrate, a binder material comprising styrene-acrylonitrile copolymer resin plasticized with a plasticizer comprising at least one nitro aromatic compound, and a combustion

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catalyst, which grain will flex and not fissure in range of temperature between about 170° F. and —75° F. Still another object is to produce a gas-generating composition comprising ammonium nitrate, a binder material comprised essentially of plasticized styrene-acrylonitrile copolymer resin, and an inorganic combustion catalyst, which gas-generating composition is suitable for use in rockets and assist take-off units. Yet another object is the preparation of a composition which is suitable for use as a binder for a mixture of ammonium nitrate and a combustion catalyst. A further object is to provide an improved grain which is useful as a rocket fuel and as fuel for a jet assisted take-off unit. This grain is characterized by having a burning rate at 1000 p.s.i., of at least 0.10 inch per second and which is preferably of the order of 0.10 to 0.20 inch per second. Other objects will be apparent as the detailed description of the invention proceeds.

The composition of this invention comprises a combustible binder material comprised of about 20% to about 40% by weight of styrene-acrylonitrile copolymer and about 60% to about 80% by weight of at least one nitro-substituted aromatic plasticizer. To the nitro-substituted plasticizer may be added a minor amount of high oxygen-containing plasticizer containing no nitro substituent groups to improve the low temperature physical properties of the binder. The binder material is particularly suitable for incorporation in an ammonium nitrate based gas-producing propellant composition which also contains inorganic combustion catalyst and to which may be added finely divided carbon and a small amount of a surfactant such as a sorbitan oleate. Such gas-producing propellant corresponds on a weight basis to the following composition:

		Percent
(A) Plastic binder		8 to 25
	Percent	
(a) Styrene-acrylonitrile copolymer	20–40	
(b) Plasticizer	80–60	
(B) Inorganic combustion catalyst		1 to 10
(C) Carbon		0 to 5
(D) Surfactant		0 to 1
(E) Remainder of composition essentially ammonium nitrate.		

The styrene-acrylonitrile resins of the binder material of this invention are solid copolymers, preferably reduced to fine particles before mixing with the plasticizer. The copolymer contains from about 15 to about 40 mol percent, preferably about 29 mol percent of acrylonitrile units and from about 85 to about 60 mol percent, preferably about 71 mol percent of styrene units. The binder material contains on a weight basis from about 20% to about 40% of the styrene-acrylonitrile, the remainder of the binder, that is, about 80 to about 60% being plasticizer for the syrene-acrylonitrile copolymer.

The plasticizers in the binder material consist predominately of nitro aromatic compounds the nitro substituent groups of which are attached to the phenyl nuclei of the aromatic compounds. The nitro aromatics contain from one to 2 phenyl groups per molecule and not more than 2 nitro substituent groups on any phenyl nucleus of the compound. These nitroaromatics may be classified as the dinitrobenzenes, dinitrotoluenes, dinitrodiphenyl ethers, dinitrostilbenes, dinitrophenyl allyl ethers, dinitrophenyl propyl ethers, dinitroanisoles, bis (dinitrophenyl) propyl ethers and bis (dinitrophenyl) triglycol ethers. Examples of these are orthodinitrobenzene, 2,4-dinitrotoluene, 2,4-dinitrodiphenyl ether, 2,4- dinitrostilbene, 2,4-dinitrophenyl allyl ether, 2,4-dinitrophenyl propyl ether, 2,4-dinitroanisole, bis(2,4-dinitrophenyl) propyl ether and bis(2,4-dinitrophenyl) triglycol ether. Mixtures containing at least 2 of these nitroaromatic compounds are preferred in the plasticizer. However, binder compositions which contain only one nitroaromatic compound as plasticizer may be used.

In the choice of plasticizer components for the binder of the ammonium nitrate based compositions preference is reserved for highly oxygenated material other factors being equal. At least one plasticizer material containing no nitro substituent groups may be used in minor amount in the plasticizer material. Suitable non-nitro group containing plasticizers are esters of polyhydric alcohols or esters of polycarboxylic acids. For example, dialkyl phthalates containing from 1 to 8 carbon atoms in the alkyl groups thereof, triethyl citrate, tributyl citrate, diethyl tartrate, dibutyl tartrate, triethylene glycol-di-2-ethylbutyrate (Flexol 3GH) or triethylene glycol-di-2-ethylhexoate may be added in minor amounts up to 40% by weight of the total plasticizer of the binder. Still another plasticizer component which has been found to be effective in adding body to the binder is known commercially as Poly-pale Resin and when used in the plasticizer is added in minor amounts only and is a hard thermoplastic polymerized rosin having a softening point of 198–208° F. by the A.S.T.M. Ring and Ball Test E–28–42T, a Cleveland Open Cup flash point of about 424° F., an acid number of 140–155, as an average about 150, a specific gravity of about 1.072 (20° C.) and an index of refraction of about 1.544 (20° C.). The Ubbelohde viscosity of a 60% solution of this product in toluene is about 25 centipoises.

Normally liquid plasticizer such as the above esters must be compatible with the styrene-acrylonitrile and the nitroaromatic components. Oxygen balance is important and esters of higher oxygen content are preferred when they have no undesirable effects. Some plasticizers impart good properties with regard to impact resistance, hot aging, and cycling of the shaped ammonium nitrate propellant grains through extreme temperature changes. These are usually preferred regardless of oxygen balance in the composition.

The dinitrodiphenyl ethers of the plasticizer may be prepared by reacting, in alkali media, the appropriate nitro substituted chlorobenzene with phenol in substantially equal molar concentrations of the reactants according to the Williamson reaction. Likewise the nitrophenyl propyl ethers and nitrophenyl allyl ethers may be produced by reacting the alcohol with the nitro substituted chlorobenzene in alkali media. The bis (dinitrophenyl) propyl ether may be prepared by condensing 1 molecule of propylene glycol with 2 mols of the dinitrochlorobenzene in an alkali media and the bis (dinitrophenyl) triglycol ether may be prepared by condensing one mol of triethylene glycol ether with 2 mols of the dinitrochlorobenzene in alkali media. The dinitrostilbene is prepared by condensing 1 mol of dinitrotoluene preferably 2,4-dinitrotoluene with 1 mol of benzaldehyde. The phenyl nuclei and the aliphatic groups of the ethers as well as the dinitrostilbenes contain only nitro substituent groups.

The relative amounts of the defined nitro substituted aromatics or mixtures of these where used in the binder may be varied over a wide range. Thus the plasticizer may consist entirely of 2,4-dinitrodiphenyl ether, entirely of 2,4-dinitrotoluene or a mixture of these, or one or more of the other dinitro substituted aromatic compounds may be mixed with either or both of these as plasticizer in the binder. The plasticizer contains a major part, that is, at least about 60% by weight of the nitro aromatic compound plasticizer which plasticizer may consist entirely of the nitro aromatics. Not more than 40% by weight of the plasticizer may consist of the above esters.

Examples of inorganic combustion catalysts which may be used in the grain compositions are the Prussian blues and ammonium dichromate. The term "Prussian blue" as used herein is defined to include the ferric ferrocyanide, insoluble Prussian blues and also the soluble Prussian blues. The Prussian blue and the ammonium dichromate catalytic material are preferably used as mixtures

of these catalytic materials and are usually incorporated in the compositions intermixed as a finely divided powder with the ammonium nitrate. The amount of inorganic catalyst used is usually within the range of from about 1 to about 10% preferably from about 1 to about 5%, for example about 3% by weight of the composition. When using mixtures of the Prussian blue and ammonium dichromate catalyst the ratio of Prussian blue catalyst to dichromate catalyst is preferably in the range of from about 1 part of Prussian blue to 2 parts of ammonium dichromate and 2 parts of Prussian blue to 1 part of ammonium dichromate although the ratios of the two types of catalysts in the mixtures is not critical since the soluble Prussian blue, insoluble Prussian blue or ammonium dichromate may be used alone as the sole inorganic combustion catalyst in the compositions.

Finely divided carbon may be added to the gas-producing composition in amounts up to about 5% by weight, preferably in amounts of 0.5 to 3.0% by weight of the finished grain for the purpose of improving burning rate. Highly adsorptive activated carbons such as "Norit" and "Nuchar" make up one class of effective burning rate additives. A second general type of carbon useful for increasing the burning rate of compositions are the carbon blacks, roughly classified as the channel blacks and the furnace combustion blacks. The carbon blacks are characterized by low ash content, and by having extremely small particle size, that is, 50 to 5000 A. In order to avoid dusting and afford convenience in handling, some carbon blacks are available in "bead" form. The "beads" are extremely soft and disintegrate during the mixing of the composition. Examples of "bead" type carbon blacks are Micronex beads (channel blacks) and Statex beads (furnace blacks).

A third type of carbon which may be used in the composition is finely ground petroleum coke, particularly petroleum coke obtained as residue in the pipestilling of mid-continent heavy residuums. Such coke usually contains less than about 1% ash and hence, like the carbon blacks, is particularly suitable in gas-producing grains where it is desirable to keep to a minimum solid inorganic particles in the combustion gas. The coke may be activated by methods well known in the art to improve the efficiency thereof as a burning rate promoter and it is preferably ground to pass through a #325 U.S. Standard sieve.

The burning rate of grains shaped from the compositions of this invention varies with pressure, the higher the pressure the higher the burning rate. If strands of the compositions are burned at successively higher pressure, usually within the range of 600 to 1800 p.s.i. in the presence of an inert gas such as nitrogen, plotting of the burning rate in inches per second versus pressure on log-log paper gives a straight line. The burning rate at 1000 p.s.i. is an interpolated value obtained from the burning rate-pressure straight line plot. Burning rate strands are usually ¼" x ¼" in cross section and about five inches in length. These may be cut from molded slabs or burning rate strands may be obtained by extruding the composition.

It has been found that the addition of a small amount of sorbitan oleate containing from 1 to 3 oleyl radicals per molecule as a surface modifying component reduces the power requirement to extrude the composition and also provides improved uniform texture of the composition. The surfactant may be added in amounts up to 1% by weight of the composition preferably in amounts within the range of 0.05 to about 0.5% by weight of the composition. Sorbitan sesquioleate is very effective for this service.

The major part of the composition, that is, the component exclusive of binder, catalyst, and other components added in minor amounts to improve specific properties in the composition, consists essentially of ammonium nitrate. One of the particular advantages of the styrene-acrylonitrile based binder is that a relatively small percentage of the composition may be used as binder material for the ammonium nitrate thus making possible the fabrication of ammonium nitrate propellant grains of balanced oxygen content to produce upon combustion carbon monoxide and carbon dioxide without producing smoke in the exhaust gas. In general the amount of ammonium nitrate in the composition varies from about 70% to about 90% by weight of the composition. Since ammonium nitrate is the principal oxygen-affording component, relatively high proportions of the oxygen are available for the combustion of the compositions containing low binder content.

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 which may be coated with a small amount of moisture-resisting material such as petrolatum or paraffin; or to mean miltary grade ammonium nitrate or mixtures of minor amounts (usually less than 10%) of other inorganic nitrates such as sodium nitrate or potassium nitrate with the ammonium nitrate. A mixture of finely ground and coarsely ground ammonium nitrate is preferred, and the major proportion of the ammonium nitrate is finely ground. I prefer to grind the ammonium nitrate with a part or all of the catalyst component of the composition.

Preparation of the compositions of this invention may consist of these two steps, i.e., making the binder and mixing binder with ammonium nitrate and other ingredients to form a homogeneous solid composition or all components of the propellant grain material may be mixed in a single mixing operation. In the stepwise method the binder is prepared by adding the styrene-acrylonitrile copolymer to a mixture of nitro compounds and the styrene-acrylonitrile copolymer is completely plasticized. This occurs readily, requiring from about one-half to two hours depending on the efficiency of the mixing. Blending of the binder with ammonium nitrate and the other components of the formulation may be carried out in the same mixer if desired. A mixing temperature of 90–120° C. which temperature should not exceed 120° C. and preferably not over 110° C. after addition of ammonium nitrate. A homogeneous somewhat dough-like solid results from thorough mixing. If desired, mixing may be carried out under reduced pressure in order to remove any moisture present in the raw materials.

Gas-producing grains are prepared from the above compositions containing ammonium nitrate, combustion catalyst and binder material by molding under a pressure of about 2000 to 4000 p.s.i. The size and shape of the grains are dependent upon their intended use. Grains are provided with centrally located holes of different shapes, that is, starform, cruciform or circular. Each grain has at least a part of the external surface inhibited by a coating of a material such as asphalt, cellulose acetate or a 80%–20% mixture of Vistanex and carbon black to restrict burning to a selected surface. The gas-producing material may be molded into disc-form, stacks of discs being used as gas-forming propellant material for missile rockets or the material may be molded into cylinders, i.e. grains, having differently shaped internal apertures to permit internal burning. Cylindrical assist take-off grains, about 2.75" in diameter and about 4.0" in length with starform aperture, may be inserted in a conventional case provided with a suitably placed ignited charge of cannon powder were test fired as indicated below. Cylindrical grains having a diameter of about 5" and length of 4.0", provided with a 1.0" internal cylindrical aperture are suitable as turbine starter propellant grains.

The grains are given a thermal shock test which is referred to herein as the cycling test. In this test, grains of a given composition are held in an oven at a temperature of 170° F. for a period of two hours, following which the grains are immediately subjected for a period of two hours to a temperature of −75° F. to complete one cycle.

After a second cycle, the grains are permitted to come to room temperature, i.e., about 75° to 80° F. These grains are examined for indications of cracking, crystallinity, and resistance to deformation and shattering when dropped on a concrete surface. Grains are then fired at −75° F., 170° F. and normal ambient temperatures following the cycle treatment. In general, grains made with the plasticized styrene-acrylonitrile copolymer of this invention show no physical defects following the thermal cycling test, and show firing qualities after the cycling test identical with grains which have not been submitted to the high and low temperature cycles.

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

Example 1

Seventy parts by weight of a mixture of 2,4-dinitrotoluene and 2,4-dinitrodiphenyl ether in equal weight proportions in said mixture were melted and blended at a temperature of about 120–140° C. in a sigma blade dough mixer. To this 70 parts by weight of blended plasticizer was added 30 parts by weight of styrene-acrylonitrile copolymer having an acrylonitrile content of about 29 mol percent and mixing was continued for a period of 2–4 hours to obtain a homogeneous binder material. This binder material was quite tough and flexible at room temperature and showed no tendency for the components of the binder to separate upon aging of the binder material. The binder consisted of 70% by weight plasticizer and 30% by weight styrene-acrylonitrile. To 12 parts by weight of the binder was added 83.9 parts by weight of ammonium nitrate containing intimately mixed therewith 3 parts by weight of insoluble Prussian blue catalyst and 1 part by weight of carbon black (Micronex beads), the temperature in the mixture being maintained at about 110° C. Sorbitan sesquioleate was added to the mixture in an amount of 0.1 part per 100 parts by weight of the mixture of ammonium nitrate, catalyst, carbon and binder in the mixture and mixing was continued for a period of 1–2 hours to obtain a homogeneous propellant composition. Strands prepared from this composition showed a burning rate of 0.13"/sec. at 1000 p.s.i. Molded propellant grains of 2.75" diameter and 4 inches in length and having a star-shaped internal aperture passed the thermal shock test and exhibited excellent ballistic properties when fired in the test motor following storage at 170° F. for a period of 46 days. This propellant material had the following approximate composition:

Component:	Percent by weight
Ammonium nitrate	83.9
Styrene-acrylonitrile copolymer	3.6
2,4-dinitrodiphenyl ether	4.2
2,4-dinitrotoluene	4.2
Insoluble Prussian blue catalyst	3.0
Carbon	1.0
Sorbitan sesquioleate	0.1

To 14 parts by weight of the binder material containing styrene-acrylonitrile copolymer, the dinitrodiphenyl ether and the dinitrotoluene in the same proportions as above was added a mixture containing 81 parts by weight of the ammonium nitrate, 2 parts by weight of the carbon and 3 parts by weight of the insoluble Prussian blue catalyst no surfactant being included in this composition. The burning rate at 1000 p.s.i. of extruded test strands of this material was 0.19" per second.

Example 2

A binder material was prepared according to the procedure of Example 1 the composition of which was 40.8% by weight of 2,4-dinitrotoluene, 29.2% by weight of 2,4-dinitrodiphenyl ether and 30% by weight of styrene-acrylonitrile copolymer of about 29 mol percent of acrylonitrile units. This binder had excellent physical properties with respect to flexibility and toughness. To 21 parts by weight of this binder was added an intimate mixture of 76 parts by weight of finely divided ammonium nitrate, 2 parts by weight of ammonium dichromate and 1 part by weight of insoluble Prussian blue and this mixture was added slowly and incrementally to the binder material maintained at a temperature of 100° to about 115° C. in a sigma blade mixer. The mixing was continued for a period of 1–2 hours. The composition consisted of:

Component:	Percent by weight
Ammonium nitrate	76.0
2,4-dinitrotoluene	8.6
2,4-dinitrodiphenyl ether	6.1
Styrene-acrylonitrile copolymer	6.3
Ammonium dichromate	2.0
Insoluble Prussian blue	1.0

An extruded test strand of this propellant composition indicated a burning rate at 1000 pounds p.s.i. of 0.14"/sec.

Example 3

A binder composition was prepared according to the procedure described in Example 1, which binder contained 35% by weight of 2,4-dinitrodiphenyl ether, 35% by weight of 2,4-dinitrophenyl propyl ether and 30% by weight of the same grade of styrene-acrylonitrile copolymer as used in Example 1. The binder was tough and flexible at room temperature. To 15 parts by weight of this binder was added a mixture containing 82 parts by weight of ammonium nitrate, 2 parts by weight of ammonium dichromate and 1 part by weight of insoluble Prussian blue catalyst. The mixture of ammonium nitrate, catalyst, and binder was stirred for a period of about one and one-half hours at a temperature of about 110° C. to obtain a homogeneous propellant composition. The composition consisted, on a weight basis, of 4.5% styrene-acrylonitrile copolymer having an acrylonitrile content of about 29 mol percent, 5.25% 2,4-dinitrodiphenyl ether, 5.25% 2,4-dinitrophenyl propyl ether, 2% ammonium dichromate, 1.0% insoluble Prussian blue and 82.0% ammonium nitrate. Burning rates of strands of this composition indicated a burning rate of 0.20"/sec. at 1000 p.s.i.

A very important property of gas-forming propellant material is the impulse provided by the combustion of grains produced from the material. Specific impulse is expressed in pound seconds per pound of propellant and a propellant grain having a specific impulse of 200 pound seconds per pound or higher is very satisfactory for propellant service. A grain, molded from the composition of Example 3, 8" in length and 2.5" in diameter and provided with a star-shaped aperture was tested on an air-bearing thrust stand. A specific impulse of 203 seconds was indicated for the grain material. The average specific impulse obtained for four tubular grains molded from this material, the grains having a length of 8" and a diameter of 2.25" was 208 seconds.

Example 4

Another propellant composition using the same binder material as in Example 3 was prepared. In preparing this composition 88 parts by weight of the finely divided ammonium nitrate in intimate admixture with 1.8 parts by weight of ammonium dichromate and 0.8 part by weight of insoluble Prussian blue catalyst were added to 9.4% of the binder to form a propellant composition of low binder content. The final mixture was mixed in the mixer to produce a homogeneous composition. This composition consisted on a weight basis of 88% of ammonium nitrate, 1.8% of ammonium dichromate, 0.8% of insoluble Prussian blue, 3.3% of 2,4-dinitrodiphenyl ether, 3.3% of 2,4-dinitrophenyl propyl ether and 2.8% of styrene-acrylonitrile copolymer having an acrylonitrile content of about 29 mol percent. Test strands of this composition were burned in the pressure bomb. A burning rate of 0.135"/sec. at 1000 p.s.i. was obtained. Propellant grains were molded from this material at a pressure of about 4000 p.s.i. These cylindrical grains were about 4" in length and 5" in diameter and weighed about 1750 grams. The grains were provided with cylindrical apertures one inch in diameter extending through the grain and the external end surfaces of the grain were restricted with respect to burning area by applying restrictor material thereto. The grains were subjected to thermal shock cycling tests by being subjected successively to temperatures of −75° F. and +170° F. These grains, although containing a relatively small amount of binder material, passed the cycling test without physical damage to the grains which were fired successfully in the test motor following the cycling test. Firings were made at +170° F., +70° F. and −70° F. and average gas pressures of 1300 p.s.i., 925 p.s.i. and 550 p.s.i. respectively were obtained. The grains were encased in a firing case provided with a 0.236" gas efflux nozzle in this series of firing tests.

Example 5

A binder material was prepared from the same grade styrene-acrylonitrile copolymer, 2,4-dinitrotoluene, and 2,4-dinitrodiphenyl ether as used in the above examples. The binder in addition to those components contained 2,4-dinitrostilbene which was prepared by condensing 2,4-dinitrotoluene with benzaldehyde. The finished binder contained on a weight basis 27.2% of styrene-acrylonitrile copolymer, 34.1% of 2,4-dinitrotoluene, 34.1% of 2,4-dinitrodiphenyl ether and 4.6% of 2,4-dinitrostilbene. This binder was quite gummy, rubber-like, tacky at room temperatures and very extensible.

Example 6

A binder was prepared according to the method of Example 1 from styrene-acrylonitrile copolymer (29 mol percent) acrylonitrile, 2,4-dinitrophenyl allyl ether, 2,4-dinitrodiphenyl ether and 2,4-dinitrostilbene. Poly-pale Resin, described above, was added as an additional component to the binder composition. This binder contained on a weight basis 25.0% of styrene-acrylonitrile copolymer, 31.2% of 2,4-dinitrodiphenyl ether, 31.3% of 2,4-dinitrodiphenyl allyl ether, 4.2% of 2,4-dinitrostilbene and 8.3% of the Poly-pale Resin. The composition was relatively soft and very extensible. To 20 parts by weight of this binder was added 77 parts by weight of ammonium nitrate intimately mixed with 2 parts by weight of ammonium dichromate and 1 part by weight of insoluble Prussian blue and the resulting mixture was stirred to homogeneity in the sigma blade mixer for a period of about 1–2 hours. The composition was screw extruded easily at about 100° C. The strands so formed were tough and so flexible that they could be bent in nearly a 90° arc without cracking. The strand burning rates at 1000 p.s.i. was 0.15"/sec. and the pressure exponent was 0.71. The composition consisted of the following components in the approximate percentages by weight as shown below:

Component:	Percent by weight
Styrene-acrylonitrile copolymer of about 29 mol percent acrylonitrile units	5.0
2,4-dinitrodiphenyl ether	6.2
2,4-dinitrophenyl allyl ether	6.3
2,4-dinitrostilbene	0.8
Polymerized rosin having a softening point within the range of 198–208° F.	1.7
Ammonium dichromate	2.0
Insoluble Prussian blue	1.0
Ammonium nitrate	77.0

The above examples show that ammonium nitrate-based propellant compositions containing, as binder material, the defined styrene-acrylonitrile copolymer plasticized with nitroaromatic components and mixtures of these nitroaromatic compounds with or without the addition of non-nitro substituted plasticizers in the binder composition exhibit physical properties, ballistic properties and burning properties which are desirable in shaped propellant grains.

Burning rates are expressed herein as burning rates at 1000 p.s.i. Percent compositions in this specification and in the claims are percents by weight unless specified otherwise.

Having thus described the invention, what is claimed is:

1. A gas-producing composition comprising from about 8% to about 25% by weight of a combustible binder comprising from about 20% to about 40% by weight of styrene-acrylonitrile copolymer containing about 15 mol percent to about 40 mol percent of acrylonitrile units per molecule and from about 80% to about 60% by weight of at least one nitro-substituted aromatic compound plasticizer selected from the class consisting of dinitrobenzene, dinitrotoluene, dinitrodiphenyl ether, dinitrostilbene, dinitrophenyl allyl ether, dinitrophenyl propyl ether, dinitroanisole, bis (dinitrophenyl) propyl ether and bis (dinitrophenyl) triglycol ether, from about 1% to about 10% by weight of at least one inorganic combustion catalyst selected from the class consisting of Prussian blue and ammonium dichromate and the remainder of said composition essentially ammonium nitrate.

2. The composition of claim 1 wherein the styrene-acrylonitrile copolymer contains about 29 mol percent acrylonitrile units and about 71 mol percent of styrene units.

3. The composition of claim 1 wherein the plasticizer consists essentially of 2,4-dinitrodiphenyl ether.

4. The composition of claim 1 wherein the binder

consists essentially of the defined styrene-acrylonitrile plasticized with a mixture of 2,4-dinitrophenyl propyl ether and 2,4-dinitrodiphenyl ether.

5. The composition of claim 1 wherein the binder consists essentially of about 30% by weight of the styrene-acrylonitrile copolymer, the remainder of said binder consisting essentially of a mixture of 2,4-dinitrodiphenyl ether and 2,4-dinitrotoluene.

6. The composition of claim 1 wherein the catalyst is a mixture of insoluble Prussian blue and ammonium dichromate.

7. The composition of claim 1 wherein the catalyst content of the composition consists of about 3% of insoluble Prussian blue based on the weight of the composition.

8. A shaped propellant grain consisting essentially, on a weight basis of about 4.5% styrene-acrylonitrile copolymer containing about 29 mol percent acrylonitrile units, about 5.25% 2,4-dinitrodiphenyl ether, about 5.25% 2,4-dinitrophenyl propyl ether, about 1.0% insoluble Prussian blue, about 2.0% ammonium dichromate and about 82.0% ammonium nitrate.

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