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AMMONIUM NITRATE PROPELLANTS CONTAINING AMINE SALTS OF NITROSALICYLIC ACID AS COMBUSTION CATALYST

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This invention relates to ammonium nitrate propellant compositions which contain an ash-free catalyst for promoting the combustion of the ammonium nitrate.

In ammonium nitrate compositions which consist essentially of ammonium nitrate particles and an oxidizable organic binder material, which permits the shaping of the composition into a definite configuration or grain, it is necessary to promote the combustion of the composition by the use of a catalyst. Commonly used catalysts are the inorganic chromium compounds, particularly ammonium dichromate and the Prussian blues. These and other heavy metal catalysts have the drawback of forming solid oxide products in the combustion gases which cause nozzle erosion which erosion results in erratic change in gas pressure within the rocket motor. Sodium salts of some organic compounds also function as catalysts. However, the sodium reacts in the combustion gases to form solid sodium carbonate in substantial yield. This solid forms objectionable ash deposits for some uses.

For many purposes, it is very desirable to minimize the production of solid by-products of the combustion of ammonium nitrate propellants. Organic compounds are known which function as combustion catalysts. These compounds either do not produce high burning rate propellants or produce compositions which do not ignite readily or have trouble maintaining smooth burning. Even the inorganic catalysts have difficulty in maintaining smooth burning of the propellant when the catalyst content is lowered so as to produce a relatively slow burning composition.

It has been discovered that the amine salts of nitrosalicylic acids function as an effective combustion catalyst for ammonium nitrate propellant compositions and simultaneously function as ignition aids permitting better ignition of compositions at low temperatures and also give smooth burning at low burning rates. The ignition aid function and burning smoothness function carry throughout the entire class of the salts. Particularly with the salts of the more basic amines, it has been observed that the high temperature storage stability of compositions containing this class of catalyst is improved over other conventional catalyst containing compositions. The burning rate obtainable varies with the particular salts; it is possible to obtain relatively high burning rate compositions and also extremely low burning rate compositions.

The catalytic activity for the combustion of ammonium nitrate is present with any product of a nitrosalicylic acid and an organic compound containing an amino group. The amines which contain carbon, hydrogen and nitrogen atoms and the amines containing carbon, hydrogen, oxygen and nitrogen atoms are especially suitable. The amines which are strongly basic are preferred when the composition needs exceptionable storage stability. Illustrative of especially suitable amines for the preparation of the catalyst used in the composition of the invention are ethylene diamine, monoethanol amine, piperazine and guanidine.

Any of the various nitro group substituted salicylic acids may be used. One or more nitro groups may be present. Alkyl substituted acids may be used. Also, the disalicylic acids which are joined through an alkylene

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bridge may be used, for example, dinitromethylene disalicylic acid.

Sufficient catalyst must be introduced into the composition to promote the burning of the composition. The amount of catalyst used is also influenced by the rate of burning desired. The more catalyst present, the faster the combustion of the composition. (It is to be understood that the burning rate is also affected by the particular oxidizable organic binder material present.) In general, the composition will contain between about 0.1 and 15 weight percent of the catalyst. (Hereinafter all percentages are to be understood as weight percent.) With the thermoplastic matrix formers or binders obtained from cellulose esters and plasticizers therefor, between about 1 and 7% of catalyst produces satisfactory burning rates for typical military gas generation and rocketry usages.

In its broadest aspect, the novel composition of the invention consists essentially of ammonium nitrate as the major component; an oxidizable organic binder material in an amount of about 10-40 weight percent and as a combustion catalyst, an amine salt of a nitrosalicylic acid in an amount of about 0.1-15 weight percent.

The ammonium nitrate may be the high purity material commonly produced by synthetic plants today, or it may be technical grade containing small amounts of inorganic impurities. In addition to the ammonium nitrate, for special purposes, sodium nitrate or potassium nitrate may be present in an appreciable amount. The decomposition rate of the ammonium nitrate is influenced by the particle size. For gas generation purposes, the ammonium nitrate is finely divided. Particularly suitable ammonium nitrate will contain about 80 weight percent of material having a screen size greater than 80 mesh and smaller than 30 mesh. The more finely powdered ammonium nitrate is used where higher burning rates are desired. Usually the propellant composition will contain between about 60 and about 80% of ammonium nitrate. In all cases, the major component present in the composition is ammonium nitrate.

In order to permit the shaping of the ammonium nitrate composition into definite configurations, a matrix former or binder material is present. When ammonium nitrate decomposes, free-oxygen is released. The existence of this free-oxygen permits oxidizable organic materials to be used as the binders and thereby obtain additional gas production. These oxidizable organic materials may contain only carbon and hydrogen, for example, high molecular weight hydrocarbons such as asphalts or residuums, and rubbers, either natural or synthetic. Or, it may contain other elements in addition to carbon and hydrogen, for example, as in Thiokol Rubber and neoprene. The stoichiometry of the composition is improved, with respect to smoke production, by the use of organic materials containing combined oxygen as the binders. The binder or matrix former may be a single compound such as a rubber or asphalt or it may be a mixture of compounds. The mixtures are particularly suitable when special characteristics are to be imparted to the propellant which cannot be obtained by the use of a single compound.

Multi-component binder, or matrix former, consists of a polymeric base material and plasticizer therefor. Particularly suitable polymeric base materials are cellulose esters of alkanolic acids containing from 2 to 4 carbon atoms such as cellulose acetate, cellulose acetate butyrate and cellulose propionate. The polyvinyl resins such as polyvinylchloride and polyvinyl acetate are good bases. Styreneacrylonitrile is an example of a copolymer which forms a good base material. Polyacrylonitrile is another suitable base material.

The plasticizer component of the binder also, preferably, contains combined oxygen. The oxygen may be present in the plasticizer as an ether linkage and/or hydroxyl and/or carboxyl; also the oxygen may be present as a part of an inorganic substituent, particularly, a nitro group. In general, any plasticizer which is adapted to plasticize the particular polymer may be used in the invention. A single plasticizing compound may be used; more usually two or more compounds are used in conjunction. Exemplary classes of plasticizers which are suitable are set out below. (It is to be understood that these classes are illustrative only and do not limit the types of organic compounds which may be used to plasticize the polymer.)

Di-lower alkyl-phthalates, e.g., dimethyl phthalate, dibutyl phthalate, dioctyl phthalate and dimethyl nitrophthalate.

Nitrobenzenes, e.g., nitrobenzene, dinitrobenzene, nitrotoluene, dinitrotoluene, nitroxylenes, and nitrodiphenyl. Nitrodiphenyl ethers, e.g., nitrodiphenyl ether and 2,4-dinitrodiphenyl ether.

Tri-lower alkyl-citrate, e.g., triethyl citrate, tributyl citrate and triamyl citrate.

Acyl tri-lower alkyl-citrate where the acyl group contains 2-4 carbon atoms, e.g., acetyl triethyl citrate and acetyl tributyl citrate.

Glycerol-lower alkanates, e.g., monoacetin, triacetin, glycerol tripropionate and glycerol tributyrates.

Lower alkylene-glycol-lower alkanates wherein the glycol portion has a molecular weight below about 200, e.g., ethylene glycol diacetate, triethylene glycol dihexoate, triethylene glycol dioctate, polyethylene glycol dioctate, dipropylene glycol diacetate, nitromethyl propanediol diacetate, hydroxyethyl acetate and hydroxy propyl acetate (propylene glycol monoacetate).

Dinitrophenyl-lower alkyl-lower alkanates, e.g., dinitrophenyl ethylacetate, and dinitrophenyl amyloctate.

Lower alkylene-glycols wherein the molecular weight is below about 200, e.g., diethylene glycol, polyethylene glycol (200), and tetrapropylene glycol.

Lower alkylene-glycol oxalates, e.g., diethylene glycol oxalate and polyethylene glycol (200) oxalate.

Lower alkylene-glycol maleates, e.g., ethylene glycol maleate and

Bis-(diethylene glycol monoethyl ether) maleate.

Lower alkylene-glycol diglycollates, e.g., ethylene glycol diglycollate and diethylene glycol diglycollate.

Miscellaneous diglycollates, e.g., dibutyl diglycollate, dimethylalkyl diglycollate and methylcarbitol diglycollate.

Lower alkyl-phthalyl-lower alkyl-glycollate, e.g., methyl phthalyl ethyl glycollate, ethyl phthalyl ethyl glycollate and butyl phthalyl butyl glycollate.

Di-lower alkyloxy-tetraglycol, e.g., dimethoxy tetra glycol and dibutoxy tetra glycol.

Nitrophenylether of lower alkylene glycols, e.g., dinitrophenyl ether of triethylene glycol and nitrophenyl ether of polypropylene glycol.

Nitrophenoxy alkanols wherein the alkanol portion is derived from a glycol having a molecular weight of not more than about 200. These may be pure compounds or admixed with major component bis(nitrophenoxy) alkane.

In addition to the main components, i.e., ammonium nitrate binder and catalyst, the propellant composition may contain other components. For example, materials may be present to improve low temperature ignitability, for instance, oximes or asphalt; surfactants may be present in order to improve the adhesion of the nitrate and the binder—also to improve the shape retention characteristics of the composition; burning rate promoters which are not considered to be true catalysts such as finely

divided carbon may also be present; other combustion catalysts may also be present.

Aromatic hydrocarbon amines may be present in order to improve storage stability, particularly at higher atmospheric temperatures. Illustrations of these aromatic amines are toluene diamine, diphenyl amine, naphthalene diamine, and toluene triamine. In general, these are present in an amount between about 0.5 and 5 percent. Better stabilization is obtained with a combination of the hydrocarbon amines and N-phenylmorpholine. In general, when aromatic hydrocarbon amines are also present, between about 0.1% and 1% of N-phenylmorpholine will be present.

A particularly good composition consists of cellulose acetate, about 6-12%; acetyltriethylcitrate, about 6-12%; dinitrophenoxyethanol, about 6-12%; carbon, about 2-6%; toluene diamine, about 0.5%; N-phenylmorpholine, about 0.5%; catalyst, about 1-7% and the remainder ammonium nitrate.

Illustrations

The amine salts of nitrosalicylic acid are easily prepared by precipitation from a common solvent for the particular nitrosalicylic acid and the particular amine. Methanol has been found to be a particularly good solvent reaction medium. It has been observed that completion of the reaction and purity of the product can be determined easily by taking the melting point of the crystalline product precipitated from the reaction medium. Ultraviolet inspection of the reaction products establish that the amine salt prepared by simple reaction of nitrosalicylic acid and an amine has the amino group joined to the carboxy group on the nitrosalicylic acid nucleus.

A composition was prepared by mixing together for one hour in a laboratory mixer a 1 quart batch having ingredients in the proportions set forth hereinbelow. The mixing temperature was about 100° C. Celanese HLFS-93 grade cellulose acetate, analyzing about 55 percent of acetic acid equivalent, was the polymer. Two plasticizers were used. One plasticizer was essentially pure dinitrophenoxyethanol. The other plasticizer was acetyl triethyl citrate.

After mixing the resulting pasty mass was compression molded into a slab approximately one-half inch in thickness. The slab was subsequently sawed into strips for the burning rate test. The burning rate tests were conducted in a Crawford Bomb pressured at 1000 p.s.i.a. and at 25° C.

Composition Mark 5328 has the component analysis:

	Percent
Ammonium nitrate	62.0
Cellulose acetate	10.0
Acetyl triethyl citrate	11.0
Dinitrophenoxyethanol	10.0
Carbon black (EPC)	3.0
Toluene diamine	1.0
Piperazine 3,5-dinitrosalicylate	3.0

In addition to obtaining the burning rate of inches per second at 1,000 p.s.i.a., the pressure exponent "n" was obtained for each composition. The burning characteristics of nondetonating explosives are dependent upon the temperature and pressure in the combustion chamber. The relationship of burning rate and pressure at constant temperatures is expressed by R. N. Wimpers in "Internal Ballistics of Solid Fuel Rockets" (1950), as

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

wherein B is the linear burning rate at pressure p, β is the linear burning rate for the composition 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 versus pressure on log-log paper. A composition having a pressure exponent of the order of 1.0 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 the gas-producing component 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.

The Mark 5328 composition has a burning rate, inches per second at 1,000 p.s.i.a. and 25° C. of 0.064; the pressure exponent is 0.64.

This composition, Mark 5328, gave excellent storage stability in an accelerated test carried out at 170° F. (76.70 C.). The customary tests were run wherein pressure-time traces were obtained with the propellant at various initial temperatures; the propellant was brought to the desired test temperature by storage at that temperature until the entire mass of propellant was known to be at the desired temperature. The pressure-time traces permit determination of the ease of ignition of the propellant and also the smoothness of burning of the propellant during the test. These tests established that Mark 5328 was exceptionally easy to ignite at even the low temperature of -75° F. and was very smooth burning regardless of the initial temperature of the propellant.

In another composition the guanidine salt of 3,5-dinitrosalicylic acid was used as a catalyst. For purposes of comparison, a composition containing none of the amine salt was prepared and tested. The component analysis of the two compositions are: (The DNPOE plasticizer contained about three parts of dinitrophenoxyethanol and one part of bis(dinitrophenoxy)ethane, obtained by the reaction of dinitrochlorobenzene and ethylene glycol in the presence of aqueous sodium hydroxide solution.)

	Mark I, percent	Mark IV, percent
Ammonium nitrate.....	61.00	61.00
Cellulose acetate.....	11.15	10.15
Acetyl triethyl citrate.....	12.60	11.60
DNPOE.....	11.25	10.25
Carbon black.....	3.00	3.00
Toluene diamine.....	0.50	0.50
N-phenylmorpholine.....	0.50	0.50
Guanidine 3,5-dinitrosalicylate.....	None	3.00

Composition Mark I had a burning rate of 0.05 and a pressure exponent of 0.75. This composition was increasingly difficult to ignite and to continue burning after ignition as the temperature of the composition was lowered. At the lowest temperature required by military specifications of -75° F., composition Mark I would not support combustion.

Composition Mark IV had a burning rate of 0.065 and a pressure exponent of 0.57. At all temperatures this composition ignited easily and was very smooth burning.

Thus having described the invention, what is claimed is:

1. A propellant composition consisting essentially of about 0.1-15 weight percent, as a combustion catalyst, of an amine salt of a nitrosalicylic acid; ammonium nitrate as the major component; and between about 10 and 40 weight percent of oxidizable organic binder material selected from at least one member of the class consisting of hydrocarbon, rubber containing essentially hydrogen, carbon and chlorine, rubber containing essentially hydrogen, carbon and sulfur, and polymeric base material and plasticizer adapted to plasticize said polymeric base material, said polymeric base material selected from at least one member of the class consisting of cellulose esters of alkanolic acids containing from 2-4 carbon atoms, polyvinylchloride, polyvinylacetate, styrene acrylonitrile copolymer and polyacrylonitrile.
2. The composition of claim 1 wherein said catalyst is guanidine 3,5-dinitrosalicylate.
3. The composition of claim 1 wherein said catalyst is piperazine 3,5-dinitrosalicylate.
4. A propellant composition consisting essentially of about 0.1-15 weight percent, as a combustion catalyst, of an amine salt of a nitrosalicylic acid; ammonium nitrate as the major component; and between about 10 and 40 weight percent of oxidizable organic binder material consisting of a cellulose ester of alkanolic acid having from 2 to 4 carbon atoms and a plasticizer adapted to plasticize said ester.
5. A propellant composition consisting essentially of cellulose acetate, about 6-12%; acetyl triethyl citrate, about 6-12%; about 6-12% of dinitrophenoxyethanol; carbon, about 2-6%; toluene diamine, about 0.5%; N-phenylmorpholine, about 0.5%; piperazine 3,5-dinitrosalicylate, about 1-7%; and the remainder ammonium nitrate.

No references cited.