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PRESSED SOLID PROPELLANT PELLETS

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This invention relates to pellets of ammonium nitrate-base propellant and a process for the preparation thereof.

In the preparation of igniters or propulsion powders for large guns it is desirable to have the propellant composition in the form of pellets or tablets. These pellets may be cylindrical, egg-shaped, flat tablets or wafers (with or without perforations), etc. These pellets are normally made by introducing into a mold cavity the necessary amount of propellant composition and applying an elevated pressure to the mold until the pellet of desired shape has been formed. This operation is normally carried out at ambient temperatures. These pellets are not distinguished for strength; they crumble easily to applied pressure and wafer type pellets are readily broken by finger pressure.

For military purposes, particularly, it is desirable to have pellets which are strong enough to withstand fairly severe handling in transportation and other movement of the article housing the pellet. Also, it is a problem to handle these pellets in the subsequent manufacture of igniters or propulsion powders without breakage or excess amount of scrap formation. The objects of the instant invention are to produce an ammonium nitrate-base propellant pellet which does not suffer from these disabilities.

It has been discovered that an ammonium nitrate-base propellant pellet prepared by the usual molding techniques is convertible to a strong, durable, compacted pellet by heat treatment thereof at a temperature from about 70° C. to 85° C. for a time between about 1 hour and 2 hours and subsequent cooling of the hot propellant to ambient temperatures. It is to be understood that the time of heat treatment is dependent upon the shape of the particular pellet; in the case of tablets or wafers, the thickness of the tablet has a bearing on the time of heat treatment.

The invention is particularly applicable to propellant compositions consisting of essentially between about 0.5 to 15 weight percent of a catalyst for promoting combustion of ammonium nitrate, between about 10 and 40 weight percent of an oxidizable organic binder material, hereinafter defined, for ammonium nitrate and the other components of the composition. The pellet is formed from the composition by the application of pressure between about 3,000 p.s.i. and 8,000 p.s.i. for a short time between about 0.05 and 0.25 seconds. In a particular embodiment wherein the pellet is a wafer about 0.5 inch in diameter and about 0.2 inch thick the pellet is molded at a pressure of about 6,000 p.s.i. with application of such pressure for a time of about 0.1 second. A strong compressed propellant pellet is obtained by heat treating this particular molded pellet at a temperature of about 75° C.–80° C. for a time of about 1–1.5 hour; greater strength is obtained when the heat treated pellet is cooled in a substantially dehumidified atmosphere.

The term "dehumidified atmosphere" applies to ordinary atmospheric air or similar gaseous material whose moisture content has been controlled to on the order of 40–50% at temperature on the order of 18–25° C.

The propellant pellets of the invention contain ammonium nitrate as the major component. The ammonium nitrate may be either C.P. or ordinary commercial ammonium nitrate such as is used for fertilizers. This

commercial grade material contains a small amount of impurities and the particles are usually coated with moisture resisting material such as paraffin wax. Military grade ammonium nitrate which is almost chemically pure is particularly suitable. The ammonium nitrate is preferably in a finely divided particulate form which may be either produced by prilling or by grinding. The ammonium nitrate is the major component of the propellant composition and usually the composition will contain between about 65 and 80% of ammonium nitrate.

In order to permit the shaping of the ammonium nitrate composition to definite configurations a matrix former or binder material is present. When ammonium nitrate decomposes free-oxygen is formed. Advantage of the existence of this free-oxygen is taken and oxidizable organic materials are used as the binders. The stoichiometry of the composition is improved, with respect to smoke production by the use of oxygenated organic material as the binders. The binder is usually present in an amount between about 10 and 40 weight percent of the propellant composition.

The multi-component binder or matrix former commonly consists of a polymeric base material and a plasticizer therefor. Particularly suitable polymeric base materials are cellulose esters of alkanoic 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 also good bases; acrylonitrile is good; styrene-acrylonitrile is an example of a copolymer which forms a good base material. In general the binder contains between about 15 and 45% of the particular polymeric base material.

The plasticizer component of the binder is broadly defined as an oxygenated hydrocarbon. The hydrocarbon base may be aliphatic or aromatic or may contain both forms. The oxygen may be present in the plasticizer in ether linkage and/or hydroxyl group and/or carboxyl groups; also the oxygen may be present in inorganic substituents particularly nitro groups. In general any plasticizer which is suitable for work with the defined polymers may be used in the invention. 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 oxygenated hydrocarbons which may be used to plasticize the polymer.

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

Nitrobenzene, e.g. nitrobenzene, dinitrobenzene, nitrotoluene, dinitrotoluene, nitroxylene, and nitrodiphenyl.

Nitrodiphenyl ethers, e.g. nitrodiphenyl ether and 2,4-dinitrodiphenyl ether.

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

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

Glycerol-lower alkanoates, e.g. monoacetin, triacetin, glycerol, tripropionate and glycerol tributyrate.

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

Dinitrophenyl-lower alkyl-lower alkanoates, e.g. dinitrophenyl ethylacetate and dinitrophenyl amyloctoate.

Lower alkylene-glycols wherein the molecular weight is

below about 200, e.g. diethylene glycol, polyethylene glycol (200), and tetrapropylene glycol.

Lower alkylene-glycol oxolates, e.g. diethylene glycol oxolate and polyethylene glycol (200) oxolate.

Lower alkylene-glycol maleates, e.g. ethylene glycol maleate and bis-(diethylene glycol monoethyl ether)maleate.

Lower alkylene-glycol diglycolates, e.g. ethylene glycol diglycolate and diethylene glycol diglycolate.

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.

Nitrophenyl ether 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.

A single plasticizer may be used or more usually two or more plasticizers may be used in conjunction. The particular requirements with respect to use will determine not only the polymer but also the particular plasticizer or combination of plasticizers which are used.

In addition to the basic components, i.e. ammonium nitrate binder and catalyst, the gas generator propellant composition may contain other materials. For example, materials may be present to improve low temperature ignitability, for instance oximes may be present or, asphalt may be present. Surfactants may be present in order to improve the coating of the nitrate with the binder and to improve the shape characteristics of the composition. Various burning rate promoters, which are not catalyst per se, may also be present.

The aromatic hydrocarbon amines are known to be gas evolution stabilization additives. Examples of these aromatic amines are toluene diamine, diphenyl amine, naphthalene diamine, and toluene triamine. In general the aromatic hydrocarbon amines are used in amounts between about 0.5 and 5 percent.

The mixture of ammonium nitrate, polymeric base and oxygenated hydrocarbon is essentially as insensitive to shock as is ammonium nitrate itself. It is extremely difficult to get this particular mixture to burn. Smooth burning is attained by the addition of a catalyst to the mixture. (This catalyst is distinguished from the well known sensitizers. For example, nitro starch or nitroglycerin may be added to ammonium nitrate in order to increase its sensitivity to shock and enable it to be more easily detonated for explosive use. Catalysts as a class do not promote sensitivity and are used to cause the ammonium nitrate composition to burn for example, like a cigarette.) The effectiveness of the catalyst is in general measured by its ability to impart a finite burning rate to a cylindrical strand of ammonium nitrate composition. The burning rate is specified as inches per second at a given pressure and temperature; usually these burning rates are obtained by a bomb procedure operating at 1000 p.s.i. and about 75° F. temperature.

Many catalysts which promote the burning of ammonium nitrate compositions are known. The inorganic chromium salts form the best known classes of catalysts. The better known members of this class are ammonium chromate, ammonium polychromate, the alkali metal chromates and polychromates, chromic oxide, chromic nitrate, and copper chromite. Ammonium dichromate is the most commonly used chromium salt. Various hydrocarbon amine chromates such as ethylene diamine chromate and piperidine chromate are also excellent chromium catalysts. Certain heavy metal cyanides particularly those of cobalt, copper, lead, nickel, silver and zinc are effective catalysts. The cyanamides of barium, copper, lead, mercury and silver are effective catalysts. The various Prussian blues are excellent catalysts.

In addition to the above primarily inorganic catalysts various organic catalysts are known. The organic catalysts are particularly useful when it is desired to have combustion products which are gases or vapors and thereby do not erode gas exit orifices. Catalysts which do not contain any metal components are triethanolamine, N-(hydroxyethyl)-morpholine, pyrogene blue (Color Index 956–961), hydrogen phthalocyanine and methylene blue. Other suitable catalysts are the alkali metal barbiturates, alkali metal parabanates, alkali metal anthranilates and sodium glutamate.

These combustion catalysts are present in amounts needed to give, within limits, the desired burning rates. While amounts from about 0.5 to as much as 15 weight percent may be present, in general amounts above about 8% do not boost the burning rate greatly. Usually the catalyst is present in amounts between about 2 and 5 weight percent.

Finely divided carbon such as carbon black present in amounts of several percent is effective alone as a catalyst, however, carbon is generally used in combination with another catalyst as a burning rate promoter.

Example

For purposes of illustration the preparation of pellets suitable for use in a gas generator igniter is described. The propellant compostiion consisted of an ammonium nitrate composition as follows: cellulose acetate 12%, acetyl triethyl citrate 9%, 9% of a 2:1 mixture of dinitrophenoxyethanol and bis(dinitrophenoxy)ethane, carbon black 4%, toluene diamine 1%, sodium barbiturate catalyst 3% and ammonium nitrate 62%. The pellets (tablets) in this illustration were 0.5 inch in diameter and 0.18 inch thick.

These pellets were prepared using a commercial tableting machine providing a mold pressure of approximately 6000 p.s.i.; the pressure was maintained on the composition in the mold for approximately 0.1 second. The molding operation was carried out in a room whose temperature was held at about 20° C. and had a relative humidity of about 40%.

The pellets, as they came from the pelleting press, broke easily between the fingers and tended to crumble when handled with ordinary care.

Pellets were heat treated in an oven at a temperature of 75–80° C. Various heat treating times were used. It was observed that for these particular pellets times below 1 hour did not increase the strength of the pellets substantially over the strength of the non-heat treated pellets. At about 1.5 hours the strength of the pellets had leveled off and no significant improvement in strength was obtained by heating for more than 2 hours. It was also observed that there was some additional strength gained in a period of 18–24 hours holding at ambient temperature following the cooling of the pellet to ambient temperature.

It was also observed that the strength of the heat treated pellets was improved when the cooling to ambient temperature was carried out in a dehumidified atmosphere equivalent to about 40–50% relative humidity at about 20° C. temperature.

The heat treated pellets could not be broken by the finger pressure test and did not crumble even though handled fairly roughly in the subsequent manufacture of igniters for use in gas generator cartridges.

Thus having described the invention what is claimed is:

1. A process for producing a propellant pellet which process comprises introducing into a mold cavity a predetermined amount of a propellent composition consisting essentially of between about 0.5 and 15 weight percent of a combustion catalyst, and between about 10 and 40

weight percent of oxidizable organic binder material wherein said binder material consists of a polymeric base selected from the class consisting of cellulose esters of alkanoic acids containing from 2 to 4 carbon atoms, polyvinylchloride, polyvinyl acetate, acrylonitrile and styrene-acrylonitrile, and an oxygenated hydrocarbon plasticizer therefor said plasticer containing said oxygen in chemical combination, and the remainder essentially only ammonium nitrate, applying to said composition in said mold cavity a pressure between about 3000 p.s.i. and 8000 p.s.i. for a time between about 0.05 and 0.25 second to form said composition into a pellet of the desired shape, removing said pellet from said mold, heat treating said pellet at a temperature from about 70° C. to 85° C. for a time between about 1 hour and 2 hours and cooling said hot pellet to ambient temperature to obtain a strong compressed propellant pellet.

2. A process for producing a strong compressed propellant-pellet which process comprises inserting into a mold a predetermined amount of ammonium nitrate-base propellant composition consisting of ammonium nitrate, 62%; combustion catalyst, 3%; carbon black, 4%; toluene diamine, 1%; cellulose acetate, 12%; acetyl triethyl citrate, 9% and a 2:1 mixture of dinitrophenoxyethanol and bis (dinitrophenoxy) ethane, 9%; applying to said composition in said mold a pressure of about 6000 p.s.i. for a time of about 0.1 second to form a pellet about 0.5 inch in diameter and about 0.2 inch thick, removing said pellet from said mold, heat treating said pellet at a temperature of about 75–80° C. for about 1–1.5 hour, and cooling said heat treated pellet in a substantially dehumidified atmosphere to ambient temperature to obtain a strong compressed propellant pellet.

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