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# GUN PROPELLANT

Wayne A. Proell, Chicago, Ill., and Norman J. Bowman, Hammond, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to a gas-generating composition which can be used as a propellant in guns.

In firearms such as pistols and rifles and in cannon accuracy is attained because the bullet or shell rotates on its axis during its passage through the barrel of the firearm. Corrosion or erosion of the rifling very markedly affects the accuracy of the piece. It has been known that the powder which drives the bullet or shell is primarily responsible for the erosion and corrosion of the rifling; the gas produced in the decomposition of the powder erodes and the decomposition products deposited in the barrel corrode. The ordinary nitrocellulose powders now used primarily as gun propellants have this serious defect; in addition to their effect on the barrel these propellants are marked by more or less undesirable amount of smoke production and muzzle flash. Still further the nitrocellulose powders are relatively expensive because of the method of manufacture required in the handling of relatively sensitive materials.

An object of the invention is a gun propellant suitable for use in firearms and artillery. Another object is a gun propellant which has very little adverse effect on the rifling present in the piece. A further object is a gun propellant which is essentially smoke-free and flash-free. A still further object is a gun propellant based on cheap ammonium nitrate. Other objects will become apparent in the course of the detailed description.

The gun propellant composition of the instant invention consists of ammonium nitrate, a binder and combination combustion promoter. The combustion promoters are phenotiazine and carbon black. The binder which permits the formation of shaped particles of the composition is made up from cellulose acetate, as defined hereinafter, a polyester condensation product of a hereinafter defined glycol and a hereinafter defined alkyl dicarboxylic acid and a hereinafter defined nitrodiphenyl oxide. The composition can be readily formed into granules suitable for use in cartridges such as pistol cartridges, rifle cartridges or shotgun shells; or it can be formed into more complicated shapes suitable for use in large caliber pieces such as field artillery, or cannon; or it can be formed into shapes suitable for use in mortars. In addition to its use as a gun propellant the composition may be used as a blasting explosive or for the generation of gas by controlled burning in a chamber provided with an orifice. The composition is extremely insensitive to shock and can be ignited only by the use of the conventional explosive primers, blasting caps or means suitable for igniting nitrocellulose powders.

The ammonium nitrate utilized in the composition may be ordinary commercial grade ammonium nitrate or it may be military grade ammonium nitrate or ammonium nitrate containing very small amounts of inorganic nitrate material such as sodium nitrate or potassium nitrate. The ammonium nitrate may or may not be coated with moisture resisting materials such as paraffins or clays.

In order to obtain a composition which may not only be formed into shapes which are stable at atmospheric temperatures, it is necessary that the shapes resist cracking or break up due to the effect of the ammonium nitrate phase changes when the composition passes through temperatures of about −18° C. and about 32° C. This difficulty is overcome by using as the binder for the ammonium nitrate particles a material which is thermoplastic



and is able to take up the volume changes of the ammonium nitrate particles without disrupting the shape imparted to the composition during the manufacturing process. The binder utilized in the composition consists of three components.

Strength and rigidity is imparted to the binder by the use of cellulose acetate as one component. The cellulose acetate utilized herein is described as having an acetic acid content between about 52 and 58 weight percent. The term "acetic acid content" denotes the amount of acetic acid formed on saponification of the cellulose acetate and is expressed as weight percent based on the cellulose acetate. The commercial grade cellulose acetates described as LL–1, analyzing from about 55–56 weight percent of acetic acid and FM–3 analyzing between 56 and 56.6%, of acetic acid are preferred for use as the acetate component. The binder contains between about 20 and 30 weight percent of the defined cellulose acetate component.

In addition to the cellulose acetate the binder contains a plasticizer component. The binder itself is thermoplastic and has a melting point in the region of 90° C. to 110° C. The thermoplastic characteristics are imparted to the binder by the use of two plasticizers. One plasticizer is nitrodiphenyl oxide material. The mononitrodiphenyl oxide and the various dinitrodiphenyl oxides are particularly suitable. The dinitrodiphenyl oxides wherein both nitro groups are joined to the same benzene nucleus are preferred. The trinitrodiphenyl oxides are not suitable because of their low compatibility with the cellulose acetate. Mixtures of either nitrodiphenyl oxide, or dinitrodiphenyl oxide, or mixtures of these two, and trinitrodiphenyl oxide may be used when the average nitro content of the total mixture is less than 2.5 nitro groups per diphenyl oxide molecule present. Because trinitrodiphenyl oxide having all three nitro groups on the same benzene nucleus is extremely sensitive to physical and thermal shock the trinitrodiphenyl oxide used contains essentially not more than two nitro groups on any benzene nucleus. The nitrodiphenyl oxide component of the binder is present in an amount between about 35 and 40 weight percent.

The second plasticizer utilized consists essentially of the polyester condensation product of a dihydric alcohol and a dicarboxylic acid wherein a molar excess of alcohol has been used. In order to obtain a plasticizer of the desired thermoplastic characteristics and having the proper solvent action on the acetate, it is necessary to use a dihydric alcohol wherein the hydroxyl groups are the only functional groups and a dicarboxylic acid wherein the carboxylic groups are the only functional groups, i.e., a polyester having substantially no cross linkages is obtained. The polyester component is present in the binder in an amount between about 35 and 40 weight percent. It is preferred to use about equal amounts of the polyester component and nitrodiphenyl oxide component.

The dihydric alcohol used in the preparation of the plasticizer is selected from at least one of the dihydric alcohols in the class consisting of ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, n-butylene glycol and poly n-butylene glycol; the polyglycols must have a molecular weight of less than about 400 in order to produce a polyester of the desired properties.

The dicarboxylic acid utilized in the preparation of the plasticizer is selected from at least one member of the class consisting of alkyl dicarboxylic acids and alkyl oxydicarboxylic acids, which acids have between 2 and 6 carbon atoms in the molecule. Examples of the dicarboxylic acids are malonic acid, succinic acid, glutaric acid and adipic acid. Examples of the oxydicarboxylic acids are diglycolic acid, oxyacetic-propanoic acid and

oxydipropanoic acid. It is preferred to use the oxydicarboxylic acids because of their favorable effect on the oxygen demand of the binder.

It has been discovered that the molecular weight of the product of the polyester condensation has a considerable effect on the plasticizing properties of the product. A low molecular weight is desirable and this desired molecular weight is obtained by using a molar excess of alcohol over acid. The mole ratio of alcohol to acid should be between about 1.02 and 1.3, preferable between about 1.15 and 1.25.

The polyester plasticizer is prepared by any of the conventional methods known to the art, e.g., the desired amounts of alcohol and acid are charged to a heated reaction zone wherein the temperature of the materials is maintained at about 150° C. The water evolved in the reaction is withdrawn from the reaction zone by means of a condenser which refluxes back to the reaction zone any glycol and acid which may have vaporized. Preferably, the reaction zone is operated under vacuum. The reaction is continued until the evolution of water has substantially ended. The contents of the reaction zone, hereinafter known as reaction product of the polyester condensation, are cooled and sent to storage for future use in the preparation of the binder of this invention. Various methods of preparing polyester condensation products are set out in Synthetic Resins and Rubbers (copyright 1943) by Paul O. Powers, John Wiley and Sons, Inc.

The ammonium nitrate-binder composition is extremely stable to physical shock and even thermal shock. The binder-nitrate material may be maintained at a temperature of about 120–130° C. without appreciable gassing. In order to obtain a usable propellant it is necessary to add to the binder and ammonium nitrate combustion promoters. The combustion promoters utilized in the composition herein are two. The first promoter is phenotiazine which is present in the total composition in an amount between about 1 and 4 weight percent. Variation in the amount of phenotiazine present has an effect on the burning rate of the composition. In general, about 2 percent of phenotiazine is sufficient for the majority of uses in gun propulsion. The phenotiazine may be used as chemically pure material or in the various grades sold commercially which contain appreciable amounts of impurities.

The phenotiazine combustion promoter is particularly effective in this composition because it eliminates the smoking tendency imparted to the composition by the nitrodiphenyl oxide plasticizer.

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

A 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. They prefer graphite of colloidal or semi-colloidal particle size.

Another general class 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.

Still another type of useful carbon 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 their propellant composition.

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.

The binder of this invention is preferably prepared by heating the polyester plasticizer to a temperature between about 100° and 150° C. and adding to the hot plasticizer the desired amount of diphenyl oxide plasticizer. The mixture is agitated while being maintained at the elevated temperature above the melting point of the diphenyl oxide plasticizer and the agitation is continued until a substantially homogeneous mixture has been attained. The mixture is maintained above the melting point of the diphenyl oxide plasticizer while the desired amount of cellulose acetate is added thereto. A suitable temperature is between about 100° and 150° C. The three-component mixture is agitated while being maintained at the elevated temperature until a smooth homogeneous plastic mass is obtained. When cooled to ambient temperature the binder is a hard, tough material which has thermoplastic properties. The binder is readily converted to a viscous liquid by heating to a temperature above about 90° C. While the order of component addition need not be as above, the blending process is simplified by the order given.

In general, after the three-component binder has been prepared the phenotiazine and carbon are added to the binder while it is in the molten or pasty state. The phenotiazine and carbon were uniformly distributed throughout the plastic binder by stirring. This mixture may then be allowed to cool and stored as such for

future use or finely divided ammonium nitrate may be added to the vessel containing this plastic material and thoroughly agitated while the composition is present as a plastic solid. The plastic composition may be permitted to solidify by cooling; the solid may be divided into granules by grinding and screening to obtain a fraction of approximately the same particle size. The plastic composition may be formed into various shapes such as threads, strands, tubes—all these in variations of conventional shapes—by extrusion through a suitable dye. Also the plastic composition may be formed into sheets or plates which can be cut up into the shapes needed for a particular use. In general, for hand-arms screened powders are preferred whereas for artillery uniform shapes provided with perforations are preferred. The composition is extemely stable to both mechanical and thermal shock and may be stored with perfect safety under conditions suitable for nitrocellulose powders.

Results obtainable with the composition of the instant invention are illustrated by the following working example.

*Test*

The cellulose acetate component of the binder was a commercial LL–1 grade material analyzing 55–56 weight percent of acetic acid. The diphenyl oxide component was technical grade 2,4-dinitrodiphenyl oxide.

The plasticizer was prepared by reacting ethylene glycol and diglycolic acid in a mole ratio of glycol-to-acid of 1.2. The glycol and acid were placed in a reactor which was provided with an agitator and a reflux condenser. A vacuum pump was connected to the condenser. The reactants were heated to about 150° C. Water formed in the reaction was withdrawn and the reaction continued until substantially no water was being evolved. The total reaction time was about 4 hours. The polyester condensation product had the following physical properties at 25° C.: Specific gravity, 1.35; refractive index, 1.475; viscosity, 578 centistokes at 100° F.

The ammonium nitarte used was technical grade and has a particle size as follows:

| Mesh size: | Wt. percent retained |
|---|---|
| +35 | Trace |
| 35–60 | 5 |
| 60–80 | 7 |
| 80–120 | 16 |
| 120–200 | 28 |
| 200–325 | 19 |
| −300 | 8 |
| Dust | 17 |

The polyester plasticizer and dinitrodiphenyl oxide plasticizer were added in equal amounts into a small dough mixer heated to 150° C. The plasticizers were mixed until a viscous liquid was obtained. The cellulose acetate was then added and the mixing continued at the temperature of 150° C. until a homogeneous viscous mass was obtained. The binder components were added in such amounts that the binder consisted of cellulose acetate 25 weight percent; polyester plasticizer 37.5 percent and dinitrodiphenyl oxide plasticizer 37.5 weight percent. Phenotiazine and commercial grade carbon black were added in equal amounts to the vessel and thoroughly intermingled into the binder. The phenotiazine and carbon black were added in amount such that each was present in the final composition to the extent of 2.0 weight percent. Ammonium nitrate was added to the other components in the mixture at a temperature of about 120° C. and the mixture stirred for about 30 minutes until a uniform plastic mass was obtained. In this instance the mixer was allowed to cool while the blades were rotated; in this procedure the composition was obtained as a coarse powder when room temperature was reached.

The powder was removed from the mixer and sieved for the test firings. The fraction which passed 30 mesh and was retained on a 40 mesh was used. The firings were carried out with a 30 caliber rifle. The cartridges were provided with a standard commercial primer and were loaded with a 169 grain bullet.

Three series of firings were made using cartridges loaded respectively with 25, 30, and 32.5 grains of propellant. A wood block target was set at a distance of 40 feet from the rifle. Shots were made with each loading and the penetration of the bullet into the wood in each shot determined.

The bullets penetrated the wood block for a distance varying from 9 inches to 11 inches. In all cases there was no observable smoke produced in the firings and no observable muzzle flash. After the firings the bore of the rifle was completely clean and had a polished appearance.

The composition used in the above tests consisted of binder, 20 weight percent; phenotiazine, 2 weight percent; carbon black, 2 weight percent; and ammonium nitrate 76 weight percent. In order to obtain a comparison another series of firings was made wherein 4 weight percent of Prussian blue was substituted for the phenotiazine and carbon black of the above composition and in another test 4 weight percent of ammonium dichromate was substituted for the phenotiazine and carbon black. After the firings with the inorganic catalyst the rifle bore contained appreciable amounts of ash and had a dirty appearance. These series of firings show the very important advantage of the composition of the invention in the cleanliness of the rifle bore after the firings, owing to the completely organic nature of the combustion promoter utilized in the instant composition.

The illustrative composition contained only the binder, the phenotiazine, the carbon black and technical grade ammonium nitrate. However, it is to be understood that other materials which are commonly added to ammonium nitrate explosives may also be present; these materials do not change the essential features of the composition of the invention. For example, the high temperature stability of the composition may be improved by adding small amounts of aromatic hydrocarbon amines such as diamino toluene or diphenylamine. Also the mixing of the ingredients may be helped by the presence of a very small amount of a surface active agent; any of the conventional commercial agents which do not react with one or more of the components may be used, for example, alkylarylsulfonate.

Thus, having described the invention, what is claimed is:

A gun propellant consisting of (1) about 20 weight percent of a binder consisting of (A) about 25 weight percent of cellulose acetate analyzing between about 55 and 57 weight percent of acetic acid, (B) about 37 weight percent of the polyester condensation product of ethylene glycol and diglycollic acid, the mole ratio of glycol to acid being about 1.2 and (C) about 37 weight percent of dinitrodiphenyl oxide, (2) about 2 weight percent of phenothiazine, (3) about 2 weight percent of carbon black and about 76 weight percent of ammonium nitrate.

No references cited.