

1

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## PROCESS FOR PREPARING COMPOSITE PROPELLANTS

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This invention relates generally to a propellant composition suitable for projectiles of the reaction-impulse types. The herein described propellant composition is particularly useful where the reactive effect of a high velocity gas jet is employed for the propulsion of rocket shells, as for example, anti-aircraft, anti-tank, gas shells, etc. It may also be employed for assisting in the take-off of airplanes.

Propellants of the present class are generally burned in a fuel chamber, which chamber is provided with an orifice, the chamber being of such construction as to withstand the high gas pressure developed by the combustion of the fuel. The impulse is developed in such projectiles by the reactive effect of the gases issuing at high velocity, the effect being directed along the axis of the gas orifice, which orifice is usually of the venturi type.

For the propulsion of artillery shells for anti-tank or anti-aircraft use the fuel chamber containing the propellant is generally attached to the base of a shell, the whole then forming a projectile of the rocket type. For firing purposes the projectile is fired from a smooth bore tube, which is sufficiently light so that it may be conveniently handled by personnel without additional supporting structure, although for certain purposes it may also be mounted in a fixed or semi-fixed position. Ignition of the fuel may be effected by electrical means employing a miner's squib or other suitable ignition device.

When used in the assisted take-off of airplanes one or more of the fuel chambers may be mounted upon the plane in such a way that the impulse imparted to the chamber by the high velocity gases issuing from the jet is transmitted directly to the plane.

From the above brief description it follows that certain important requirements must be met by the propellant. These requirements, as now understood, comprise the following:

(a) The propellant should burn uniformly without disintegration under the high pressure existing in the fuel chamber and by uniform combustion generating a steady stream or jet of high velocity propelling gas.

(b) The rocket principle of propulsion, employing as it does the reactive effect of a high velocity gas stream, requires that the fuel chamber be of light construction consistent with safety so as not to burden the projectile with excess dead weight. This requirement, in terms of the propellant, requires substantial reproducibility of the internal ballistics of the propellant, particularly a reproducible relationship between the gas pressure generated in the fuel chamber and the area or diameter of the gas orifice.

The relationship between the gas pressure generated in the fuel chamber and the diameter of the orifice is expressed by the equation:

$$2 \log \phi = \log K + (n-1) \log P_m$$

where  $\phi$  is the orifice diameter,  $K$  is a constant which is proportional to the burning area of the fuel grain,  $n$  is

2

another constant and  $P_m$  is the maximum gas pressure developed in the fuel chamber.

The above equation, when plotted on log-log paper, will be found to describe a straight line having the slope-intercept form, the slope of the line being the constant

$$\frac{n-1}{2}$$

while the intercept will be  $\frac{1}{2} K$ .

From an inspection of the above equation it will be seen that the larger the value of the constant  $n$  the more rapidly will the pressure vary with the inverse of the area of the orifice, in other words, the more sensitive does the system become to small variations in the conditions of burning. On the other hand, the smaller the value of  $n$  the less rapidly does the pressure increase with a decrease in the area of the orifice and hence the safer the fuel becomes. Thus, the constant  $n$  is seen to be an important property of the fuel, which property must be taken into account for the design of the fuel chamber.

(c) Another important property of the propellant is the effect of its initial temperature (usually called the ambient temperature) on the rate of burning of the propellant. For example, if the pressure developed by the combustion of the propellant is increased by from 75% to 100% by a 50° F. rise in ambient temperature, a firing chamber designed to withstand the pressures developed at the highest temperatures encountered in its use will be needlessly heavy at lower temperatures. Furthermore, the differences in total time of burning between different temperatures will make the external ballistics of the projectile a function of the ambient temperature.

From the above considerations it will be apparent that the temperature coefficient of the rate of burning or of the maximum pressure developed should be as low as possible in order that a standard design of fuel chamber may be adopted which may be used under various climatic conditions.

(d) A further important characteristic of a rocket propellant is what is loosely called its "power," meaning by this its effectiveness in imparting forward motion to a projectile by reaction of the gases expelled through the jet. From an analysis of the factors entering into this relationship, it has been found that the projectile velocity is determined only by the ratio of fuel mass to load and by the gas-velocity; and furthermore, that for a given ratio of fuel mass to projectile mass the velocity of the projectile is directly proportional to the velocity of the ejected gases.

(e) The density of the propellant should be as high as possible, because a high density permits the use of a smaller and hence a lighter firing chamber with the same weight of fuel, thereby making it possible to decrease the size of the fuel chamber of the projectile and hence to decrease its air resistance.

(f) Ease of production-fuels of the type herein described are most readily produced in large quantities either by pressing or by extrusion of a plastic mass by means of an intermittently operated press or by means of a continuous extrusion machine. For the present composite propellant, the gas generating ingredients of which consist of a mixture of an oxidizer such as sodium nitrate and an oxidizable substance such as ammonium picrate, it is possible by means of the present invention to produce safely, cheaply and in large quantities accurately formed grains of a variety of shapes and sizes. When the individual grains are produced by pressing in a die, such grains are generally of a length not appreciably greater than the diameter. When such relatively short grains are produced it is possible to cement together a plurality of short grains in order to form a single long grain with-

3

out adversely affecting the burning rate or characteristics of the composite cemented charge. When producing long grains by means of an extrusion press the grains may, of course, be produced of indefinite length since a continuous rod or tube may readily be produced by extrusion of the plastic mass. Such an extruded grain may be cut into individual grains of any desired length.

According to the present invention I have found that the gas generating ingredients of the fuel, which ingredients are preferably an oxidizing substance such as sodium nitrate and an oxidizable material such as ammonium picrate can be formed by cold molding into a grain or cylinder of any reasonable size by the incorporation with such gas generating ingredients of a thermosetting resin. In order to make possible a thorough incorporation of the resin with the solid materials of the fuel, the thermosetting resin is employed in the partly condensed liquid state and is hence in a condition where, upon further exposure to slightly elevated temperatures a further advancement of the resin may be caused to take place. With the present resins I have found that the resin ingredients are conveniently first partly condensed, which condensation may take place either in the absence of or in the presence of a solvent. In order not to affect adversely the internal ballistics of the propellant it is necessary that a restricted amount of the resin be employed and that such restricted amount be sufficient to enable a mechanically strong grain to be produced. Employing my present invention, it is possible to produce satisfactory grains using only 5% to 10% by weight of resin in the finished grain.

The incorporation of the liquid resin or the liquid resin solution with the solid gas forming ingredients may be effected by mechanically mixing together the various ingredients. After thorough incorporation of the liquid thermosetting resin with the gas forming ingredients, the compounded material may be molded by pressing or extruding as above mentioned and the grain produced in a sufficiently strong state so as to readily permit further curing and handling without danger of breakage. I have also discovered that the gas forming ingredients herein employed may assist or hasten the further polymerization or curing of the resin in such a manner as to considerably accelerate the rate of cure.

Various thermosetting resins may be employed for the bond of the herein described fuel. Such resins comprise the phenol-aldehyde type, which is preferably utilized in the "A" stage where the ratio of phenol to formaldehyde is employed in substantially 1:1 molecular proportions. I may also utilize the casting type of phenol-formaldehyde resin in which the proportions of phenol to formaldehyde are in the neighborhood of 1:2 to 1:6 molecular proportions. Other resins may comprise the alkyl substituted phenols, particularly the tertiary butyl and tertiary amyl phenol-formaldehyde condensation products. The phenyl-phenol-formaldehyde condensation products may also be used. When such resins are condensed in the presence of a catalyst they become thermosetting in nature and may be utilized in this thermosetting form. Other resins which may be utilized are thermosetting resins prepared from melamine or substituted melamines condensed with formaldehyde. Moreover alkyd resins may also be employed. These resins are thermosetting condensation products of a polybasic acid such as phthalic anhydride and a polyhydric alcohol such as glycerine or glycol. These resins are preferably condensed in the presence of a fatty acid or a fatty oil. Resins prepared from polyvinyl acetal compositions containing plasticizers and also a sufficient amount of a urea or melamine-formaldehyde condensation product to make the material thermosetting may also be employed. I may also employ with the above resin condensation products of urea or substituted urea and formaldehyde.

Resins suitable for the present purpose are first condensed to the point where the liquid resin or a solution of the resin in a suitable solvent is condensed to the

4

point where the viscosity of the liquid resin has a viscosity of from 500 to 10,000 centipoises at 25° C. Within this range of viscosities efficient incorporation of the liquid resin may be obtained within a reasonable time. These resins at this stage are fusible, soluble in alcohol and possess heat reactive properties.

#### *Process for producing propellant*

Commercial sodium nitrate which has been first dried to contain less than 0.5% of water is ground so as to have a particle size of approximately 100 microns. This particle size corresponds to a standard screen size of from 100 to 200 mesh per linear inch. The dry powdered sodium nitrate is then mixed with finely precipitated ammonium picrate in a 1:1 ratio by weight. The mixing of the nitrate and the picrate is carried out by stirring in a ribbon type mixer for approximately 1 hour.

A liquid resin or resin solution is now made by condensing a mixture of 1 mol of phenol with 2 mols of formaldehyde in the presence of an alkaline catalyst to the point where the liquid resin has a viscosity within the limits given above. After such preliminary condensation the alkaline catalyst is desirably neutralized and replaced by an acid type catalyst so as to provide a thermosetting composition.

Ninety parts by weight of a sodium nitrate-ammonium picrate mixture is placed in an edge runner mill and over a period of from 15 to 30 minutes, 10 parts of the solution of phenol-formaldehyde liquid resin is added. In order to impart a somewhat greater plasticity to the product, 1.5 parts of a plasticizer such as a toluene sulfonamide-formaldehyde reaction product or other plasticizing material may be added to the liquid resin and the plasticizer and liquid resin thoroughly mixed into the dry powder. After all of the resin solution has been added, mixing is continued for approximately 3 to 4 hours. During the addition of the resin-plasticizer solution and while mixing the solution into the powder, a current of dry nitrogen gas or other inert gas is passed into and through the mill. The purpose of the inert gas is to remove any volatile solvents and water which may be present in the products being mixed.

At the end of the mixing period, the mixture consists of a dry, dusty powder which may have a total volatile content of not more than 1.4% by weight. The volatile content is measured by determining the loss in weight on heating a sample of the powder for 48 hours at 80° C. During the mixing of the powder and the resin-plasticizer mixture the temperature should not be allowed to exceed a temperature which will advance the resin during mixing, since it is desired not to further condense the resin while in the mixer. The bulk density of the dry powder containing the resin at the end of the mixing period is from 0.7 to 0.9 gram per cc.

The object of the mixing operation is to coat each grain of powder with a uniform coating of the liquid resin.

#### *Molding Step*

The powder as produced above is now cold molded by pressing in a mold by means of a toggle or hydraulic press. For this purpose the powder is poured into the die of the press and then by means of a plunger subjected to a pressure of from 10,000 to 15,000 lbs./sq. in. This pressure is preferably maintained by means of the plunger for approximately 30 seconds in order to permit the escape of any entrapped air and also to permit flow of the resin coated crystalline particles so that a dense mass results which is free of strains. The molded grain is then ejected from the mold and will usually be found to have a density of from 1.75 to 1.85 grams per cc. It possesses a smooth, glossy finish and is free from cracks. The temperature during pressing is substantially room temperature, i. e., within the limits of, say, 15° C. to 35° C. Molding temperatures within these limits are herein referred to as "cold molding" temperatures.

5

Since it is particularly important that the grain be free of cracks including microscopic cracks, some of the grains, after removing from the die, are inspected by painting on the outside of the grain a solution of a dye such as gentian violet dissolved in hexane. The dye causes any small microscopic cracks to become visible. At this stage the grains are strong enough to withstand normal handling.

#### Cure

In order to cure the grains they are placed in closed, sealed containers of a size just sufficient to contain one or more of said grains, and then heated in an oven at a temperature of about 60° C. for a period of from 6 to 8 days. A sealed container is employed in order to prevent evaporation of the residual solvent from the interior of the grain. If such residual solvent is permitted to evaporate freely the liberated vapors would crack the grain. It will be found that the initial curing in the sealed container has advanced the resin to a point where it is sufficiently strong so that further curing can be carried out in the open. When this has been done the grain may be removed from the sealed container and then cured for a further period of from 2 to 4 days at a temperature of 60° C. During this second open curing step the grain loses approximately from 1/2% to 3/4% or more of volatile matter. Where a solvent free resin is employed, it is practical to carry out the curing entirely in the open, that is, without first confining the grains in a sealed container. In this case the curing time for a phenol-formaldehyde thermosetting resin will vary from 8 to 12 days when such curing is effected at a temperature of 60° C. Higher rates of cure may be employed by using a higher temperature, however, generally the cure should be carried out at temperatures below 80° C. Curing at temperatures below 80° C. is herein referred to as curing at "slightly elevated" temperatures.

After the curing has been completed it has been found that the grain is sufficiently strong so that it will withstand repeated exposure to high and to low temperatures without cracking. I have been able to subject grains made as described herein to alternate extremes of temperature without developing cracks or breaking of the grain. Such exposure of the grains to extremes of temperature for testing purposes is best done by first heating the grain to a temperature of 60° C. for 4 hours then allowing the grain to cool to room temperature for one hour and then cooling the grain to a temperature of -40° C. for 4 hours. Such a cycle of temperature changes should be repeated approximately 10 times and if the grain withstands this treatment without developing cracks or without breaking it is considered satisfactory for the present purpose.

#### Performance characteristics

A propellant produced as described above will be found to burn uniformly without disintegration and to be mechanically strong enough to withstand ordinary handling. Upon experimentally burning grains as produced above and determining from the experimental measurement thereon the value of quantity  $n$ , given in Equation 1 above, I have found that for thermosetting resins generally the value of  $n$  will lie between 0.4 and 0.6, as compared with a value of 0.7 to 0.8 for cordite or other double base powders hitherto proposed for similar purposes.

I have determined, moreover, that the temperature sensitivity of the propellant, i. e., the increase in chamber pressure produced with the ambient temperature changes from -40° F. to 90° F. is approximately 10% as compared with a pressure increase of about 64% for double base powders of the cordite type.

#### I claim:

1. The process of producing a propellant for jet actuated devices which comprises the following steps: (a) intimately mixing finely divided sodium nitrate and finely

6

divided ammonium picrate in a ratio of about 1:1 by weight, (b) intimately mixing with the mixture formed in step (a) a liquid thermosetting synthetic resin having a viscosity of from about 500 to about 10,000 centipoises at 25° C. and in such amount that the propellant will contain about 5 to 10 per cent by weight of resin, (c) cold molding under pressure the mixture formed in step (b), and (d) curing the cold molded mixture at a temperature below 80° C.

2. The process of producing a propellant for jet actuated devices which comprises the following steps: (a) intimately mixing finely divided sodium nitrate and finely divided ammonium picrate in a ratio of about 1:1 by weight, (b) intimately mixing with the mixture of sodium nitrate and ammonium picrate a liquid thermosetting synthetic resin having a viscosity of from about 500 to about 10,000 centipoises at 25° C. and in such amount that the propellant will contain about 5 to 10 per cent by weight of resin, (c) cold molding under pressure the mixture of sodium nitrate, ammonium picrate and thermosetting resin, (d) heating the cold molded mixture in a sealed container at about 60° C. to prevent free evaporation of any volatile solvent and to advance the condensation of the resin to a point where the molded mixture is sufficiently strong so that further heating can be conducted in the open, and (e) thereafter heating the product obtained from step (d) in the open at a temperature of about 60° C. to further advance the condensation of the resin.

3. The process in claim 1 wherein the liquid thermosetting resin is an alkyl substituted phenol.

4. The process in claim 1 wherein the liquid thermosetting resin is phenol-formaldehyde.

5. The process in claim 1 wherein the liquid thermosetting resin is a phenylphenol-formaldehyde condensation product.

6. The process in claim 1 wherein the liquid thermosetting resin is a tertiary butyl phenol-formaldehyde condensation product.

7. The process in claim 1 wherein the liquid thermosetting resin is a tertiary amyl phenol-formaldehyde condensation product.

8. The process in claim 1 wherein the liquid thermosetting resin is a phenol-aldehyde.

9. The process of producing a propellant for jet actuated devices which comprises the following steps: (a) intimately mixing finely divided sodium nitrate and finely divided ammonium picrate in a ratio of about 1:1 by weight, (b) intimately mixing with the mixture formed in step (a) a liquid thermosetting phenol-aldehyde resin selected from the group consisting of, phenol-formaldehyde, phenylphenol-formaldehyde condensation products, tertiary butyl phenol-formaldehyde condensation products and tertiary amyl phenol-formaldehyde condensation products, said resin having a viscosity of from 500 to about 10,000 centipoises at 25° C. and in such amount that the propellant will contain about 5 to 10 percent by weight of resin, (c) cold molding under pressure the mixture formed in step (b), and (d) curing the cold molded mixture at a temperature below 80° C.

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