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PROCESS FOR PREPARING COMPOSITE PROPELLANTS

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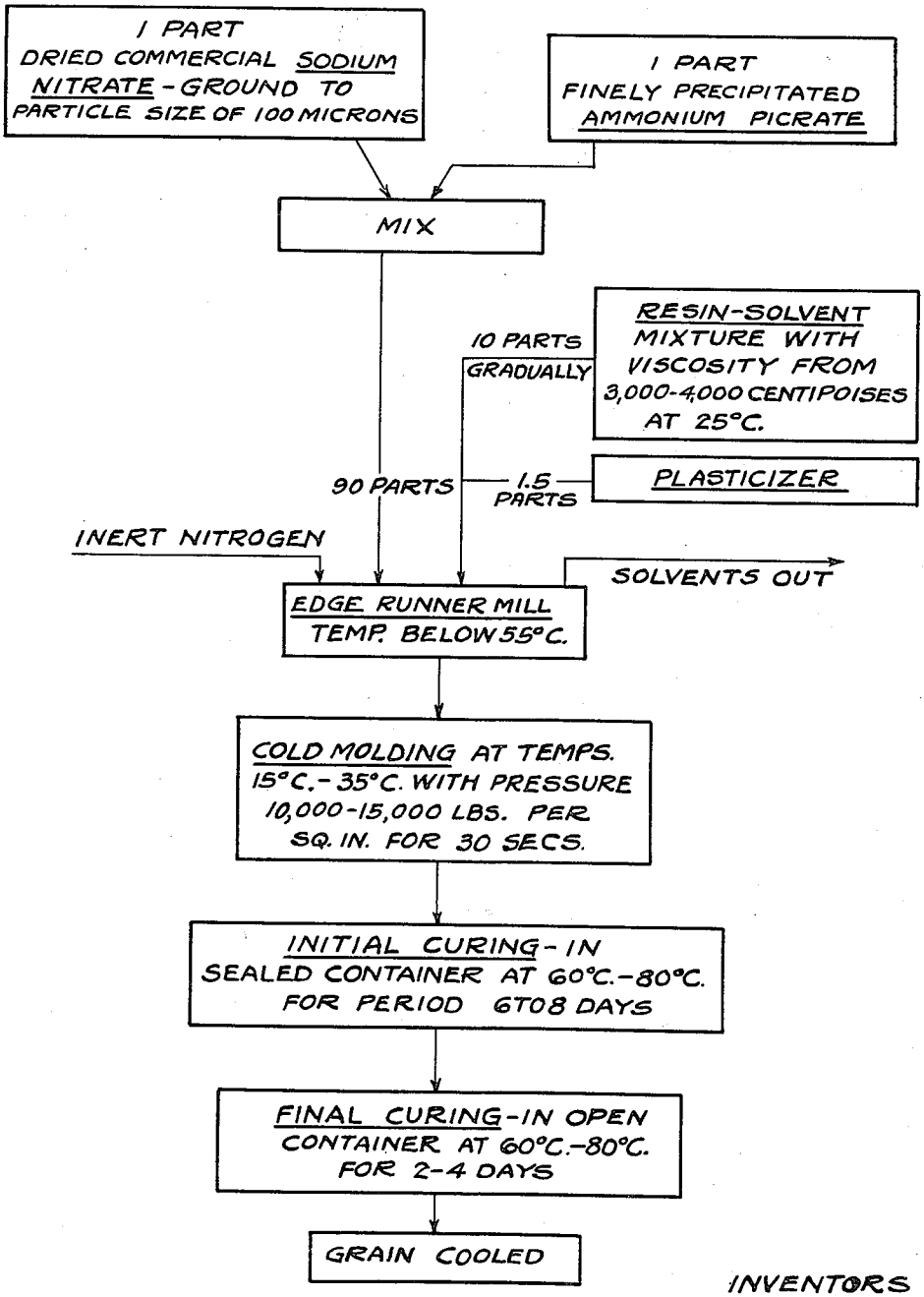

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PROCESS FOR PREPARING COMPOSITE PROPELLANTS

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This invention relates generally to a propellant composition for projectiles of the reaction-impulse type. 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 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 the 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 devices.

When used in the assisted take-off of airplanes one or more of the 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 generate a steady stream or jet of 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

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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:

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

where ϕ is the orifice diameter, K is a constant which is proportional to the burning area of the fuel grain, n is 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 ½ 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 area of the orifice, in other words, the more sensitive does the system become to small variation 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 (referred to herein as 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 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 determined 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 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 long grain without 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 be of indefinite length since a continuous rod or tube may readily be produced by extrusion. Such an extruded grain may be cut into individual grains of any desired length.

According to the present invention we have now found that the gas generating ingredients of the fuel, which ingredients are preferably an oxidizing substance such as sodium nitrate and an oxidizable substance 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 of the urea-aldehyde type. In order to make possible a thorough incorporation of the resin with the solid materials the thermosetting resin is only partly condensed and is hence in a condition where, upon further exposure to slightly elevated temperatures, a further condensation may be caused to take place. With the herein preferred resin we have found that the resin ingredients are conveniently first partly condensed while dissolved in a solvent. The quantity of resin ingredients so dissolved should preferably be in the neighborhood of from 50% to 65% by weight of the resin solution. After incorporation of the resin solution with the solid gas forming ingredients the compounded material may be pressed or extruded as above mentioned and the grain produced in a sufficiently strong state as to permit further curing and handling without danger of breakage. It has also been found that the gas forming ingredients exhibit an accelerated action on the further polymerization or curing of the resin, thereby considerably accelerating the rate of cure.

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 urea-formaldehyde resins according to my present invention it is possible to produce satisfactory grains using only 5% to 10% by weight of resin in the grain.

While various urea-aldehyde condensation products may be used for the bond of the herein fuel we have found that most satisfactory results, in meeting the exacting requirements outlined above, are obtained by employing as the bonding resin a mono-N-butyl urea-formaldehyde condensation product, as described more particularly below. Such a condensation product is produced by condensing a mixture of N-butyl urea and urea with formaldehyde in a mixed solvent consisting of equal volumes of normal butanol and xylene. The mixture preferably consists of 70% by weight of N-butyl urea and 30% of urea. Condensation is carried out in the presence of condensation catalysts by the application of a moderate degree of heat, the condensation being carried to the point where the viscosity of a 50% solution of the resin is of the order of 3,000 to 4,000 centipoises at 25° C. At this viscosity, efficient incorporation of the liquid resin solution may be obtained in reasonable time.

Process for producing propellant.—Commercial sodium nitrate is first dried to less than ½% of water, then ground so as to have a particle size of approximately 100 microns. This corresponds to a standard screen size of from 120–200 meshes per inch. The dry powdered sodium nitrate is then mixed with finely precipitated ammonium picrate in the proportions of 1:1 by weight. The mixing of the nitrate and the picrate is carried out for approximately one hour in a ribbon type mixer.

A liquid resin is made by condensing mono-N-butyl urea and formaldehyde in a mixture of butanol and xylene as a solvent so that the solution contains 50% solids, i. e., resin by weight. The viscosity of the resin-solvent mixture employed is of importance. The viscosity of the resin solution should be of such a degree as to afford thorough mixing in the time allotted therefor without introducing into the mixture an excessive amount of solvent. The object to be achieved is the coating of each grain of powder with a uniform coating of the resin solution. As stated above the preferred viscosity of the resin is in the neighborhood of from 3,000 to 4,000 centipoises at 25° C.

Ninety parts by weight of the sodium nitrate-ammonium picrate mixture is now placed in an edge runner mill and over a period of 15 to 30 minutes 10 parts of the solution of the N-butyl urea-formaldehyde resin, together with 1.5 parts of a plasticizer such as toluene sulfonamide-formaldehyde reaction product, is added and the plasticized 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 the mixing of this solution with 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 the volatile solvents (butanol and xylene) in a safe manner.

At the end of the mixing period the mixture consists of a dry, dusty powder which should have a total volatile content of between 1% and 1.4% by weight. The volatile content is measured by determining the loss in weight on heating a sample 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 55° C., since it is desired not to advance 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.

Molding step.—The powder as produced above is now molded by pressing in the cold in a toggle or hydraulic press. For this purpose the powder is poured into the die of the press and then by means of the plunger subjected to a pressure of from 10,000 to 15,000 lbs. per sq. inch. The pressure is preferably maintained by means of the plunger for approximately 30 seconds in order to permit the escape of entrapped air and a flow of the fine resin coated crystalline particles so that a dense grain free of strains is formed. The grain is 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 of cracks. The temperature during pressing is substantially room temperature, i. e., within the limits of from, say, 15° C. to 35° C.

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.

Curing step.—In order to cure the grains they are confined in closed, sealed containers having a volume only slightly greater than the grains and then heated in an oven at a slightly elevated temperature (about 60° C.) for a period of from 6 to 8 days. A sealed container is used to prevent evaporation of the residual solvents from the interior of the grain while the initial stage of the resin cure is carried out. If such residual solvent is permitted to evaporate freely the result would be to crack the grain.

As a result of the initial curing in the sealed container the resin has advanced to the point where it is sufficiently strong so that further curing can be carried out upon the unconfined grain, under conditions of free evaporation of volatile constituents. Accordingly, the grain is removed from the sealed container and 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 ½ to ¾ of a percent of volatile matter.

The purpose of the curing step is to further advance the initially partly condensed condensation product so as to complete the condensation of the resin and to produce a mechanically strong grain having the desired burning characteristics. While temperatures in the neighborhood of 60° C. are preferred temperatures as high as 80° C. may be employed. Temperatures below 80° C. may be referred to herein as "slightly elevated temperatures."

After curing has been completed, we have found that the grain is sufficiently strong so that it will stand repeated exposure to high and to low temperatures without cracking. In order to test the grain for resistance to extremes of temperature the test grains are first heated to a temperature of 60° C. for 4 hours then removed from the oven and allowed to cool at room temperature for one hour, and then cooled to a temperature of −40° C. for 4 hours. Such a cycle of temperature changes is repeated 20 times and a grain is considered satisfactory if it withstands this temperature change without developing cracks or breaking and will further show the proper characteristics on burning.

Performance characteristics.—A propellant produced as 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 the value of n in the equation given above, we have found that the value of n will lie between 0.4 and 0.5 as compared with a value of 0.7 to 0.8 for cordite or other double base propellants hitherto proposed for similar purposes.

The temperature sensitivity of the propellant, i. e., the increase in chamber pressure produced when 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. In other words, the prior propellants were over six times as sensitive to temperature changes as is the propellant produced in accordance with the present invention.

The velocity of the exhaust gases through the nozzle for the present propellant is in the neighborhood of 5300 ft./second, when the chamber pressure is 2000 lbs./sq. in., while the corresponding value for the double based powder, cordite, is 6300 ft./second. This yields a specific impulse in pound seconds per pound of fuel of 170 for the present propellant and 200 for the double base powders. Since the specific gravity for the above-named propellants are 1.80 and 1.55, respectively, a proportionally higher loading density can be obtained with the present propellant. Therefore, the specific impulse per unit of volume is 98% as compared to 100% for the cordite propellant.

When a propellant is used as a rocket fuel, it is desirable that the rate of burning be as rapid as possible, since the accuracy of the rocket is proportional to the speed of burning. With a high rate of burning the rocket reaches its maximum velocity in free flight at an earlier stage of its trajectory. Measurements of the rate of burning of the herein described propellant are in the neighborhood of 1.3 inches per second at 2000 pounds chamber pressure, while the double base type has a rate of burning, under similar conditions, of 0.8 inch per second. Such an increase in the rate of burning also permits a grain to be designed with a thicker web to give the same burning time, this permits a higher loading density to be attained in the fuel chamber.

The drawing illustrates in flow design form the above process.

We claim:

1. The process for producing a propellant for jet actuated devices which comprises the following steps: (*a*) intimately mixing finely divided sodium nitrate and ammonium picrate in about equal parts by weight; (*b*) intimately mixing

with the mixture resulting from step (*a*) partially condensed N-butyl urea-formaldehyde resin in solution in a solvent that may be vaporized during the mixing of this step; (*c*) evaporating solvent during the mixing of step (*b*) until the mixture assumes the condition of a substantially dry, dusty powder having a total volatile content of about 1 to 1.4 per cent; (*d*) cold molding, under pressure, the powder resulting from step (*c*); (*e*) confining the molded product resulting from step (*d*) in a closed container and heating to a temperature below 80° C. to further condense the resin to a point where the molded product is sufficiently strong so that further condensation of the resin can be carried out upon the unconfined molded product; (*f*) and thereafter additionally heating the product resulting from step (*e*) while unconfined to a temperature below 80° C. to further condense the said resin; the said resin being used in sufficient amount to provide about 5 to 10 per cent by weight of the resin in the finished product.

2. The process of producing a propellant for jet actuated devices which comprises the following steps (*a*) intimately mixing finely divided sodium nitrate and ammonium picrate in 1:1 ratio by weight; (*b*) partially condensing N-butyl urea-formaldehyde resin in solution in a vaporizable solvent to a point where the viscosity of said resin is between 3000–4000 centipoises at 25° C.; (*c*) mixing said resin with the mixture of step (*a*) while simultaneously vaporizing said solvent until the mixture assumes the condition of a substantially dry, dusty powder having a total volatile content of about 1 to 1.4 per cent; (*d*) cold molding at ambient temperature and at a pressure ranging from 10,000 p. s. i. to 15,000 p. s. i. the powder resulting from step (*c*); (*e*) confining the molded product resulting from step (*d*) in a sealed container and heating to a temperature below 80° C. to further condense the resin to a point where the molded product is sufficiently strong so that further condensation can be carried out upon the unconfined product; (*f*) and thereafter additionally heating the product resulting from step (*e*) while unconfined to a temperature below 80° C. to further condense the resin; the said resin being used in sufficient amount to provide between 5–10 per cent by weight of the resin in the finished propellant.

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