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PROPELLENT POWDER

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This invention relates to the manufacture of propellent explosives and more particularly to the production of rocket powder.

Giant grains of propellant suitable for use as rocket powder by the military or for use as jet-assisted take-off rockets for aircraft ordinarily have a grain diameter of from one to several inches and lengths sometimes over one foot or more. Heretofore, such large grains have been prepared by extruding the explosive composition which had previously been prepared in gelatinized sheet form. The production of such sheets has required a series of rolling operations, removal of volatile matter being accomplished during the final rolling steps, or by a subsequent drying treatment. Gelatinization was effected by the rolling, frequently supplemented by intermediate kneading operations, with the rolls ordinarily being heated. The resulting sheet or carpet of explosives was then rolled into a bundle to be inserted in the extruding die.

Such a process has the disadvantage that huge presses, rolls, and other explosive equipment capable of producing extremely high pressures are required, and the operation is, at best, very slow and hazardous, requiring many precautions to avoid explosion during extrusion. Furthermore, when the composition contains nitroglycerine, considerable nitroglycerine may be lost by volatilization during the extensive rolling resulting in variations of the composition of the ultimate grains. Such large grain propellants have likewise been produced by casting methods, but such prior casting methods have likewise had attending disadvantages. For instance, Silk and Dintelmann in U.S. Patent 2,417,090 disclose a casting process in which pellets of double base powder having their surface rendered tacky by means of a plasticizer are compressed and heated to form a homogeneous powder grain. Such a process, although well suited for certain types of large grains, is not well adapted for the manufacture of single base grains, requires the use of pressure with the attending hazards, and does not lend itself to the manufacture of grains of irregular configuration such as may be necessary to fit in certain types of rocket motors to provide the desired type of ballistic functioning.

The present invention has as an object the provision of a simplified and improved process for manufacturing rocket powder grains whereby the aforementioned and other disadvantages of prior procedures are overcome. Another object of this invention is to provide a process for producing rocket powder grains of either single or double base composition in which the use of extrusion, rolling, and other pressure methods and devices are eliminated. A further object is to provide an improved casting process for making rocket powder grains of any desired configuration or design.

The foregoing objects and advantages, as well as others which will become apparent from the following detailed description, are accomplished in accordance with this invention, generally started, by providing particles or pellets of a propellant, uniformly mixing therewith a

plastisol solvent in a sufficient amount to provide a pourable and flowable paste, forming the paste into the shape of a rocket powder grain as by pouring into a mold or by otherwise shaping, and then maintaining the mixture in the desired shape for a sufficient time to cause the paste to set-up or solidify and thereby form the desired rocket powder grain. The setting-up step is preferably carried out at elevated temperature to hasten the action. By "plastisol solvent" as used herein is meant a relatively non-volatile liquid which is a slow acting solvent or one having only little or no solvent power for the spherical particles of propellant at low or ordinary room temperatures, but being rapidly acting and having a relatively great solvent power therefor at elevated temperatures.

It has been found that the particles of propellant are advantageously formed by agitating nitrocellulose and a solvent therefor, such as ethyl acetate, with an excess of a non-solvent, such as water, in the presence of a protective colloid, removing the solvent, and thereafter drying the resulting spherical pellets of nitrocellulose. Such a process is described in U.S. Patent 2,027,114 and for spherical pellets of high density in U.S. Patent 2,160,626. Such spheres are particularly advantageous in the present invention because of their inherent characteristic of being relatively free-flowing, even in the dry state, and because of their "case-hardened" surface characteristic which tends to resist initial attack by the solvent. This surface characteristic is undoubtedly the result of a "skin effect" occasioned by surface tension and removal of the solvent in the formation of the spheres. Other ingredients, such as dioctyl phthalate, lead stearate, red lead, centralite, carbon black, dinitrotoluene, and the like, may be incorporated with the nitrocellulose in the formation of the spherical pellets to obtain particular ballistic properties as desired. Using such spherical particles, a relatively free-flowing paste is obtained in accordance with this invention when the spheres are mixed with the proper proportion of the plastisol solvent, whereas if irregular shaped particles, such as may be obtained by merely grinding cannon powder or the like, are utilized, the desirable free-flowing characteristics of the paste are not obtained. Although the spheres of propellant may be of any desired size, large diameter spheres require relatively longer periods of time in order to effect their solution and resultant solidification of the grain, whereas with smaller spheres, the time is correspondingly reduced. It is preferred therefore to utilize spheres having a diameter not greater than about 0.005 inch and preferably of much smaller diameter, such as 0.001 inch or less.

The ordinary liquid deterrents are generally solvents for nitrocellulose and are admirably suited as the plastisol solvent in the present process, it only being necessary that such deterrent have relatively poor solvent power for the propellant at ordinary room or low temperatures. In other words, the solvent power of such solvent should be insufficient to effect any substantial solution of the propellant at ordinary temperatures during the time required for uniformly mixing the solvent and propellant together and shaping the resultant mixture. Furthermore, if it is desired to prepare double base rocket powder grains, energizing modifiers, such as nitroglycerine, butane triol trinitrate, diglycol dinitrate, ethylene glycol dinitrate, and the like, may be mixed with one or more miscible deterrents, such as dibutyl phthalate, dimethyl sebacate, dibutyl succinate, dibutyl adipate, triacetin, ethyl diphenyl phosphate, tributyl phosphate, and the like, to provide plastisol solvents admirably suited for the purpose. If it is desired to produce single base rocket powder grains, the energizing modifier may be omitted from the composition and the plastisol solvent will be composed only of a liquid deterrent, such

as one of those set forth above or mixtures of them. Other deterrents suitable therefor at temperatures above their melting points are dimethyl phthalate, dioctyl sebacate, ortho nitro biphenyl, butyl benzyl phthalate, octyl diphenyl phosphate, triethylene glycol di-2-ethyl butyrate (i.e. triglycol dihexoate), and the like.

The amount of plastisol solvent should be such that it forms at least about 25% of the volume of a mixture of the solvent and the propellant. Substantially lesser amounts of the plastisol solvent tend to result in voids or air pockets in the resulting rocket grain and the mixture with such lesser amounts is generally not sufficiently fluid for the purpose. Greater amounts of plastisol solvent may be utilized to good advantage to increase the fluidity of the mixture, vary the ballistic properties of the resulting rocket grain as desired, and insure absence of voids or air spaces in the grains, but the amount utilized should preferably not be sufficiently great to result in segregation or settling out of the propellant during the period required to cause the mixture to set up.

In operation, the plastisol solvent is preferably desiccated or otherwise treated to reduce any traces of moisture to a minimum, and both the propellant and plastisol solvent are preferably evacuated prior to mixing to an absolute pressure of about ten millimeters or less of mercury for several hours and then are intimately mixed in any suitable mixer, such as a sigma blade mixer, while the pressure of about ten millimeters or less is maintained, and the resultant mixture is then poured into a mold, or otherwise shaped, in such a manner as to avoid entrapment of air and give the desired design of rocket powder grain. Such precautions as desiccating and evacuating are preferably observed in order to minimize the possibility of undesirable voids in the resulting rocket powder grain. After the mixture has been given the desired shape, heat is applied to elevate the temperature of the mixture to a temperature preferably in the range of about 50° C. to 90° C. and such temperature is maintained for a time sufficient to cause solution of the propellant and setting-up of the mixture, at which time the temperature may be reduced. As a general rule, the higher the temperature used during this treatment the shorter the period required in order to cause the grain to satisfactorily set up or harden, but precaution should be observed not to exceed the combustion or explosive temperature of the mixture. Grains so formed are of uniform composition throughout, may be of any desired design or configuration, and all pressure extrusion steps and undesirable casting techniques are avoided.

In order that the invention may be further clarified, following is an example illustrating a typical embodiment of the invention. Two hundred fifty parts of nitrocellulose having a nitrogen content of about 12.6% are agitated with 4100 parts of water at about 50° C. to form an aqueous slurry. A suspension of carbon black in ethyl acetate is separately prepared by first thoroughly mixing 0.705 part of carbon black with 100 parts of ethyl acetate. This mixture of carbon black and ethyl acetate is then added to 1250 parts more of ethyl acetate, and the resultant dilute carbon black-ethyl acetate mixture is agitated to insure uniform distribution of the suspended particles of carbon black. Thirty-one and four-tenths parts of dinitrotoluene and 2.8 parts of ethyl centralite are then added to the carbon black-ethyl acetate mixture. When the dinitrotoluene and the ethyl centralite are dissolved, the resulting mixture is then added to the nitrocellulose slurry while the slurry is under agitation. The temperature is raised to 68° C. and the complete charge vigorously agitated for one hour at which time the nitrocellulose is dissolved. Twenty-five parts of a protective colloid of the type derived from animal protein dispersed in 150 parts of water is then added and the agitation is continued until the nitrocellulose solution is formed into globules of the desired small size. Vigorous agitation is required in order to form very small particles. The addition of an emulsifying agent, such as the water soluble salts of fatty acids, sulphonated oils, the so-called water-soluble oils, and the like, greatly facilitates the formation of small particles of the nitrocellulose solution, and for this reason, twenty-four parts of a 40% aqueous solution of the sodium sulphate derivative of 2-ethylhexanol is added to the bath. One hundred twenty-five parts of sodium sulfate dissolved in 300 parts of water is added over a one hour period and agitation continued for an additional three hours. The globules are then hardened to form powder grains by removal of the ethyl acetate during continuous agitation and heating up to about 99° C. in accordance with the practice set forth in U.S. Patent 2,027,114 referred to, hereinbefore. The resultant spherical pellets of propellant are then air dried at 50° C. and are composed of about 87.7% nitrocellulose, 11.0% dinitrotoluene, 0.3% carbon black, and 1.0% ethyl centralite and have an average diameter of about 0.001 inch, more or less, depending on the degree of agitation used in the formation thereof.

About 56.18 parts by weight of spherical pellets of propellant such as prepared by the foregoing treating steps are then placed in a sigma blade mixer and the system is evacuated to an absolute pressure of about ten millimeters of mercury and so held for about sixteen hours. Meanwhile, about 37 parts by weight of a substantially anhydrous plastisol solvent, composed of 74% by weight nitroglycerine, 25% by weight dimethyl phthalate and 1% by weight ethyl centralite, is placed in a vessel and the vessel evacuated to an absolute pressure of about 10 millimeters of mercury and so maintained for about sixteen hours. The solvent is then added to the propellant in the mixer and the mixer operated to intimately mix the solvent and propellant, while the vacuum is maintained to prevent entrapment of air. After the solvent and propellant are uniformly mixed, the mixture is then shaped by carefully pouring to avoid entrapment of air into a mold formed of nitroglycerine-resistant plastic such as cellulose acetate, methyl methacrylate, or ethyl cellulose. Inasmuch as the plastisol solvent has a specific gravity of about 1.5, the percent by volume of plastisol solvent in the mixture is about 41.3%.

The mold containing the mixture of solvent and propellant is then placed is an oven, heated to about 75° C. and maintained at this temperature until the propellant is substantially dissolved by the solvent and the grain has set up. This solution and setting up of the grain is readily accomplished in a relatively short time, but for instance, may be conveniently let set over night. The exact time of such heat treatment depends, of course, upon the activity of the solvent, the particle size of the propellant, and the effective resistance of the surface of the propellent grains, hereinbefore described as "case hardening." For instance, utilizing the propellant and plastisol solvent described above, the mixture, if let stand at the relatively low temperature of about 22° C. will ordinarily set up in about 21 hours. When the grain has set up it is permitted to cool to room temperature and is removed from the mold.

Rocket powder grains prepared in accordance with the foregoing example are substantially free of undesirable voids, are substantially uniform in composition throughout the grain, and have the strength and other physical properties requisite for rocket powder grains. It will be apparent that the method is relatively simple lending itself to mass production and that no costly apparatus such as is needed for developing high pressures is needed. It will likewise be apparent that the propellant and plastisol solvent may vary appreciably in composition and that rocket powder grains having substantially any desired ballistic characteristics can be prepared in accordance with this invention. While the foregoing embodiment has been set forth in considerable de-

tail, it is to be distinctly understood that many modifications and variations will naturally present themselves to those skilled in the art without departing from the spirit of this invention or the scope of the appended claims.

Having thus described the invention, what I claim and desire to secure by Letters Patent is:

1. In the art of making powder grains by a molding process, the method which comprises preparing a substantially uniform pourable paste by mixing together particles of gelatinized nitrocellulose propellant and a liquid plasticizer for the nitrocellulose in the amount of at least about 25% by volume of the resulting mixture and at a temperature at which substantially no dissolution of the nitrocellulose particles in the plasticizers takes place and thereafter maintaining said composition at atmospheric pressure, and at a temperature at which the nitrocellulose will dissolve, until the nitrocellulose is completely dissolved and the resulting substantially homogeneous mass has solidified into a powder grain.

2. In the art of making powder grains by a molding process, the method for making substantially homogeneous and substantially non-porous propellent grains which comprises preparing a pourable paste having a substantially uniform composition by mixing together pellets of gelatinized nitrocellulose propellant and a liquid plasticizer for nitrocellulose in the amount of at least about 25 percent by volume of the resulting mixture and at a temperature at which substantially no dissolution of the pellets in the plasticizer takes place during said mixing, shaping said paste in a suitable mold, and thereafter maintaining said paste in said mold at atmospheric pressure, and at a temperature at which the nitrocellulose will dissolve, until the nitrocellulose has completely dissolved in said plasticizer and the substantially homogeneous mass has solidified into a propellent powder grain having dimensions and shape conforming substantially to those of said mold.

3. In the art of making powder grains by a molding process, the improved method for making propellent powder grains having a substantially homogeneous nonporous composition which comprises preparing a pourable paste of substantially uniform composition by agitating together pellets of gelatinized nitrocellulose propellant and a liquid plasticizer for nitrocellulose in the amount of at least about 25 percent by volume of the resulting mixture and at a temperature at which substantially no dissolution of the pellets in the plasticizer takes place during said agitation, said plasticizer including in its composition an energizing modifier of the resulting propellent grain, shaping said paste in a suitable mold, and, thereafter, maintaining said paste in said mold at atmospheric pressure and at a temperature at which the nitrocellulose will dissolve until the nitrocellulose has completely dissolved in said plasticizer and the substantially homogeneous mass has solidified into a propellent powder grain having dimensions and shape conforming substantially to those of said mold.

4. In the art of making powder grains by a molding process, the improved method for making propellent powder grains having a substantially homogeneous nonporous composition which comprises preparing a pourable paste of substantially uniform composition by agitating together pellets of gelatinized nitrocellulose propellant and a liquid plasticizer for nitrocellulose in the amount of at least about 25% by volume of the resulting mixture and at a temperature at which substantially no dissolution of the pellets in the plasticizer takes place during said agitation, shaping said paste in a suitable mold, and, thereafter, heating said paste in said mold at atmospheric pressure and to a temperature at which the nitrocellulose will dissolve until the nitrocellulose has completely dissolved in said plasticizer and the substantially homogeneous mass has solidified into a propellent powder grain having dimensions and shape conforming substantially to those of said mold.

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