3,702,272
Patented Nov. 7, 1972

3,702,272

SPHERICAL ROCKET PROPELLANT CASTING GRANULES AND METHOD OF PREPARATION

Thomas F. McDonnell, Collinsville, and Ralph E. Coffee, Alton, Ill., assignors to Olin Mathieson Chemical Corporation

No Drawing. Continuation-in-part of application Ser. No. 176,424, Feb. 28, 1962. This application Jan. 10, 1964, Ser. No. 337,099
Int. Cl. C06d *5/00*
U.S. Cl. 149—19 **36 Claims**

This invention relates to spherical rocket propellant casting granules and to rocket propellant grains prepared therefrom.

This patent application is a continuation-in-part application of a patent application Ser. No. 176,424, filed Feb. 28, 1962 by Thomas F. McDonnell and Ralph E. Coffee, entitled Process and Composition.

Crystalline high explosive compounds have been used extensively as oxidizers and finely divided metals have been used extensively as fuels in the preparation of rocket propellant grains. However several serious problems have been encountered in the use of these materials. First, the explosive compounds and powdered metals in a dry form may explode when subjected to a sharp impact, friction, heat or electrostatic discharge from a human body or other source. Thus special handling and storing techniques must be employed. Second, the explosive compositions and metals in finely divided form are extremely dusty, thus creating a health problem and increasing the explosion problem. Third, when the explosive compositions and metals are used in the preparation of castable rocket propellant grains, dry particles of the explosive composition or metal cling together tenaciously during mixing to form lumps, which cause a marked variation in the ballistic properties of the resulting rocket propellant grain, as well as between different batches of rocket propellant grains. Thus extended mixing periods must be employed in the preparation of the rocket propellant grains in order to obtain some degree of dispersion of the particles of explosive composition or powdered metal throughout the fluid propellant mix. Fourth, the irregular shapes of the explosive powder particles and metal powder tend to shorten the pot life of the fluid propellant mix, which causes the loss of some mixes which set-up before casting of the rocket grain can be effected. Fifth, the fluid propellant mix containing powdered explosive composition or powdered metal has a very high viscosity and uniform dispersion of the components throughout the mix is not easily attained.

The term "sensitive solid" as used throughout the description and claims is intended to include the finely divided crystalline high explosive oxidizer compositions and the metal fuels defined more fully hereinafter which are sensitive to explosion by sharp impact, friction, heat, or electrostatic discharge, and/or finely divided materials of this type which adversely increase the viscosity of fluid uncured solid propellant mixes and/or finely divided materials of this type which are chemically unstable under storage conditions and the conditions obtained in the preparation of solid propellants therefrom.

Several techniques have been developed in an effort to overcome these problems. In one process, the particles of explosive composition are coated with a wax or resinous material. However these coating materials seriously dilute the effectiveness and reduce the explosive power of the explosive composition. In another process, particles of explosive composition are admixed with a single- or double-base powder in a colloiding operation, then the resulting mixture is pressed into strands, the strands are cut into the desired grain size, and thereafter dried, glazed and sieved. This technique has some effect on reducing the sensitivity of the explosive composition. However the irregular shape of the grains formed by extrusion and cutting according to this technique markedly decreases the castability by a great reduction in the fluidity of rocket propellant mixtures containing these irregular shaped grains.

It is a primary object of this invention to overcome the disadvantages inherent in the handling of finely divided particles of a sensitive solid, and during the mixing of these particles in the preparation of fluid castable rocket propellant formulations.

Another object of this invention is to provide novel rocket casting powder compositions.

A further object of the invention is to provide an improved method for stabilizing finely divided particles of a sensitive solid against unprogrammed explosions.

Still another object of the invention is to provide an improved method for stabilizing finely divided particles of crystalline high explosive compositions against unprogrammed explosions.

It is another object of the invention to provide an improved method for stabilizing finely divided particles of a powdered metal against unprogrammed explosions.

A further object of the invention is to provide an improved method for preparing castable rocket propellant formulations.

Another object of the invention is to provide a novel rocket casting powder which can be added in larger proportions than previously to fluid castable rocket propellant formulations without adversely affecting the fluidity thereof.

It is another object of the invention to provide novel castable rocket propellants having improved physical properties.

These and other objects of the invention will be apparent from the following detailed description thereof.

It has now been discovered that novel rocket casting powders can be prepared by admixing an aqueous slurry of finely divided particles of a sensitive solid with a lacquer of either nitrocellulose or a mixture of nitrocellulose and nitroglycerin, in a substantially water immiscible volatile solvent, agitating the resulting mixture to form globules of the lacquer having the particles dispersed therein, partially evaporating the solvent, admixing a dewatering agent with the residue, and then evaporating the remainder of the solvent. The residue is an aqueous slurry of substantially spherical granules of the particles firmly embedded in a matrix of nitrocellulose, or a mixture of nitrocellulose and nitroglycerin, as the case may be. The slurry is dewatered, the granules are sized, dried, and, if desired, are glazed.

The term "matrix" is used throughout the description and claims to define the solid nitrocellulose or mixture of nitrocellulose and nitroglycerin portions of the granules, which includes the portions, filling the spaces between the particles of sensitive solid on the interior of the granules as well as that portion near and at the ing the outer surfaces of the particles near and at the exterior of the granules.

Any sensitive solid such as the crystalline high explosive compounds used as oxidizers and powdered metals used as fuels in the preparation of solid propellants, which is substantially insoluble in the water immiscible solvent or water used in preparing the lacquer of nitrocellulose, can be used in the preparation of the novel rocket casting granules of this invention. Typical examples of suitable crystalline high explosive compositions of this type include HMX (cyclotetramethylenetetranitramine), RDX (cyclotrimethylenetrinitramine), PETN (pentaerythritol tetranitrate), 2,4,6-trinitrophenylmethylnitramine, nitroguanidine, and mixtures thereof.

Typical examples of suitable metal fuels of this type in finely divided form which can be encapsulated in accordance with the process of this invention include zirconium, aluminum, beryllium, zinc, and the like and mixtures thereof. When it is desired to encapsulate powdered aluminum, the aluminum is first washed with an aqueous potassium dichromate solution to inhibit reaction with the aqueous component of the lacquer suspension. It will be recognized by those skilled in the art that a mixture of two or more of the oxidizer compounds, or a mixture of two or more of the metal fuels, or a mixture of one or more oxidizer compound with one or more metal fuel may be encapsulated in accordance with the technique of this invention.

HMX is one of the preferred crystalline high explosive compositions because of its high oxygen content. It is well known that HMX exists in the form of several species of crystals, i.e., it exhibits polymorphism in the solid state. The four known crystal forms of HMX are the alpha, beta, gamma and delta isomorphs. The commercial form of HMX predominates in the beta-isomorph, which is one stable at ordinary temperatures and pressures, and also one which is the safest to handle from the impact sensitivity standpoint. Recent findings indicate that the beta-isomorph may undergo a transition to the other forms (mainly to the alpha form) in the presence of liquid ingredients, and under the environmental conditions existing in certain solid rocket propellant formulations. Such a transition results in a mixture of polymorphs of HMX which is of greatly increased sensitivity to detonation by impact, which increases the hazards during handling. It is believed that the individual HMX particles in the novel granules of the instant invention are immobilized within the granule matrix during the initial phases of preparing the rocket propellant formulation, and transition of the beta-isomorph to an undesired form is thus markedly inhibited.

Sensitive solids in finely divided form, for example, particles having a diameter between about 0.1 and about 150 microns, and preferably between about 1 and about 30 microns are used in the preparation of the novel granules. However, particles of any size that can be uniformly dispersed in a lacquer containing nitrocellulose under the reaction conditions described more fully below may be employed.

Particles of the sensitive solid are preferably admixed with the nitrocellulose base lacquer as an aqueous slurry containing, for example, between about 2 and about 10 percent by weight of solids, but a higher or lower concentration of solids in the slurry may be employed if desired. Explosive compositions such as HMX are available commercially as alcohol slurries or as aqueous slurries containing alcohol. If alcohol is present in the slurry, it should be removed by distillation or the like prior to adding the HMX to the lacquer. Dry particles of the sensitive solid may be added to an aqueous dispersion of the lacquer, if desired, but more severe agitation is required to obtain the desired degree of dispersion of the particles in the lacquer.

Nitrocellulose-base lacquer is prepared by dissolving nitrocellulose in a volatile solvent therefor. The nitrocellulose may be wholly or partially purified fibrous nitrocellulose in the form of nitrated flakes, linters, or wood pulp; it may be dense colloided nitrocellulose in the form of existing powder, whether fresh or deteriorated, or of good, poor, or indifferent stability; it may be nitrocellulose from other processes such as dust and mud or bulk powder and cannon powder. The nitrocellulose may be of any suitable degree of nitration, such as having a nitrogen content between about 11.0 and about 13.9 percent by weight.

Any volatile solvent for nitrocellulose which has a boiling point below that of water or other non-solvent vehicle and which is substantially immiscible or only partially immiscible with water may be employed in the preparation of the lacquer. In addition, the volatile solvent should be one in which the sensitive solid is substantially insoluble. Typical examples of suitable solvents of this type include ethyl acetate, methyl ethyl ketone, ethyl formate, isopropyl acetate, diethyl ketone, and mixtures thereof. Sufficient solvent is employed to provide a weight ratio of solvent to nitrocellulose of between about 6:1 and about 15:1, and preferably between about 7:1 and about 10:1.

The lacquer is preferably made by adding solid nitrocellulose and the volatile solvent to the aqueous slurry of particles of the sensitive solid in a suitable mixing vessel and agitating the ingredients. When solid nitrocellulose is contacted with the volatile solvent in this manner, the solvent dissolves the nitrocellulose to form a lacquer. Agitation of the resulting lacquer in the aqueous slurry causes formation of spherical lacquer globules which are dispersed in the aqueous medium. In addition, substantially all of the particles of sensitive solid present in the aqueous slurry become dispersed in the lacquer globules. In another embodiment, the lacquer is prepared separately by admixing solid nitrocellulose with the volatile solvent at a temperature below the boiling point of the solvent until substantially all of the nitrocellulose is dissolved. The resulting lacquer is then admixed with the aqueous slurry to form substantially spherical lacquer globules as described above. If desired, the lacquer may be formed in water or added to water in a suitable mixing vessel, and after formation of lacquer globules in the water, dry particles of the sensitive solid, or an aqueous slurry thereof, are added to the aqueous suspension of lacquer globules in the mixing vessel.

Sufficient water should be present during mixing of the lacquer and aqueous slurry and during formation of the lacquer globules to provide a water content equivalent to a weight ratio of water to nitrocellulose of between about 25:1 and about 180:1, and preferably between about 50:1 and about 80:1.

Sufficient sensitive solid in finely divided form is mixed with the nitrocellulose lacquer to provide a weight ratio, on a dry basis, of sensitive solid to nitrocellulose of between about 1:1 and about 9:1, and preferably between about 2:1 and about 6:1.

Mixing of the lacquer and aqueous slurry, and formation of the globules having particles of sensitive solid dispersed therein may be carried out at a temperature between about 10° and about 75° C., or any temperature above the freezing point of the mixture and below the boiling point of the volatile solvent.

Agitation of the lacquer in the aqueous slurry for a period of at least about ½ hour, and as long as 1½ hours or more is generally necessary to form globules of the desired size and shape and to effect substantially complete dispersion of the particles of sensitive solid in the lacquer globules.

Other materials may be added to the laquer or aqueous medium prior to or during the formation of the lacquer. A suitable protective colloid such as corn starch, gum arabic, animal bone glue, dextrin, bentonite, or the like, is added to the lacquer prior to formation of the globules in a proportion equivalent to between about 0.2 and 1.0 percent by weight of the water present in the mixture. Nitroglycerin may be added with the lacquer in a proportion equivalent to between about 1 and about 50 percent by weight of the nitrocellulose in order to improve the specific gravity of the rocket propellant casting granules ultimately produced.

If desired, other materials, for example, stabilizers such as diphenyl amine, 2-nitrodiphenyl amine, ethyl centralite, and the like; deterrents such as dinitrotoluene, dibutyl phthalate, and the like; and other modifying agents such as lead compounds, carbon black, powdered aluminum, and the like, may be included in the lacquer prior to formation of the globules.

In addition, other substances which are volatile nonsolvents for nitrocellulose, and which are miscible with the volatile solvent for nitrocellulose and immiscible with water may be added as a diluent. Typical examples of suitable diluents include the liquid hydrocarbons, xylene, benzene, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and other compatible water-immiscible diluents such as isopropyl ether, propyl ether, cyclohexane, methyl cyclohexane, toluene and the like.

After formation of the lacquer globules having the particles of sensitive solid dispersed therein, sufficient volatile solvent is removed to effect partial hardening of the lacquer globules. Some of the factors affecting the proportion of volatile solvent which must be removed in order to effect this partial solidification include the solvent employed, the weight ratio of solvent to nitrocellulose initially present, and the weight ratio of sensitive solid to nitrocellulose initially present. For example, when the volatile solvent is ethyl acetate, the weight ratio of solvent to nitrocellulose originally present is about 7.5:1, and the weight ratio of sensitive solid to nitrocellulose is about 3:1, then the proportion of ethyl acetate which must be removed to effect partial solidification of the globules is between about 35 and about 45 percent by weight of the solvent initially present. However, greater or lesser proportions may be removed if the above mentioned factors are varied.

Partial removal of the solvent is preferably effected by air stripping, wherein air is bubbled through the aqueous suspension of lacquer globules by means of a sparging system while agitating the suspension. Partial solidification of the lacquer globules in this manner inhibits coalescence and/or distortion of the spherical globules during subsequent processing steps, and increases the specific gravity of the rocket casting granules ultimately produced. If desired, partial removal of the volatile solvent may be effected by distillation or other solvent separation techniques, either individually or in combination with the air stripping technique.

After partial removal of the solvent and partial solidification of the globules are effected, a dewatering agent is admixed with the aqueous suspension. Typical examples of suitable dewatering agents include water soluble metal salts such as sodium sulfate, magnesium sulfate, aluminum sulfate, sodium chloride or sodium nitrate, and mixtures thereof. The dewatering agent is preferably dissolved in water to form a solution having a concentration of at least about ten percent by weight up to about the saturation concentration, and the resulting solution is then added to the aqueous globule suspension with agitation. However, the dewatering agent may be added in dry powder form to the aqueous suspension of globules, if desired. The proportion of dewatering agent added is equivalent to a weight ratio of water (total weight of water present in the aqueous suspension of globules plus water in the solution of dewatering agent) to dewatering agent (dry basis) of between about 50:1 and about 20:1. Addition of the dewatering agent to the aqueous suspension increases the specific gravity of the rocket casting granules ultimately produced. The dewatering agent is added slowly to the aqueous dispersion of globules, the total requirement being added over a period of at least about 15 minutes, and preferably between about 30 minutes and about 60 minutes. Agitation of the dispersion is continued after addition of the dewatering agent for a period of between about 1 hour and about 5 hours to effect substantially complete dispersion of the dewatering agent throughout the system. During this latter agitation period the dispersion is heated to a temperature above the boiling point of the volatile solvent but below the boiling point of water to effect substantially complete removal of the solvent and complete solidification of the globules into solid, substantially spherical, granules. The resulting aqueous slurry of solid granules is dewatered to remove the aqueous medium by decanting or other suitable dewatering technique, and the granules are washed with fresh water to remove the dewatering agent and other water soluble substances that may adhere to the granules.

After washing, the wet granules may be screened or subjected to another suitable sizing technique to recover a first size fraction and a second size fraction. The first size fraction predominates in larger granules having a minimum diameter of between about 0.025 and about 0.045 inch, the maximum diameter being about 0.090 inch. The first size fraction may be recycled to the lacquer make-up step, where the nitrocellulose portion of the granules is dissolved in the volatile solvent, and the resulting lacquer containing particles of the explosive composition is used in the preparation of additional novel granules of this invention. The second size fraction predominates in smaller granules having a maximum diameter of between about 0.020 and about 0.025 inch, the minimum diameter being about 0.002 inch. The second size fraction, which generally constitutes between about 80 and about 99 percent of the granules produced, is suitable for use after drying, in the preparation of castable rocket propellant compositions. However, the size separation step may be omitted when the granules are used in the processes where the diameter of the granules is of little or no importance.

The washed granules, with or without sizing, as the case may be, are then dryed by heating to remove substantially all of the moisture, preferably to less than about 1 percent moisture by weight. The drying temperature should be less than about 70° C. to avoid adverse effects of heat on the stability of the granules. If desired, the granules may be admixed with graphite, tumbled, and heated to yield a glazed surface on the granules.

The sensitivity of the novel granules prepared in accordance with the technique of the instant invention compares favorably with the sensitivity of conventional smokeless powders used in the preparation of small arms ammunition. The novel granules of this invention resist uncontrolled explosion due to impact or electrostatic discharge, and thus can be stored, processed, and/or otherwise handled with comparative safety. In addition, the granules are substantially free of dust and thus do not create a health problem for personnel handling them. The novel granules contain between about 50 and about 90 percent by weight of the sensitive solid; the remainder being comprised of the nitrocellulose matrix or nitrocellulose-nitroglycerin matrix, as the case may be. The specific gravity of the novel granules is generally greater than about 1.60 and may be as high as 1.75 or greater.

The novel spherical granules of the instant invention recovered in the second size fraction are particularly suitable for use in preparing castable rocket propellants. A typical castable rocket propellant formulation utilizing the novel granules is prepared as follows: About 20 parts of powdered aluminum, about 30 parts of triethyleneglycol dinitrate (TEGDN), about 6 parts of nitrocellulose powder, and about 44 parts by weight of the novel granules (containing about 80 percent of sensitive solid and about 20 percent by weight of nitrocellulose) are admixed until substantially homogeneous to yield a fluid curable slurry. The slurry is then poured into a cylindrical mold or mold of other desired grain configuration and cured to effect solidification. The triethyleneglycol dinitrate and nitrocelluolse powder act as a thermosetting binder. Curing of the slurry in the mold can be effected by heating to an elevated temperature, for example, up to about 70° C. for several days. The solidified grain, after removal from the mold is suitable for use as a propellant grain in rocket motors. It will be recognized by those skilled in the art that the above mentioned proportions and the components of the rocket propellant formulation can be varied to yield propellants of the desired characteristics.

The novel granules of the instant invention markedly increase the fluidity of castable rocket propellant formulations containing them because of their spherical shape. When irregular shaped or cylindrical shaped sensitive solids, either coated or uncoated, as in the prior art, are used in the preparation of the propellants, the fluidity of the propellant mixture is substantially reduced. In addition, when the novel granules of this invention are employed, a higher concentration of sensitive solid can be incorporated in the propellant formulation and easily mixed to obtain a substantially uniform dispersion throughout the formulation, as compared to forms of sensitive solids available heretofore. The novel granules of the instant invention also increase the pot life of the propellant during mixing over similar compositions in which the sensitive solid is added separately as a finely divided powder directly to the other components of the propellant mix.

The following examples are presented to further illustrate the invention without any intention of being limited thereby. All parts and percentages are by weight unless otherwise specified.

EXAMPLE I

Water (538 pounds) was placed in a 100 gallon capacity vessel equipped with a motor driven agitator. Dry powdered HMX (28.8 pounds) was then added to the water, with the agitator operating, to disperse the powder in the water. Powdered nitrocelluose (12.6 percent N) (9.6 pounds) and 2-nitrodiphenyl amine (0.14 pound) were admixed with the powder slurry. Ethyl acetate (71.4 pounds) was added to the slurry in the vessel and agitation was continued while maintaining the temperature of the mixture in the vessel at about 68° C. Agitation was continued for about 1 hour to dissolve the powdered nitrocellulose in the ethyl acetate to form a lacquer, or organic phase, which became dispersed in the water or aqueous phase. During this time the powdered HMX particles transferred from the aqueous phase to the organic phase or lacquer.

At the end of this 1 hour period a solution of animal bone glue (3 pounds) dissolved in water (30 pounds) was admixed with the aqueous and organic phases, and agitation was continued for an additional period of about 1 hour. During this time, spherical globlules were formed of lacquer having HMX particles dispersed therein. At the end of this latter period air was introduced into the vessel containing the aqueous dispersion of globules at the rate of about 3 cubic feet per minute for a period of about 20 minutes to remove a portion of the ethyl acetate from the globules. About 30 pounds of ethyl acetate was removed with the air during the 20 minute period. Removal of a portion of the ethyl acetate caused partial solidification of the globules, which inhibited coalescence of the globules and assisted in maintaining the spherical shape of the globules in subsequent processing.

An aqueous solution of 20 pounds of sodium sulfate dissolved in 60 pounds of water was added slowly during a ½ hour period to the aqueous dispersion of globules, with agitation. The sodium sulfate served as a dewatering agent which increased the specific gravity of the granules ultimately produced. After the addition of tthe sodium sulfate solution, agitation was continued for about 3 hours, while the ingredients in the vessel were gradually heated to raise the temperature from about 68° C. to about 99° C. During this period substantially all of the ethyl acetate was removed by distillation from the globules, and solid, substantially spherical granules were formed in the aqueous phase. The aqueous phase was decanted and the granules were washed several times with fresh water to remove sodium sulfate and other water soluble substances adhering to the surfaces of the granules. The granules were then screened on a screen having openings of about 0.025 inch to separate granules having a diameter of greater than about 0.025 inch from those having a diameter of about 0.025 inch or less. The granules retained on the screen were stored for use in adding to the lacquer make-up step during the preparation of another batch of granules.

The granules having a diameter of about 0.025 inch or less were heated to dryness at a temperature of about 65° C. for about 10 hours. The granules, after drying, had a moisture content of less than about 1 percent and an HMX content of about 72 percent, the remainder being nitrocellulose (about 26.5 percent) and 2-nitrodiphenylamine (about 0.5 percent).

EXAMPLE II

A sigma-blade type mixer equipped with a jacket for circulating cooling water was used in the preparation of a fluid rocket propellant composition. Liquid triethylene glycol dinitrate (300 parts) was admixed with powdered aluminum (200 parts) in the mixer until the powder was dispersed in the liquid. HMX-containing granules (440 parts) produced in Example I having a diameter of less than 0.025 inch were added to the slurry in the mixer and agitated for about 2 minutes. Nitrocellulose powder (60 parts) was then added to the mixer and agitated for about 30 minutes to obtain a substantially homogeneous slurry. During this latter mixing period a vacuum of about 28″ Hg was applied to the mixer to remove entrapped air from the slurry. The resulting fluid mixture was poured into a cylindrical mold and cured in an oven at a temperature of about 55° C. for about 3 days. The resulting solid propellant grain had good elastic and tensile strength properties.

EXAMPLE III

The same equipment used in Example II was used to prepare the following castable rocket propellants. Liquid casting solvent (298 parts nitroglycerine and 75 parts di-n-propyl adipate) was admixed with powdered aluminum (150 parts) by a procedure similar to Example II. HMX-containing granules (417 parts) produced in Example I were added to the slurry and agitated for about 2 minutes. Nitrocellulose powder (50 parts) was then added to the mixer and agitated for about 30 minutes to obtain a substantially homogeneous slurry with the vacuum application, molding, and curing as in Example II. For purposes of comparison, the same chemical composition propellant was prepared using instead, finely powdered HMX to replace the HMX-containing granules. The same quantities of powdered aluminum and nitroglycerine, di-n-propyl adipate casting solvent were admixed as before and to the mixture was added dry HMX crystals (300 parts). After agitating for about 2 minutes, nitrocellulose powder (167 parts) was added and the final mixing, molding and curing operations were carried out in the exact manner used for the propellant mixture containing the HMX powder granules.

Measurements were made of the viscosity of these two mixes just prior to molding and also of the physical properties of the cured propellant. The use of the HMX-containing granules resulted in marked advantages by a factor of at least about three in both of these important factors as shown in the table below:

Type mixture	Mix viscosity (centipoise at 75° F.)	Physical properties at 75° F.	
		Tensile strength (lbs./in.^{2})	Elongation (percent)
HMX-containing granules	18,400	87	45
Loose, crystalline HMX	54,800	23	12

EXAMPLE IV

Water (400 parts) was placed in a vessel provided with a motor-driven agitator and 33.3 parts of HMX (cyclotetramethylenetetranitroamine) were added with agitation, followed by the addition of powdered nitrocellulose

(6 parts of 12.6 percent by weight N), 0.09 part of 2-nitrodiphenylamine, and 72 parts of ethyl acetate. Agitation was continued until the powdered nitrocellulose dissolved in the ethyl acetate to yield a lacquer or organic phase.

At the end of this period 3 parts of animal colloid were admixed with the aqueous and organic phases and agitation was continued, while heating the vessel contents at a temperature of 68° C., until the lacquer formed spherical globules having HMX particles dispersed therein. Air was then bubbled through the aqueous dispersion of globules until about 18 parts of ethyl acetate were vaporized and removed with the air.

An aqueous solution of sodium sulfate (20 parts) was added slowly to the aqueous dispersion of globules with agitation to serve as a dewatering agent, which increased the specific gravity of the granules ultimately produced. After addition of the sodium sulfate the temperature of the ingredients in the vessel was increased with agitation to about 99° C. During this period the remainder of the ethyl acetate was evaporated and the globules solidified in a substantially spherical form. The aqueous phase was decanted, the solid spherical granules were washed several times with water and screened to remove particles having a diameter above about 0.025 inch. The spherical granules comprised of HMX particles embedded in a matrix of nitrocellulose having a diameter of less than about 0.025 inch were found to have a specific gravity of 1.74.

For purposes of comparison, the above described ingredients were admixed in the following proportions:

Ingredients:	Parts
HMX	4
Nitrocellulose	1
2-nitrodiphenylamine	0.015
Water	40
Ethyl acetate	10
Animal colloid	0.34
Sodium sulfate	1.2

The above described two-step evaporation procedure was employed but was modified by adding the sodium sulfate dewatering agent prior to any evaporation of ethyl acetate, and then evaporating all of the ethyl acetate in one step in accordance with the procedure set forth in various conventiontl prior art patents. The resulting granules containing particles of HMX embedded in a matrix of nitrocellulose, after screening to remove +0.025 inch diameter particles had a specific gravity of 1.58. The resulting granules were less desirable for use as a component of solid rocket propellant since the lower specific gravity of the material prepared by the one-step evaporation technique limits the weight of granules that can be loaded in a given size propellant grain and thus results in poor rocket performance.

EXAMPLE V

The two-step evaporation procedure set forth in Example IV above was repeated employing the following ingredients in the following proportions:

Ingredients:	Parts
RDX	28.8
Nitrocellulose	11.2
2-nitrodiphenylamine	0.16
Water	400
Ethyl acetate	101
Animal colloid	3
Sodium sulfate	20

The sodium sulfate was added after the first evaporation step during which time 60 parts of ethyl acetate had been removed by evaporation. The resulting spherical granules containing RDX had a specific gravity of 1.63.

The one-step evaporation procedure of Example IV above was repeated employing the following ingredients in the following proportions:

Ingredients:	Parts
RDX	144
Nitrocellulose	56
2-nitrodiphenylamine	0.8
Water	3000
Ethyl acetate	494
Animal colloid	3
Sodium sulfate	150

The specific gravity of the resulting spherical granules was 1.36, thus yielding a composition that was less desirable for use as a component of solid rocket propellants.

EXAMPLE VI

To a vessel equipped with an agitator was added 22,700 parts of water, 438 parts of nitrocellulose of 12.6 percent nitrogen content, and 2,197 parts of pure zirconium metal dust. This mixture was then stirred and the temperature raised to 68° C. Then added was 5,260 parts of a solvent for the nitrocellulose (ethyl acetate) and a lacquer of nitrocellulose-solvent formed having the zirconium entrapped in it. This lacquer suspension was then formed into lacquer droplets suspended in water by the addition of 170 parts of an animal derived colloid dissolved in 900 parts of water. At this point 1,310 parts of the solvent were removed as the first step of a two-step distillation technique. Nine hundred eight parts of sodium sulfate dissolved in 2,724 parts of water was next added to the still in order to obtain high density grains. Finally the remainder of the solvent was removed by slowly raising the temperature to 100° C. The resulting solid particles were separated from the aqueous phase and dried. The product consisted of essentially all spherical particles of about 0.020″ average grain diameter. The grains were measured to have a density of 94.3 percent of theoretical and analyzed at 78.5 percent zirconium content.

In electrostatic tests comparing the pure zirconium dust with the zirconium filled propellant casting powder, the latter had distinctly lower sensitivity. Lower sensitivity means an appreciable safety advantage when using these materials to formulate solid propellants. For instance, an 80 percent zirconium filled powder or a 50 percent zirconium filled powder would not fire in the test at an energy level as high as 12.5 joules, while the zirconium dust gave fires at the very low energy level of 0.00125 joule, which is at least a 10,000 fold difference.

EXAMPLE VII

The same type equipment and procedure was used as described above in Example VI. To 500 parts of water was added 12 parts of nitrocellulose and 28 parts of fine size aluminum dust which had been surface treated with potassium dichromate so that it would not react with water. Then 84 parts of ethyl acetate solvent was added and a lacquer suspension in water formed at 68° C. This lacquer was then made into a droplet form by adding 3 parts animal glue dissolved in 30 parts of water. A first step distillation removed 22 parts of solvent. Then 20 parts of sodium sulfate dissolved in 60 parts of water was added and the lacquer globules were dewatered. Finally the remainder of the solvent was removed. After drying, the product was found to be essentially all spherical particles between approximately 0.005″ and 0.0035″ in diameter. A specific gravity 94.8 percent of theoretical was measured.

The use of the aluminum filled powder thus prepared in solid propellant formulation was found to result in reduced propellant mix viscosity over the same formulation in which aluminum dust was added directly to the propellant mix. In the case of the propellant mix using the filled aluminum powder, the mix viscosity was measured as 30 poise while for the case in which the aluminum was added directly to the propellant mix, the viscosity was measured as 490 poise. The lower viscosity is advantageous in processing since the mix is initially more fluid and easier to handle while casting into rocket motors. Also the inherent lower viscosity makes it possible to formulate propellants having a higher proportion of metal fuel and oxidizer at a given viscosity level, with resultant increase in propellant and rocket motor performance due to the higher energy which is ordinarily obtained when this is done.

EXAMPLE VIII

A procedure similar to Example I was employed with the exception that both HMX and powdered aluminum (which had been first washed with an aqueous potassium dichromate solution followed by a water wash) were admixed with a suspension of ethyl acetate lacquer of nitrocellulose and nitroglycerin.

The resulting granules had the following composition:

Ingredients:	Percent
HMX	43.7
Aluminum	27.0
Nitrocellulose	22.5
Nitroglycerin	5.8
2-nitrodiphenylamine	1.0

The resulting granules had a gravimetric density of 1.074 and a specific gravity of 1.895, which was equivalent to 97 percent of the theoretical proportion.

The resulting casting granules containing both HMX and aluminum were used to prepare solid propellants by two different techniques. In the first technique, a slurry of the casting granules in a liquid casting solvent comprised of a mixture of nitroglycerin and triacetin was poured into a mold and cured to form a solid rocket propellant. The slurry had very satisfactory mix viscosity and the resulting solid rocket propellant had a tensile strength of 136 p.s.i. and elongation of 60.5 percent at 75° F.

In the second technique, the solid granules were first placed in the mold and the liquid casting solvent was poured into the mold and the resulting mixture was then cured to form a solid rocket propellant. The solid propellant had properties corresponding to those obtained by the first technique.

It will be recognized by those skilled in the art that various modifications of the invention, some of which have been referred to above, are possible without departing from the spirit of the invention.

Having thus described the invention, what is claimed and desired to be secured by Letters Patent is:

1. A process for preparing spherical rocket propellant casting granules which comprises admixing a lacquer of nitrocellulose in a volatile solvent therefor with an aqueous slurry of finely divided particles of a sensitive solid which is substantially insoluble in said volatile solvent, said sensitive solid being selected from the group consisting of a crystalline high explosive composition, a metal fuel for solid propellants, and mixtures thereof, agitating the resulting mixture to yield an aqueous suspension of spherical globules of the lacquer having said particles dispersed therein, evaporating a sufficient proportion of said volatile solvent to effect partial solidification of said globules, admixing a dewatering agent with the resulting aqueous suspension of partially solidified globules, evaporating the remainder of the solvent from the globules, whereby solid spherical granules of said particles firmly embedded in a matrix of nitrocellulose are formed from said partially solidified globules, washing said granules with water, and drying said granules.

2. The process of claim **1** wherein a protective colloid is added to said mixture prior to formation of said spherical globules.

3. The process of claim **1** wherein said granules, after washing and prior to drying, are separated into a first size fraction predominating in granules having a minimum

diameter of between about 0.025 and about 0.045 inch, and a second size fraction predominating in granules having a maximum diameter between about 0.020 and about 0.025 inch, admixing said first size fraction with a volatile solvent therefor, and drying said second size fraction.

4. The process of claim **1** wherein nitroglycerin is added to said lacquer in a proportion equivalent to between about 1 and about 50 percent by weight of said nitrocellulose.

5. A process for preparing spherical rocket propellant casting granules which comprises admixing a lacquer of nitrocellulose in a volatile solvent therefore with an aqueous slurry of finely-divided particles of a crystalline high explosive composition, said crystalline high explosive composition being substantially insoluble in said volatile solvent, agitating the resulting mixture to yield an aqueous suspension of spherical globules of the lacquer having said particles dispersed therein, evaporating a sufficient proportion of said volatile solvent to effect partial solidification of said globules, admixing a dewatering agent with the resulting aqueous suspension of partially solidified globules, evaporating the remainder of the solvent from the globules, whereby solid spherical granules of said particles firmly embedded in a matrix of nitrocellulose are formed from said partially solidified globules, washing said granules with water, and drying said granules.

6. The process of claim **5** wherein a protective colloid is added to said mixture prior to formation of said spherical globules.

7. The process of claim **5** wherein said granules, after washing and prior to drying, are separated into a first size fraction predominating in granules having a minimum diameter of between about 0.025 and about 0.045 inch, and a second size fraction predominating in granules having a maximum diameter between about 0.020 and about 0.025 inch, admixing said first size fraction with a volatile solvent therefor, and drying said second size fraction.

8. The process of claim **5** wherein nitroglycerin is added to said lacquer in a proportion equivalent to between about 1 and about 50 percent by weight of said nitrocellulose.

9. The process of claim **5** wherein said explosive composition is cyclotrimethylenetrinitramine.

10. The process of claim **5** wherein said explosive composition is cyclotrimethylenetrinitramine.

11. A process for preparing spherical rocket propellant casting granules which comprises admixing a lacquer of nitro-cellulose in a volatile solvent therefor with an aqueous slurry of finely-divided particles of a metal fuel which is substantially insoluble in said volatile solvent, agitating the resulting mixture to yield an aqueous suspension of spherical globules of the lacquer having said particles dispersed therein, evaporating a sufficient proportion of said volatile solvent to effect partial solidification of said globules, admixing a dewatering agent with the resulting aqueous suspension of partially solidified globules, evaporating the remainder of the solvent from the globules, whereby solid spherical granules of said particles firmly embedded in a matrix of nitrocellulose are formed from said partially solidified globules, washing said granules with water, and drying said granules.

12. The process of claim **11** wherein a protective colloid is added to said mixture prior to formation of said spherical globules.

13. The process of claim **11** wherein said granules, after washing and prior to drying, are separated into a first size fraction predominating in granules having a minimum diameter of between about 0.025 and about 0.045 inch, and a second size fraction predominating in granules having a maximum diameter between about 0.020 and about 0.025 inch, admixing said first size fraction with a volatile solvent therefor, and drying said second size fraction.

14. The process of claim **11** wherein nitroglycerin is added to said lacquer in a proportion equivalent to between about 1 and about 50 percent by weight of said nitrocellulose.

15. The process of claim **11** wherein said metal fuel is zirconium.

16. The process of claim **11** wherein said metal fuel is aluminum which has been washed with an aqueous solution of potassium dichromate.

17. A solid rocket propellant grain comprised of spherical propellant casting granules embedded in a cured thermosetting binder, said spherical propellant casting granules being comprised of finely divided particles of a sensitive solid selected from the group consisting of a crystalline high explosive composition, a metal fuel for solid propellants, and mixtures thereof, firmly embedded in a matrix of nitrocellulose, said sensitive solid being substantially insoluble in a water immiscible solvent for nitrocellulose.

18. A solid rocket propellant grain comprised of spherical propellant casting granules embedded in a cured thermosetting binder, said spherical propellant casting granules being comprised of finely divided particles of a crystalline high explosive compound firmly embedded in a matrix of nitrocellulose, said crystalline high explosive compound being substantially insoluble in a water immiscible solvent for nitrocellulose.

19. The grain of claim **18** wherein said granules have a maximum diameter of between about 0.020 and about 0.025 inch.

20. The grain of claim **18** wherein said explosive compound is cyclotetramethylenetetranitramine.

21. The grain of claim **18** wherein said explosive compound is cyclotrimethylenetrinitramine.

22. A solid rocket propellant grain comprised of spherical propellant casting granules embedded in a cured thermosetting binder, said spherical propellant casting granules being comprised of finely divided particles of a metal fuel for solid propellants firmly embedded in a matrix of nitrocellulose, said metal fuel for solid propellants being substantially insoluble in a water immiscible sovent for nitrocellulose.

23. The grain of claim **22** wherein said granules have a maximum diameter of between about 0.020 and about 0.025 inch.

24. The grain of claim **22** wherein said metal fuel is zirconium.

25. The grain of claim **22** wherein said metal fuel is aluminum which has been washed with an aqueous solution of potassium dichromate.

26. The process for preparing a rocket propellant grain which comprises admixing spherical propellant casting granules with a curable thermosetting binder, said granules being comprised of finely divided particles of a sensitive solid which is substantially insoluble in a water immiscible solvent for nitrocellulose, said sensitive solid being selected from the group consisting of a crystalline high explosive composition, a metal fuel for solid propellants, and mixtures thereof, said sensitive solid being firmly embedded in a matrix of nitrocellulose, molding the resulting mixture into the desired grain shape, and curing the binder to yield a solid rocket propellant grain.

27. The process for preparing a rocket propellant grain which comprises admixing spherical propellant casting granules with a curable thermosetting binder, said granules being comprised of finely divided particles of a crystalline high explosive composition firmly embedded in a matrix of nitrocellulose, said crystalline high explosive composition being substantially insoluble in a water immiscible solvent for nitrocellulose, molding the resulting mixture into the desired grain shape, and curing the binder to yield a solid rocket propellant grain.

28. The process of claim **27** wherein said granules have a maximum diameter of between about 0.020 and about 0.025 inch.

29. The process of claim **27** wherein said explosive composition is cyclotetramethylenetetranitramine.

30. The process of claim **27** wherein said explosive composition is cyclotrimethylenetrinitramine.

31. The process for preparing a rocket propellant grain which comprises admixing spherical propellant casting granules with a curable thermosetting binder, said granules being comprised of finely divided particles of a metal fuel for solid propellants which is substantially insoluble in a water immiscible solvent for nitrocellulose, said metal fuel being firmly embedded in a matrix of nitrocellulose, molding the resulting mixture into the desired grain shape, and curing the binder to yield a solid rocket propellant grain.

32. The process of claim **31** wherein said granules have a maximum diameter of between about 0.020 and about 0.025 inch.

33. The process of claim **31** wherein said metal fuel is zirconium.

34. The process of claim **31** wherein said metal fuel is aluminum which has been washed with an aqueous solution of potassium dichromate.

35. Spherical granule rocket propellant casting composition comprising between about 50 and about 90 percent by weight of finely divided particles of cyclotetramethylenetetranitramine embedded in a matrix of nitrocellulose, said spherical composition having a maximum diameter of between about 0.020 and about 0.025 inch.

36. The composition of claim **35** wherein said matrix is a mixture of nitrocellulose and nitroglycerin.

References Cited

UNITED STATES PATENTS

2,967,098	1/1961	Weil	149—19
2,970,898	2/1961	Fox	149—19 X
3,325,420	6/1966	Murphy	149—2

BENJAMIN R. PADGETT, Primary Examiner

U.S. Cl. X.R.

149—2, 18, 20, 21, 92, 99, 111, 114; 264—3

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,702,272 Dated November 7, 1972

Inventor(s) Thomas F. McDonnell and Ralph E. Coffee

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 57, "near and at the" should read as --completely coat- --

Signed and sealed this 1st day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,702,272 Dated November 7, 1972

Inventor(s) Thomas F. McDonnell and Ralph E. Coffee

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 57, "near and at the" should read as --complete coat- --

Signed and sealed this 1st day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR
Attesting Officer

ROBERT GOTTSCHAL
Commissioner of Paten