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**NITROCELLULOSE PRODUCT AND METHOD OF
MANUFACTURE OF PROPELLANT GRAINS EM-
PLOYING SAME****Robert M. Brooks, Milltown, and William H. Gardner,**
Dover, N.J., assignors to Hercules Incorporated, a cor-
poration of Delaware

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This invention relates to propellant grains, particularly double-base propellant grains, to the manufacture thereof by an improved slurry casting method and to a novel nitrocellulose product employed therein.

Heretofore large grains of double-base solid propellant suitable for propelling military rockets and missiles, or for actuating sizable jet devices have been manufactured by various "in-situ" casting techniques. The distinguishing characteristic of all such in-situ casting methods is that the casting powder, consisting of precolloided, solid particles or granules of nitrocellulose composition, is first loaded dry into a suitable casting mold and then a predetermined quantity of casting liquid comprising nitroglycerin and suitable desensitizing plasticizers, with or without stabilizers and/or other adjuvants included to control or regulate burning rate of the resulting propellant grain when fired, is then introduced into the mold to completely fill all voids between the dry casting powder granules and to just cover the casting powder granules. The mixture of precolloided nitrocellulose particles and casting liquid is then cured in the mold, usually at a suitable elevated temperature until the particles of nitrocellulose casting powder absorb all of the casting liquid and the whole mass in the mold consolidates and welds together into a solid, unitary, colloided structure conforming to the shape of the mold.

Thus, to anyone skilled in the art of manufacturing propellant grains it is apparent that in-situ casting of propellant grains is subject to certain restrictions and limitations. For example, in-situ casting methods have required a relatively large inventory of casting powder formulations. Moreover, in-situ casting requires relatively long curing times. Furthermore, known methods for preparing casting powder formulations are tedious and expensive, since these methods involve all of the steps necessary in the manufacture of smokeless powder granules, since in reality casting powder granules heretofore have been smokeless powder granules.

In attempts to overcome the limitations and disadvantages of in-situ casting as set forth above, it has been proposed to prepare propellant grains by "slurry casting," employing very small particles of fully colloided nitrocellulose. For example, one proposed slurry casting method, a typical plastisol application, involves the preparation and use of fully colloided spheroidal nitrocellulose particles on the order of 5-10 microns in size. Another proposed slurry casting method involves the use of fully colloided spheroidal nitrocellulose particles of about 100 microns in size. In these prior proposed slurry casting processes, the very finely divided casting powder particles and casting liquid are mixed together to form a pourable slurry which is then poured into the mold, and the mixture is then cured in the usual way in the mold to form the propellant grain.

Although the above previously proposed slurry casting methods have some advantages over in-situ casting methods in simplicity of casting technique involved, they are still subject to undesirable limitations and disadvantages which are inherent in the use of the very small particles of fully colloided nitrocellulose. This is because the very small particle sizes specified are difficult and expensive to

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prepare, and also involve much rework of material to obtain the particle sizes specified. In all of these systems, the small particle nitrocellulose is prepared by totally dissolving the nitrocellulose in suitable volatile solvent to form a solution, forming an emulsion or suspension of the resulting nitrocellulose solution in water, and then precipitating the nitrocellulose in fine particle size from the emulsified solution or suspension by removing substantially all solvent by some suitable means such as emulsion boil-off, steam stripping, spray drying, elution, etc. Thus, large amounts of solvent must be employed to prepare the nitrocellulose solutions, on the order of 2.5 to 20 or more parts by weight for each part of nitrocellulose processed, and this necessitates facilities for handling and recovery of large volumes of solvent. Moreover, it is apparent that these systems involve several tedious and uneconomical process steps.

Now, surprisingly, it has been discovered that large propellant grains can be manufactured without the necessity of the tedious and expensive prior preparation of smokeless powder granules, or of fully colloided tiny spheroidal particles of nitrocellulose composition.

It is an object of this invention, therefore, to provide an improved slurry casting method for manufacture of propellant grains, which has economical and procedural advantages over prior art casting methods, and which substantially overcomes the limitations and deficiencies of prior art casting methods.

Another object of the invention is to provide an improved slurry casting method for manufacture of propellant grains having a much shorter cure time than prior art methods provide.

It is a further object of the invention to provide an improved slurry casting method for manufacture of propellant grains involving employment of a novel densified nitrocellulose product which is relatively inexpensive and readily available.

A still further object of the invention is to provide a relatively inexpensive and readily available novel densified nitrocellulose product having greater utility in slurry casting of propellant grains than prior nitrocellulose products employed in manufacture of propellant grains.

These objects and others are accomplished in accordance with the present invention which, generally described, comprises agitating fibrous nitrocellulose in a heated aqueous bath containing organic liquid solvent which has active solvent power for said nitrocellulose and which forms a minimum boiling azeotropic mixture with water, said solvent being present in an amount to soften and destroy the fibrous structure of the nitrocellulose without dissolution thereof, said bath being heated to at least the boiling point of the water-solvent azeotrope, thereafter removing substantially all of the solvent by distillation while continuing agitation to form smooth, hardened, densified and irregular particles of nitrocellulose having a bulk density of at least about 40 pounds per cubic foot (dry basis), comminuting the resulting densified nitrocellulose particles by wet grinding without substantial reduction of bulk density to pass through a U.S. Standard Sieve No. 20 and substantially through a U.S. Standard Sieve No. 40, removing substantially all water from the resulting comminuted nitrocellulose particles, mixing the resulting dry comminuted nitrocellulose particles and casting liquid to form a pourable slurry of said nitrocellulose particles in said casting liquid, pouring the resulting slurry into a mold, and curing the mixture of nitrocellulose and casting liquid in the mold to form a solid, consolidated propellant grain.

More specifically, in a preferred embodiment for practicing this invention, fibrous nitrocellulose is mixed and agitated with water to produce an aqueous slurry of nitro-

cellulose. Nitrocellulose solvent is then added with agitation to the aqueous nitrocellulose slurry heated to at least the boiling point of the water-solvent azeotrope in an amount sufficient to destroy the fibrous structure of the nitrocellulose without dissolution thereof, and then removing substantially all of the solvent by distillation while continuing agitation to form smooth, hardened, densified and irregular particles of nitrocellulose. In this process the organic solvent is partitioned to the nitrocellulose which is softened and the fibrous structure thereof is destroyed. However, the nitrocellulose is not dissolved, and the particles thus modified are hardened by boiling off substantially all of the solvent. Agitation is maintained until hardening is complete in order to control agglomeration during hardening. At this point the nitrocellulose has been converted from its original fibrous form into smooth, hardened, densified and irregular particles of nitrocellulose, roughly $\frac{1}{16}$ inch to $\frac{1}{4}$ inch or more in their greatest dimension and very nonuniform in particle size, which are mixed with water.

This relatively coarse, granular nitrocellulose produced by solvent densification, as set forth above, is presently considered to be too coarse grained for slurry casting due to inability of the casting liquid to penetrate the entire granule thus leaving solvent lean areas, and also due to rapid settling of the largest particles of densified nitrocellulose. Also, when other solids are incorporated in the propellant composition, nonuniform distribution can result. Thus, all of the above factors can lead to nonuniformity in the finished grain. Accordingly, therefore, this relatively coarse, granular nitrocellulose is then comminuted by passing the mixture of solvent-densified nitrocellulose particles and water in the form of a slurry through a suitable wet mill such as a Jordan beater, a Brown mill or equivalent wet grinding equipment capable of wet-grinding the densified nitrocellulose to pass through a U.S. Standard Sieve No. 20, and substantially through a U.S. Standard Sieve No. 40 without substantial reduction of bulk density. It is presently believed that this wet-grinding step is significantly important in imparting proper sizing to the solvent densified nitrocellulose while retaining the desirable and necessary high bulk density derived from solvent densification.

After wet-grinding the solvent densified nitrocellulose to pass through a U.S. Standard Sieve No. 20, and substantially through a U.S. Standard Sieve No. 40, the resulting comminuted particles are dried to remove substantially all water from the comminuted material. At this stage the resulting dry comminuted nitrocellulose consists of smooth, hardened, densified, irregular shaped particles having a wide diversity of particle sizes less than 20 mesh per inch in size and having a bulk density of at least about 40 pounds per cubic foot.

Calculated amounts of the resulting dry comminuted nitrocellulose particles and of casting liquid comprising nitroglycerin or other explosive plasticizers desensitized with a non-explosive plasticizer are then mixed together in a suitable mixing vessel to form a free-flowing pourable slurry of the nitrocellulose particles in the casting liquid. Other propellant ingredients may be added if desired, and stirring is continued until complete mixing is obtained, usually within 5-10 minutes. The hard, horny nature of the nitrocellulose particles prevents rapid gelation of the nitrocellulose by the casting liquid, so that the slurries can be maintained in a fluid, pourable state for as much as 45 minutes or more, depending on the temperature and the composition. The mixture is preferably stirred under vacuum to remove entrained air, and after blending is complete, the slurry is poured into containers such as cellulose acetate beakers or rocket motor chambers. The propellant mixture is then cured, preferably at a suitable elevated temperature to obtain solid, well-consolidated propellant grains. During the curing operation the particles of nitrocellulose absorb all of the casting liquid and, due to the solvent action of the casting liquid on the nitro-

cellulose, the nitrocellulose particles become swollen and fully colloidized, and the whole mass in the mold consolidates and welds together into a solid, unitary, colloidized structure conforming to the shape of the mold.

The general nature of the invention having been set forth, the following examples are presented as specific illustrations thereof. It will be understood, however, that the invention is not limited to the examples but is susceptible to different modified embodiments which come within the scope of the claims.

EXAMPLE 1

Five thousand grams (5,000), dry basis of water-wet fibrous nitrocellulose of 12.6% by weight nitrogen content meeting U.S. specification JAN-N-244 was slurried with 42,815 grams of water in a 20-gallon jacketed vessel fitted with a reflux condenser and a 12-inch diameter turbine agitator driven at 200 r.p.m. The mixture was agitated, and heated to 91° C. by employing steam in the jacket of the vessel. One hundred grams (100) of 2-nitrodiphenylamine dissolved in 2,225 grams of methyl isobutyl ketone was then rapidly added to the heated agitated nitrocellulose slurry, and an additional 6,675 grams of methyl isobutyl ketone, making a total of 8,900 grams of methyl isobutyl ketone, was added, requiring about 7 minutes for the total methyl isobutyl ketone addition. The addition of methyl isobutyl ketone to the aqueous nitrocellulose slurry lowered the temperature of the mixture to the boiling point of the water-methyl isobutyl ketone azeotrope. Distillation was then carried on with continued agitation for 90 minutes, during which time the distillation temperature gradually increased to the boiling point of water. Substantially all of the solvent was removed by distillation, and the nitrocellulose was transformed, without being dissolved, from its initial fibrous state into smooth, hardened, densified, irregular particles about $\frac{1}{16}$ to about $\frac{1}{4}$ inch in their greatest dimension and having a bulk density (dry basis) of 42.9 pounds per cubic foot. Rapid, turbulent agitation was maintained throughout the above-described densification procedure.

The resulting densified particles of nitrocellulose suspended in water to form a slurry therewith were then passed in the aqueous slurry through a Brown mill to comminute the particles by wet grinding to pass substantially through a U.S. Standard Sieve No. 40. The resulting wet-ground nitrocellulose product had a bulk density (dry basis) of approximately 40 pounds per cubic foot, and a typical particle size distribution as follows:

	Percent by weight (dry basis)
Through No. 20 U.S. Standard Sieve on No. 40	
U. S. Standard Sieve -----	12
Through No. 40 U.S. Standard Sieve on No. 60	
U.S. Standard Sieve -----	43
Through No. 60 U.S. Standard Sieve on No. 80	
U.S. Standard Sieve -----	24
Through No. 80 U.S. Standard Sieve on No. 100	
U.S. Standard Sieve -----	8.5
Through No. 100 U.S. Standard Sieve on No. 200	
U.S. Standard Sieve -----	9.5
Through No. 200 U.S. Standard Sieve -----	3
Total -----	100.0

and consisted of smooth, hardened, densified, irregular particles.

The resulting densified, wet-ground nitrocellulose particles were then air dried in thin layers on trays in an air oven heated at about 55° C. until substantially all water was removed, after which the dried nitrocellulose particles were glazed with graphite.

To 20 grams of casting liquid containing

14.4 grams nitroglycerin
5.4 grams triacetin
0.2 gram 2-nitrodiphenylamine

there was added with stirring 20 grams of the above dry, comminuted, densified nitrocellulose particles (19.6 grams nitrocellulose and 0.4 gram 2-nitrodiphenylamine) to form a slurry of the nitrocellulose particles in casting liquid. To this slurry was added 15 grams of powdered aluminum (Alcoa 123, Aluminum Co. of America), and the mixture was thoroughly blended by mixing. The resulting slurry mixture was readily stirrable and pourable after 30 minutes at room temperature. The slurry was then cast by pouring into a cellulose acetate cylindrical container 8 inches high having $\frac{1}{8}$ -inch thick walls and an outside diameter of $1\frac{1}{8}$ inches, and the cast slurry mixture was then cured in the container at 55° C. for one day to form a single-end burning, tough, hard, well consolidated propellant grain.

EXAMPLE 2

Water-wet fibrous nitrocellulose of 12.6% by weight nitrogen content meeting U.S. Specification JAN-N-244 was solvent densified, wet-ground and dried substantially as set forth in Example 1. The bulk density of the densified nitrocellulose before wet grinding was 42.9 pounds per cubic foot (dry basis). After comminuting by wet grinding to pass substantially through a U.S. Standard Sieve No. 40, and drying, the comminuted material was further classified by sieving, and the material passing through a U.S. Standard Sieve No. 40 and retained on a U.S. Standard Sieve No. 60 was segregated for further processing as set forth below. This No. 40-No. 60 U.S. Standard Sieve fraction had a bulk density (dry basis) of 40.5 pounds per cubic foot.

To 120 grams of casting liquid containing

86.4 grams nitroglycerin
32.4 grams triacetin
1.2 grams 2-nitrodiphenylamine

there was added with stirring 80 grams of the above-described No. 40-No. 60 U. S. Standard Sieve fraction of densified nitrocellulose particles (78.4 grams nitrocellulose and 1.6 grams 2-nitrodiphenylamine) to form a slurry of the nitrocellulose particles in casting liquid. This slurry was stirred for 10 minutes and was then poured into a cellulose acetate container having an outside diameter of $1\frac{1}{8}$ inches. Vacuum was applied to the container to remove entrapped air, and the cast slurry mixture was cured at 55° C. for one day to form a single-end burning, well consolidated propellant grain substantially free of voids.

The cured propellant grain was fired successfully in a conventional vented vessel (rocket motor), pertinent data with respect to the firing test being as follows:

Temperature of firing, ° F. -----	70
Pressure, lbs. per sq. in.: -----	712
P ₁ * -----	712
P ₂ † -----	692
P ₃ ‡ -----	692
P average -----	699
Burning time, seconds -----	19.4
Burning rate, inches per second -----	0.177
Nozzle diameter ----- inches -----	0.0765
Grain diameter ----- do -----	$1\frac{1}{8}$
Grain length ----- do -----	$3\frac{3}{16}$
Inside chamber diameter ----- do -----	2.0
Chamber length ----- do -----	5.0

* P₁ designates pressure taken one second after ignition.

† P₂ designates pressure at midpoint of burning.

‡ P₃ designates pressure taken one second before end of burning.

Thus, the ballistic during firing of the single-end burning grain is seen from the above data to have a smooth

pressure-time relationship, indicating satisfactory homogeneity in the grain, and also indicating good consolidation.

The vented vessel employed in this example and in the other examples set forth herein was a conventional stationary rocket motor equipped with automatic devices for making a continuous record in the form of a graph of pressures developed during burning as a function of time. Such vented vessels are standard equipment in all ballistic laboratories engaged in evaluation of rocket, missile or gas generator solid propellant grains.

The residue of the comminuted wet ground and dried nitrocellulose particles remaining, after segregation and removal of the fraction passing through a U.S. Standard Sieve No. 40 and retained on a U.S. Standard Sieve No. 60, and which passed through a U.S. Standard Sieve No. 60 was then further classified into a fraction passing through a U.S. Standard Sieve No. 60 and retained on a U.S. Standard Sieve No. 80, and a fraction passing through a U.S. Standard Sieve No. 80. Each of these two latter fractions was then processed into finished propellant grains substantially exactly as set forth above for the fraction passing through a U.S. Standard Sieve No. 40 and retained on a U.S. Standard Sieve No. 60. The resulting propellant grains were well consolidated and substantially free of voids.

EXAMPLE 3

Water-set fibrous nitrocellulose of 12.6% by weight nitrogen content meeting U.S. Specification JAN-N-244 was solvent densified, wet ground and dried substantially as set forth in Example 1. The bulk density of the densified nitrocellulose before wet grinding was approximately 42.9 pounds per cubic foot. After comminuting by wet grinding to pass substantially through a U.S. Standard Sieve No. 40 and drying, the comminuted nitrocellulose material had a bulk density of approximately 40 pounds per cubic foot and a particle size distribution substantially as set forth in Example 1.

To 140 grams of casting liquid containing

100.8 grams nitroglycerin
37.8 grams triacetin
1.4 grams 2-nitrodiphenylamine

there was added with stirring 60 grams of the above dry, comminuted densified nitrocellulose particles (58.8 grams nitrocellulose and 1.2 grams 2-nitrodiphenylamine) to form a slurry of the nitrocellulose particles in casting liquid. This slurry was stirred for about 10 minutes and was then poured into a cellulose acetate container having an outside diameter of $1\frac{1}{8}$ inches. Vacuum was applied to the container to remove entrapped air, and the cast slurry mixture was cured at 55° C. for one day to form a single-end burning, well consolidated propellant grain substantially free of voids, and less rigid than the propellant grains prepared in Example 2.

The cured propellant grain was fired successfully in a conventional vented vessel, pertinent data with respect to the firing test being as follows:

Temperature of firing ----- ° F-----	70
Pressure, lbs. per sq. in.: -----	
P ₁ -----	808
P ₂ -----	1154
P ₃ -----	1346
P average -----	1103
Burning time ----- seconds -----	9.69
Burning rate ----- inches per second -----	0.254
Nozzle diameter ----- inches -----	0.765
Grain diameter ----- do -----	$1\frac{1}{8}$
Grain length ----- do -----	$2\frac{3}{8}$
Inside chamber diameter ----- do -----	2.0
Chamber length ----- do -----	5.0

EXAMPLE 4

Water-wet fibrous nitrocellulose of 12.6% by weight nitrogen content meeting U.S. Specification JAN-N-244 was solvent densified, wet ground and dried substantially as set forth in Example 1. The bulk density of the densified nitrocellulose before wet grinding was approximately 42.2 pounds per cubic foot. After comminuting by wet grinding to pass substantially through a U.S. Standard Sieve No. 40, and drying, the comminuted nitrocellulose material had a bulk density of approximately 40 pounds per cubic foot and a particle size distribution substantially as set forth in Example 1. All particles coarser than 40 mesh per inch were screened out.

To 1,025 grams of casting liquid containing

848 grams nitroglycerin
162 grams triacetin
15 grams 2-nitrodiphenylamine

there was added in a mechanical mixer 505 grams of the above dry comminuted densified nitrocellulose particles which passed through a U.S. Standard Sieve No. 40 (495 grams nitrocellulose and 10 grams 2-nitrodiphenylamine). The mixture was stirred until the nitrocellulose particles were completely wet. Then 493 grams of aluminum powder (Alcoa 123) was added and stirred until the aluminum powder was wetted and dispersed through the slurry. Finally 452 grams of ammonium perchlorate having an average particle size of 25 microns and 25 grams of CP grade magnesium oxide were added to the slurry. Vacuum was then applied to the mixer and mixing was continued at a pressure of 10 mm. of mercury for 14 minutes to thoroughly blend all ingredients. Total elapsed mixing time was 20 minutes. The slurry flowed well and was poured into a cellulose acetate cylindrical container having an outside diameter of 5.5 inches. The cast slurry mixture was cured at 55° C. for 3 days to form a single-end burning, well consolidated propellant grain substantially completely free of voids.

The cured propellant grain was fired successfully in a conventional vented vessel, pertinent data with respect to the firing test being as follows:

	Grain No. 1
Temperature of firing ----- ° F--	65
Pressure, lbs. per sq. in.:	
P ₁ -----	349
P ₂ -----	386
P ₃ -----	393
P average -----	376
Burning time ----- seconds--	3.58
Burning rate ----- inches per second--	0.472
Nozzle diameter ----- inches--	0.500
Grain diameter ----- do--	5.5
Grain length ----- do--	1.75
Inside chamber diameter ----- do--	5 $\frac{1}{16}$
Chamber length ----- do--	4.25

EXAMPLE 5

One hundred five parts by weight (dry basis) of fibrous water-wet nitrocellulose, 12% nitrogen, ½-second viscosity (ASTM Specification D-1343-56), was slurried with 945 parts of water. The slurry was heated and

agitated in a vapor-tight vessel fitted with a reflux condenser. When the temperature reached 82° C., 133 parts of methyl ethyl ketone was added under reflux conditions in three minutes. A condenser was then added for solvent removal. The agitator peripheral speed was maintained at 1,000 feet per minute as the solvent and water were distilled from the mixture until the temperature reached 100° C. Thirty minutes were required to complete the distillation. The water-wet product consisted of smooth, hard, dense irregular particles roughly ⅛ inch to ¼ inch in their greatest dimension. Bulk density was 44.1 pounds of nitrocellulose (dry basis) per cubic foot.

The resulting densified particles of nitrocellulose suspended in water to form a slurry therewith, when passed in the aqueous slurry through a Brown mill to comminute the particles by wet grinding to pass substantially through a U.S. Standard Sieve No. 40, produces a product consisting of smooth, hard dense irregular particles of nitrocellulose having a bulk density of at least about 40 pounds per cubic foot (dry basis), and having a diversity of particle sizes. This wet-ground product, upon drying to remove water, was suitable for use in manufacture of propellant grains by the slurry casting technique substantially as set forth in Examples 1 to 4.

EXAMPLE 6

One hundred five parts by weight (dry basis) of unjordaned, fibrous water-wet nitrocellulose, 12.6% nitrogen, 22 seconds viscosity (U.S. Specification JAN-N-244), was slurried with 595 parts of water. The slurry was heated and agitated in a vapor-tight vessel fitted with a reflux condenser. When the temperature reached 100° C., 144 parts of n-butyl acetate was added cooling the mixture to the boiling point of the azeotrope, 90.2° C. A condenser was then added for solvent removal. Agitation was continued as the solvent and water were distilled from the mixture until the temperature reached 100° C. Seventy minutes were required to complete the distillation. The water-wet product consisted of smooth, hard, dense, irregular particles of nitrocellulose having a bulk density of 42 pounds (dry basis) per cubic foot.

The resulting densified particles of nitrocellulose suspended in water to form a slurry therewith, when passed in the aqueous slurry through a Brown mill to comminute the particles by wet grinding to pass substantially through a U.S. Standard Sieve No. 40, produces a product consisting of smooth, hard, dense irregular particles of nitrocellulose having a bulk density of 40 pounds per cubic foot (dry basis), and having a diversity of particle sizes substantially similar to the range and proportion of sizes set forth in Example 1. This wet-ground product, upon drying to remove water, was suitable for use in manufacture of propellant grains by the slurry casting technique substantially as set forth in Examples 1 to 4.

EXAMPLE 7

The following compositions were processed into satisfactory, well-consolidated propellant grains by the slurry technique of this invention employing the comminuted, solvent densified nitrocellulose of this invention by following substantially the same procedures set for in Examples 1 to 4.

Formula number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Nitrocellulose (12.6% N.)	19.8	19.8	19.8	19.8	19.8	19.8	37.9	19.8	19.8	19.8	19.8	19.8	19.8	19.8
Nitroglycerine	33.9	33.9	33.9	33.9	33.9	33.9	50.8	33.9	33.9	33.9	33.9	33.9	33.9	33.9
Ammonium Perchlorate (average particle size of 25 microns)	9.1	13.6	4.5	18.1	18.1			9.1	4.5	13.6		23.1	18.1	11.1
RDX (Cyclotrimethylene Trinitramine)	9.0	4.5	13.6					9.0	13.6	4.5	18.1		9.8	21.8
HMX (Tetramethylene tetranitramine)								19.7	19.7	19.7	19.7	14.7	9.9	5.0
Aluminum Powder (Alcoa 123)	19.7	19.7	19.7	19.7	19.7			6.5	6.5	6.5	6.5	6.5	6.5	6.5
Triacetin (Glycerol Triacetate)	6.5	6.5	6.5	6.5	6.5	7.2		1.0	1.0	1.0	1.0	1.0	1.0	1.0
Magnesium Oxide (CP Grade)	1.0	1.0	1.0	1.0	1.0			1.0	1.0	1.0	1.0	1.0	1.0	1.0
2-nitrodiphenylamine	1.0	1.0	1.0	1.0	1.0	0.3		1.0	1.0	1.0	1.0	1.0	1.0	1.0

NOTE.—All values in above table are given as percent by weight.

Pertinent ballistic data for propellant grains of Formulas 7, 8, 12 and 13 in the above table follow:

Formula Number	7	8	12	13
Temperature of Firing, ° F	70	70	70	70
Average Pressure, lbs. per sq. in.	198	305	223	802
Burning Time, seconds	19.51	4.85	3.42	1.75
Burning Rate, inches per second	0.199	0.28	0.396	0.774
Nozzle Diameter, inches	0.210	0.332	1.38	1.07
Grain Diameter, inches	3.0	4.5	4.5	4.5
Grain Length, inches	3.87	9.0	9.0	9.0
Center Perforation, inches	None	1.8	1.8	1.8
Inside Chamber Diameter, inches	3.2	4.91	4.91	4.91
Chamber Length, inches	4.5	10.0	10.0	10.0

While 12.6% nitrogen nitrocellulose is customarily employed in the manufacture of cast double-base propellant grains, the present invention is by no means limited thereto, since all commercial types of nitrocellulose without limitation can be employed as set forth herein for the purposes of this invention. It is known, of course, that commercial grades of nitrocelluloses range in nitrogen content from about 10.7% nitrogen to about 13.6% nitrogen by weight and in viscosity from about 10 centipoises to about 377,000 centipoises or higher as measured on a solution containing 12.2% by weight concentration of nitrocellulose in a solvent composed of 90% acetone and 10% denatured ethyl alcohol (2B formula) by weight at 25° C. It is understood, of course, that both burning rate and temperature of burning are correlatable with the nitrogen content of the nitrocellulose (other factors remaining constant), with both burning rate and burning temperature increasing with increase of nitrogen content in the nitrocellulose. Thus, choice of nitrocellulose with respect to nitrogen content is one means for regulating and controlling the burning characteristics of slurry cast propellant grains.

From an economic viewpoint it is desirable to practice the invention with aqueous slurries containing as much fibrous nitrocellulose as practicable, and the upper practical limit of nitrocellulose in the slurry is governed by the ability to agitate the slurry effectively. Generally, nitrocellulose-water slurries containing from about 3% to about 15% by weight of fibrous nitrocellulose have been employed, and preferably from about 7% to about 12% by weight of nitrocellulose. Although slurry consistencies of less than 3% by weight of nitrocellulose can be employed, it is obviously less economical to do so. Furthermore, the invention is not limited to a maximum of 15% by weight of nitrocellulose in the slurry, since the upper practical limit is governed by the ability to agitate the slurry effectively. The fibrous nitrocellulose to be densified may be jordaned, or otherwise comminuted, if desired, and such comminution generally makes it possible to increase the quantity of fibrous nitrocellulose which can be effectively agitated in the slurry. Generally, somewhat smaller densified particles are produced when jordaned nitrocellulose is employed. It will be understood, however, that jordaning, or equivalent comminution of the fibrous nitrocellulose, is not necessary for the practice of this invention.

Solvent granulation and densification of nitrocellulose in accordance with this invention depends upon the action of an active solvent upon fibrous nitrocellulose suspended in water. The desired action is a softening of the nitrocellulose fibers by the solvent to eliminate the fibrous character thereof, without actually dissolving any measurable amount of the nitrocellulose. Organic liquid solvents suitable for use in practicing this invention are those having an active solvent power for nitrocellulose, and preferably having an appreciable vapor pressure at or below the boiling point of water. The most useful solvents are those which have limited solubility in water and which can be steam distilled from the slurry. Preferably, such solvents should form a minimum boiling azeotropic mixture with water. Suitable solvents include, by way of example but not in limitation of the invention, various ketones such as methyl ethyl ketone, methyl propyl ketone, methyl isobutyl

ketone, and the like, and various esters such as ethyl acetate, propyl acetate, butyl acetate, ethyl butyrate, isopropyl butyrate, ethyl propionate, β -ethoxyethyl acetate, and the like. Buyl acetate and methyl isobutyl ketone are presently preferred for densifying nitrocellulose for the purposes of this invention. The solvent treatment for densifying nitrocellulose can be accomplished by addition of the solvent to an agitated slurry of nitrocellulose in water, by addition of nitrocellulose to an agitated mixture of water and solvent, or by simultaneous addition of all ingredients, with agitation, as in a continuous process.

In the solvent granulation and densification of nitrocellulose in accordance with this invention, the ratio of active organic liquid nitrocellulose solvent to water is controlled in a range where enough solvent is partitioned to the nitrocellulose to soften and gel the nitrocellulose fibers without actually dissolving any measureable portion of the nitrocellulose. Too little solvent leaves the physical form of the nitrocellulose unaltered or not sufficiently altered, thus resulting in a product having low bulk density which tends to cause formation of soft, porous propellant grains. Too much solvent causes the product to agglomerate into large hard lumps which interfere with comminution by wet grinding. Still more solvent, of course, causes undesirable dissolving of the nitrocellulose which interferes with recovery of the nitrocellulose in proper physical form for the purpose of this invention. The desired degree of alteration of the physical structure of the nitrocellulose is to obtain a product which, after solvent removal, consists of smooth, hardened, densified, irregular shaped particles having a bulk density of at least about 40 pounds per cubic foot.

It will be apparent that solvent requirement to obtain this objective will vary somewhat with slurry consistency, initial physical form of the nitrocellulose, temperature, degree of agitation, and solvent chosen for densification purposes. In general, however, it has been found that suitable products for the purposes of this invention are obtained by using between about 15% and about 22% of either butyl acetate or methyl isobutyl ketone, based on combined weight of solvent and water in the aqueous slurry, and preferably between about 16% and 20% by weight. The minimum suitable quantity of methyl ethyl ketone is on the order of approximately one part by weight of methyl ethyl ketone for each 7.2 parts of water in the aqueous nitrocellulose slurry. Similarly, the minimum suitable quantity of ethyl acetate is on the order of approximately one part by weight of ethyl acetate for each 9.5 parts of water in the aqueous nitrocellulose slurry. However, regardless of the solvent employed for densification purposes, it is a simple expedient to carry out a preliminary densification trial, using the hereinabove quantities as a guide, and determine the degree of densification obtained, based on bulk density requirements. It will be apparent, of course, that densification as measured by increased bulk density of the densified product will improve with increasing quantity of active nitrocellulose solvent employed, until that point is reached where the softened particles tend to agglomerate into large lumps. Thus, this invention provides a basis for density control in the products produced. The phenomenon of agglomeration of the softened particles into large lumps governs the upper useful limit of active solvent which can be employed to alter the physical structure of the nitrocellulose in accordance with this invention.

In practicing this invention, it has been found that softening of the nitrocellulose fibers by the active nitrocellulose solvent occurs very rapidly upon bringing the nitrocellulose and solvent into contact with each other in the heated aqueous slurry. Accordingly, it is important to maintain vigorous agitation in the aqueous slurry from the moment that the nitrocellulose is contacted by the active solvent in the aqueous slurry until the softened nitrocellulose particles have been hardened and densified

by removal of substantially all of the solvent. Agitation prevents substantial agglomeration of the softened nitrocellulose particles into lumps.

Any desired additives, such as nitrocellulose stabilizers, plasticizers, or other desirable additives, which are soluble or dispersible in the solvent used for densification and which are insoluble in water can be introduced with the solvent and become very uniformly distributed into the nitrocellulose product during the solvent densification. Additives such as lead salts and carbon black which are not solvent soluble may be added by slurring them in finely divided form with the nitrocellulose before adding the solvent. Water-soluble additives can be introduced by first suitably saturating the water with the additive.

In the preferred practice of this invention, the solvent is added to the aqueous nitrocellulose slurry which is heated at least to the boiling point of the water solvent azeotrope, preferably under reflux conditions, since the partition of solvent to the nitrocellulose is thus aided by reduced solubility of the solvent in water. Moreover, under these conditions there is no tendency for the softened particles of nitrocellulose to puff up or "popcorn" during subsequent solvent removal, thus aiding materially in attaining a high bulk density in the densified nitrocellulose product.

Hardening of the softened nitrocellulose is carried out by boiling off the solvent from the agitated slurry until substantially all solvent is removed from the nitrocellulose slurry. This may require from about 20 minutes to about 4 hours, depending upon equipment used and the solvent which has been employed. It will be remembered, of course, that the preferred nitrocellulose solvents form a minimum boiling azeotropic mixture with water. Hence, as the solvent is removed by distillation, the boiling point of the mixture rises until it finally reaches the boiling point of water when substantially all solvent has been removed from the slurry. Observation of the boiling point during removal of solvent by distillation is, therefore, a simple method for determining when substantially all solvent has been removed from the nitrocellulose slurry. The solvent thus removed is readily recovered by conventional methods for reuse in the process.

The resulting nitrocellulose material, after solvent removal, consists of smooth, hardened, densified and irregular particles of nitrocellulose, roughly $\frac{1}{16}$ inch to $\frac{1}{4}$ inch or more in their greatest dimension, which are mixed with water, and must be further reduced in size for use in the slurry casting process for manufacturing propellant grains, since material on the order of $\frac{1}{16}$ inch or larger in size leads to nonuniformity in propellant grains prepared by slurry casting technique. Size reduction or comminution is accomplished by a wet-grinding procedure in which a slurry of the relatively coarse, densified nitrocellulose particles suspended in water is passed through a suitable wet mill such as a Jordan mill, a Brown mill, or equivalent wet-grinding equipment capable of wet-grinding the densified nitrocellulose to pass substantially through a U.S. Standard Sieve No. 40 without substantial reduction of bulk reduction of bulk density. Thus, the nitrocellulose material after the wet-grinding step consists of smooth, hardened, densified and irregular particles of nitrocellulose having a relatively wide diversity of particle sizes, as determined by screen analysis, and a bulk density of at least about 40 pounds per cubic foot. It has been found, as shown by the examples, that substantially the entire nitrocellulose product from the wet-grinding step which passes through a U.S. Standard Sieve No. 20 and substantially through a U.S. Standard Sieve No. 40, and with its relatively wide diversity of particle sizes can be employed without classification into a narrower particle size range. This discovery is indeed surprising, and is distinctly advantageous from an economic point of view, since it eliminates the necessity for reworking the nitrocellulose material. Moreover, the smaller particles help to fill in

the spaces between larger particles, thus leading to a product of higher bulk density. It is also believed that the finer particles are advantageous during the curing of the propellant grain, since these finer particles, due to their relatively greater surface to volume relationship, are more rapidly gelled by the casting liquid, thus causing an initial partial thickening of the entire mass, which thickening action restrains any marked tendency for settling of the larger particles during the curing process, thus contributing to homogeneity in the structure of the final grain. If desired, of course, the densified nitrocellulose particles produced by this invention can be classified by screening into relatively narrow fractions with respect to particle size, and the examples show that such classified fractions can be individually employed in slurry casting of propellant grains having satisfactory ballistic characteristics. However, such classification is seen to be unnecessary for the purposes of this invention. It is advisable, however, to screen out any particles retained on a U.S. Standard Sieve No. 20, since such particles usually lead to nonuniformity in slurry cast propellant grains.

Thus, the densified nitrocellulose product suitable for the purposes of this invention consists of particles having a wide diversity of particle sizes all of which pass through a U.S. Standard Sieve No. 20 and which pass substantially through a U.S. Standard Sieve No. 40. While Example 1 illustrates a typical distribution of particle sizes, the invention is by no means limited to any particular particle size distribution. In general, however, not more than about 15% of the total weight of the material should be coarser than a U.S. Standard Sieve No. 40, and preferably all of the material should pass through a U.S. Standard Sieve No. 40. Preferably not more than about 25% of the total weight of the material should pass through a U.S. Standard Sieve No. 100. It is believed that the abovedescribed physical characteristics of the wet-ground, densified nitrocellulose are directly responsible for the many advantages of this material over prior nitrocellulose products in the slurry casting of propellant grains.

Following the wet-grinding step, the bulk of the water is removed from the nitrocellulose particles by simple draining, centrifuging, or similar equivalent means, and the resulting moist particles of nitrocellulose are then dried by conventional means well known in the art to remove the remainder of the water and produce a dry product having substantially less than 1% total volatile material by weight. A convenient method for accomplishing this is to air-dry the particles in a current of warm air at a temperature of about 50–55° C. preferably with the particles spread in thin layers on a foraminous screen or belt. Those skilled in the art understand, of course, that nitrocellulose should be dried at temperatures substantially below the temperatures at which nitrocellulose begins to decompose, and will appreciate that the above suggested temperature range for drying is well below the decomposition temperature of nitrocellulose. It should be noted also that 2-nitrodiphenylamine is a well known nitrocellulose stabilizer which preferably may be added in the densification process, as illustrated in the examples, for the purpose of enhancing the stability of the nitrocellulose during subsequent drying, storage, etc. Other well-known nitrocellulose stabilizers such as diphenylamine, diethyl diphenyl urea, and others can be used for the same purpose. The dry nitrocellulose particles may then be glazed with graphite in conformance with conventional smokeless powder art, but such glazing, while desirable, is not essential in practicing this invention.

Weighed quantities of the resulting dry, comminuted, densified nitrocellulose particles and of casting liquid are then mixed together in a suitable vessel or container to form a free-flowing, pourable slurry. The usual practice in accordance with this invention is to add to the mixing vessel the calculated amount of casting liquid. Next, the calculated amount of dry, densified nitrocellulose par-

ticles is then added with stirring to form the free-flowing slurry. Then other propellant ingredients, if desired, are added to the casting liquid-nitrocellulose slurry and stirring is continued until homogeneous mixing of all the ingredients is complete. This is usually within 5 to 10 minutes. However, the slurries can be maintained in a fluid, pourable state up to 45 minutes or longer, depending on the temperature and composition of the mixture. Ordinarily, preparation of the casting slurries is carried out at room temperature, since the solvent action of even very active solvent casting liquids on the hard, horny nitrocellulose particles is sufficiently slow at room temperatures to provide an adequate period of time for mixing and pouring the slurries into molds. However, if desired, the casting slurries may be prepared by mixing the ingredients at temperatures either above or below room temperature. Temperatures below room temperature retard the solvent action of the casting liquid on the nitrocellulose particles and thereby lengthen the period during which the slurry can be stirred and poured into molds. Temperatures above room temperature, on the other hand, have the opposite effect of accelerating the solvent action of the casting liquid on the nitrocellulose particles and thereby reduce the period during which the slurry can be stirred and poured into molds. Higher temperatures also accelerate initial gelation of the cast propellant mixture, which may be desirable for certain rocket or missile applications. The slurry mixture is preferably stirred under vacuum to facilitate removal of entrained air. After mixing is complete, the slurry is poured into mold containers such as cellulose acetate beakers or rocket motor chambers, and is then cured in the container or chamber to form a uniform, well-consolidated propellant grain.

The composition of the casting slurry can be varied widely, depending upon the properties desired in the finished propellant grain. The nitrocellulose content may range from as little as 5% or less to as much as 60% or more by weight of the casting slurry. Usually, however, the proportion of nitrocellulose in the slurry will range from about 20% to about 50% by weight. It will be understood that the strength and firmness of the propellant grain increases with increase in the viscosity characteristic of the nitrocellulose and the quantity of nitrocellulose employed, and this relationship is most readily recognized in mixtures which contain lower proportions of nitrocellulose, as for example from about 5% to about 15% by weight of nitrocellulose; propellant grains made with higher viscosity types of nitrocellulose will be harder and firmer than propellant grains made with lower viscosity types of nitrocellulose.

Casting liquids in accordance with this invention are plasticizers for nitrocellulose which gel the nitrocellulose by virtue of their solvent or swelling action on the nitrocellulose. Usually the casting liquids employed are mixtures of nitroglycerin, or other liquid explosive plasticizer such as glycol nitrates, pentaerythritol trinitrate, or other polyol nitrates and a desensitizing non-explosive plasticizer such as triacetin, with or without stabilizing substances such as 2-nitrodiphenylamine. However, casting liquids in accordance with this invention may be varied in composition from all explosive plasticizer such as nitroglycerin through various mixtures of explosive and non-explosive plasticizer without restriction to all non-explosive plasticizer. Typical non-explosive desensitizing plasticizers for nitrocellulose include by way of example, but not in limitation of the invention, such compounds as triacetin (glyceryl triacetate), tripropionin (glyceryl tripropionate), dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dioctyl phthalate, methyl phthalyl ethyl glycolate, and dibutyl sebacate. Those skilled in the art will readily call to mind many other well-known nitrocellulose plasticizers equally suitable for the purposes of this invention.

In addition to nitrocellulose and casting liquid, various other substances in varying amounts can be incorporated

as desired into the casting slurries of this invention for the purpose of modifying the burning characteristics of the finished propellant grain, such as for example, aluminum powder, ammonium perchlorate, lead salts, ammonium nitrate and many other inorganic salts, carbon black, beryllium, boron, various metal hydrides, pentaerythritol tetrinitrate, cyclotrimethylene trinitramine (RDX), tetramethylene tetranitramine (HMX), and the like. Thus, it will be apparent that the properties and burning characteristics of propellant grains according to this invention can be varied over an extremely wide range by selection of nitrocellulose of different viscosity and nitrogen content, by selection of casting liquid of almost limitless variation as to composition, and selection of other propellant grain adjuvants, as necessary or desired.

The slurry of nitrocellulose particles in casting liquid, with or without additional added substances, after pouring into the mold is then cured in the mold to cause the fluid slurry to set up or gel and consolidate and weld together into a solid mass conforming to the shape of the mold. During the curing of the propellant grain, the casting liquid is all absorbed by the nitrocellulose granules, and the casting liquid swells and colloids the granules of nitrocellulose into a solid consolidated mass. Curing is usually carried out at any conveniently elevated temperature which is safely below the temperature at which any of the components in the propellant grain composition would begin to decompose. Curing temperatures on the order of about 40° C. to about 60° C. are usually employed, since at these temperatures the solvent and swelling action of the casting liquid on the nitrocellulose granules is more rapid than at lower temperatures, and curing times are, therefore, shorter. Curing can be satisfactorily carried out, however, at ordinary room temperatures, but such curing usually involves a somewhat longer curing time. Curing times will vary, of course, depending upon the composition of the slurry and the temperature of curing. Curing times of as little as 12 hours or even less are possible. Usual curing times are from about 1 to 2 days. However, under certain circumstances some compositions may require as much as 3 or 4 days to complete the curing. Durometer hardness measurements on the propellant grain during curing is a convenient simple method for determining when curing is substantially complete. Durometer hardness measurements will increase as curing proceeds and will reach a relatively constant level when curing is substantially complete. After curing, the propellant grain is ready for use in the rocket motor for which it is designed.

The advantages of this invention over prior art practices and proposals in manufacture of propellant grains are numerous. With respect to the currently standard double-base in-situ casting practices involving use of pre-manufactured granules of smokeless powder, the present invention effectively eliminates the necessity for maintaining inventories of base grain now needed in in-situ double-base casting. By the present invention any propellant can be made with the novel nitrocellulose product herein disclosed simply by mixing together the necessary ingredients to form a stirrable, pourable slurry which is then cast by pouring the slurry into the mold. Curing time, according to the present invention, is shorter than in current in-situ casting; this means a greater throughput of propellant in the curing bays per unit of time. The cost of preparing propellant by the present invention is much less than with current in-situ practices, since many tedious and expensive steps have been eliminated in preparation of the casting powder employed. The casting procedure, in accordance with the present invention, is much simplified over in-situ double-base casting, since one pouring of the propellant slurry mix suffices for casting. In current in-situ casting, base grain must first be loaded into the mold, then casting liquid is introduced into the mold as an additional step. Moreover, very sensitive materials such as many of the rocket fuels now being proposed may be incorporated

into propellant matrices by the present invention, which is not possible by current in-situ casting. The present invention is readily adaptable to both continuous processing and to remote control operation with attendant benefits of greater uniformity of product, especially with very large size propellant grains, and safety for operating personnel. Moreover, cellulose acetate restrictions can be prepared with the end inhibitor already in place by the present invention. Upon casting and curing, the propellant composition bonds with the end restriction, thus eliminating the need for adding the end restriction after the grain is cured, as in current in-situ casting. A still further advantage is that the densified nitrocellulose particles of the present invention are shipped and stored wet with water, and the particles are dried just prior to use. Cheaper freight rates and safer transportation and storage over present casting powder are thus made possible by the present invention.

The present invention also has important advantages over previously proposed slurry casting procedures employing very tiny nitrocellulose particles having rather critical particle size restrictions. The method of preparing the nitrocellulose particles of the present invention is much simpler and cheaper and far more practical than the prior processes for preparing the very tiny nitrocellulose particles required by the prior processes, since the present invention avoids the tedious and expensive solution-emulsion-precipitation route of the prior processes. Moreover, the present invention employs the entire nitrocellulose product passing through a U.S. Standard Sieve No. 20 whereas much of the nitrocellulose processed by the prior processes fails to meet critical particle size requirements and must be reworked.

A further important advantage of the present invention is that nitrocellulose of any viscosity can be used, including very high viscosity types. This can be very important in improving physical properties of propellants having low nitrocellulose content. On the other hand, very high viscosity types of nitrocellulose cannot be satisfactorily processed by the total solution-emulsion-precipitation route of prior proposed processes. Thus, it is apparent that the present invention accomplishes all of the objects of the invention and provides the art with a novel nitrocellulose product and a slurry casting method of manufacturing propellant grains employing the novel product which are both practical and economical.

U.S. application Ser. No. 774,075, filed November 17, 1958, now Patent No. 2,948,601, by Vernon R. Grassie, discloses and claims a method for the densification of nitrocellulose by using solvent to change the physical form of conventional nitrocellulose from fibrous to granular, and recognizes that the densified product so produced when comminuted by wet grinding is useful in slurry casting techniques. Application Serial No. 774,075 does not, however, deal with or disclose the present invention.

What we claim and desire to protect by Letters Patent is:

1. Smooth, hardened, densified and irregular nitrocellulose granules having a diversity of particle sizes all of which pass through a U.S. Standard Sieve No. 20, not more than about 15% by weight of which are coarser than a U.S. Standard Sieve No. 40, and not more than about 25% by weight of which pass through a U.S. Standard Sieve No. 100, and having a bulk density of at least about 40 pounds per cubic foot, dry basis, said granules having been prepared by contacting a slurry of fibrous nitrocellulose with agitation in a heated aqueous bath with an organic liquid solvent which has active solvent power for said nitrocellulose and which forms a minimum boiling azeotropic mixture with water, said solvent being present in an amount to soften and destroy the fibrous struc-

ture of the nitrocellulose without dissolution thereof, said bath being heated to at least the boiling point of the water-solvent azeotrope during the entire period of contact between said nitrocellulose and said solvent, thereafter removing substantially all of the solvent by distillation while continuing agitation to form smooth, hardened, densified and relatively coarse irregular particles of nitrocellulose having a bulk density of at least about 40 pounds per cubic foot, dry basis, and comminuting the resulting densified and relatively coarse irregular particles of nitrocellulose without substantial reduction of bulk density by wet grinding to produce densified comminuted irregular nitrocellulose particles having the aforesaid particle size distribution, said densified comminuted irregular nitrocellulose particles being adapted for producing pourable casting slurries employed for manufacture of cast propellant grains by the slurry casting process.

2. The process of preparing nitrocellulose granules especially suitable for preparing pourable casting slurries employed for manufacture of cast propellant grains by the slurry casting process which comprises in combination: contacting a slurry of fibrous nitrocellulose with agitation in a heated aqueous bath with an organic liquid solvent which has active solvent power for said nitrocellulose and which forms a minimum boiling azeotropic mixture with water, said solvent being present in an amount to soften and destroy the fibrous structure of the nitrocellulose without dissolution thereof, said bath being heated to at least the boiling point of the water-solvent azeotrope during the entire period of contact between said nitrocellulose and said solvent, thereafter removing substantially all of the solvent by distillation while continuing agitation to form smooth, hardened, densified and relatively coarse irregular particles of nitrocellulose having a bulk density of at least about 40 pounds per cubic foot, dry basis, and comminuting the resulting densified and relatively coarse irregular particles of nitrocellulose without substantial reduction of bulk density by wet grinding to produce densified comminuted irregular nitrocellulose particles having a wide diversity of particle sizes all of which pass through a U.S. Standard Sieve No. 20, not more than about 15% by weight of which are coarser than a U.S. Standard Sieve No. 40, and not more than about 25% by weight of which pass through a U.S. Standard Sieve No. 100.

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BENJAMIN R. PADGETT, *Primary Examiner*.

U.S. Cl. X.R.

149—2, 21, 111; 260—220, 223

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,422,169

January 14, 1969

Robert M. Brooks et al.

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 34, "casing" should read -- casting --. Col 3, line 57, "non-explsovie" should read -- non-explosive --. Column 4, line 2, "whoe" should read -- whole --. Column 5, lin 51, "550 C." should read -- 55° C. --; line 58, cancel "712". Columns 7 and 8, in the table, first column, line 6 thereof, "HMX (Tetrametnylene tetranitramine)" should read -- HMX (Tetramethylene tetranitramine) --. Column 10, line 26, "interfe should read -- interferes --; line 27, "purpose" should read -- purposes --. Column 11, line 60, cancel "bulk reduction of".

Signed and sealed this 17th day of March 1970.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents