A process for the preparation of spherical, multiple-base propellant powder for firearms having a low permissible maximum pressure which powder has a base of nitric acid esters of cellulose includes the steps of utilizing a mixture of nitrocellulose and at least one nitrate selected from the group consisting of glycerin trinitrate and glycol dinitrate as propellant raw material; agitating said raw material and stabilizers for the material dissolved in a water-immiscible first solvent under water to effect formation of a lacquer containing said raw material and the stabilizers in the solvent within an aqueous system; segregating the thus-produced lacquer into a plurality of particles by the addition of a protective colloid and alkaline salts; allowing the lacquer particles to flow together again by subsequently changing the agitating speed of the aqueous system and thereupon adding once more protective colloid and salt and again segregating the lacquer to form spherical particles of propellant powder by adjusting the agitating speed of the aqueous system to approximately the value at which the first segregation of the lacquer has taken place; and, after the second segregating step is finished, removing more than one-half of the solvent from the aqueous system by distillation; adding burn control moderators dissolved in a second water immiscible solvent to the aqueous system; and subsequently, removing the remaining portion of water-immiscible solvents from the aqueous system. The moderators are coated on the spherical particles of the propellant powder.

20 Claims, 1 Drawing Figure
PROCESS FOR THE PREPARATION OF MULTIPLE-BASE PROPELLANT POWDER

The present invention relates to a process for the preparation of double-base granulated propellant powder which can be utilized in weapons such as firearms with a relatively low permissible maximum burning pressure.

For certain purposes of application, for example as propellant for shot cartridges, propellant powders are required which burn with a minimum pressure. The conventional propellant powders having a base of nitrocellulose and optionally glycerin nitrate and/or glycol nitrate, however, burn with too high a pressure, unless these powders are used in modified form. Therefore, several methods have been known to modify propellant powders either by the manner in which they are manufactured or by the addition of burn-control agents, so that, inter alia, the pressure during burning is reduced.

Nitrocellulose ball powder, for example, is also utilized as the starting material for the heretofore known propellant powders for shot cartridges, which is produced, in principle, as follows: Nitrocellulose is heated, together with a stabilizer (in most cases diphenylamine and lime) under water with ethyl acetate, and the mixture is agitated. A highly viscous solution of nitrocellulose in ethyl acetate is thus produced, called NC lacquer. While continuing the agitation, a protective colloid and an alkali salt (e.g. Na₂SO₄) are added, and the agitation speed is slowed down. The lacquer is thereby segregated into particles of various sizes, which assume a spherical shape and harden during the subsequent removal of the ethyl acetate by distillation. The spheres obtained after the distillation step are then screened into fractions with defined spherical diameters.

These spheres, which are also called "ball powder", are used either directly or are further processed to form double- or multiple-base powders in a coating process. If a nitrocellulose powder is desired as the starting material which has a particularly low bulk density (0.4 - 0.6 g/cm³), the NC lacquer is allowed to flow together once again before the solvent is distilled off, by varying the agitation speed; then, the protective colloid and salt are once again added, and the lacquer is again allowed to coat the spherical particles, the agitation speed being reset approximately to the value during which the first segregation took place. After the segregation step is terminated and small spheres have been formed, the solvent is distilled off, and the nitrocellulose granules are separated.

During the coating process, which often follows the formation of the granules, a nitrocellulose grain powder having a given particle size is again combined under water with ethyl acetate, wherein glycol dinitrate and/or glycerin trinitrate have been dissolved, and is maintained for several hours at the boiling point of the mixture of ethyl acetate and water. Thereafter, the ethyl acetate is removed by evaporation.

Such a soluble-base ball powder likewise is not as yet suitable for shot cartridge powder. Therefore, this powder must furthermore be provided with burn-control agents, such as phthalic acid esters or urea derivatives or dialkyl diphenylureas, which are applied to the powder in a further operating step.

A propellant powder manufactured in this way can be used as shot cartridge powder, but certain ballistic properties still cannot be attained with this powder. For this reason, such a powder is often aftertreated with camphor, or a ball powder is processed into flake powder by rolling the particles between steel rolls. The thus-produced flakes normally have a layer thickness of between 0.01 and 0.035 mm. The production of such flakes is cumbersome and difficult, since the rolls must be accurately adjusted, and the flakes often break apart easily, especially when brittle powders are being processed.

Although it is possible in this way to prepare propellant powders burning, upon an appropriate ignition, with a pressure of below 600 atmospheres, it is self-evident that the above-described manufacturing method is cumbersome, time-consuming, and connected with great solvent losses. Therefore, there has been the problem of finding a simpler manufacturing process for such propellant powders, which can also be used in firearms having a low permissible maximum pressure. This pressure is not to exceed 600 atmospheres, if possible.

A process has now been found for the production of spherical, multiple-base propellant powders, for firearms with a low permissible maximum pressure, on the basis of nitrocellulose, glycerin (glycerol) trinitrate and/or glycol dinitrate and burn-control agents, which process is characterized by using, as the crude i.e. raw, propellant material during the granule formation, nitrocellulose together with glycol dinitrate and/or glycerin trinitrate and adding, after removing more than half of the solvent by distillation, the burn moderators, in a dissolved form, preferably in the same solvent wherein the crude material was dissolved, and then completing the distillative removal of the solvent. The granule formation takes place by agitating the crude propellant composition, provided with stabilizers, while dissolved in a water-insoluble solvent, under water; segregating the thus-produced lacquer under agitation by the addition by the addition of a protective colloid and alkali and/or alkaline earth salts; allowing the lacquer to flow together again by a subsequent change in the agitation speed; and thereupon again adding protective colloid and salt and segregating the lacquer by agitation again to spherical particles by setting the agitation speed to approximately the value at which the first segregation of the lacquer took place; and removing the solvent by distillation after the segregating step has been completed.

A propellant charge powder produced according to this process has better ballistic properties as compared to a rolled propellant powder produced in several working steps, although the powder need not be rolled, and an aftertreatment with, for example, camphor is unnecessary.

It is furthermore likewise unnecessary to separate the nitrocellulose balls produced according to the present process into individual screen fractions -- as was heretofore necessary. For it was found that the ball diameter in the present case has no effect on the ballistic properties. In case of the nitrocellulose grains manufactured according to the previous processes, the ball powder had to be screened into fractions with defined diameter ranges, in order to satisfy certain ballistic properties. Only fractions within these ranges satisfied the desired requirements.

These improved properties can be seen from a comparison of a powder A prepared according to the present invention (see Example) with a commercially avail-
able powder MI produced in several working steps and rolled. The firing values for both powders were determined in a pressure-measuring pipe with the aid of a commercial shot cartridge. In this procedure, the final velocity V is measured after traversing a distance of 12.5 m, and the pressure P in the firearm is determined. The final velocity is to be maximally high, and the pressure P maximally low. The following results were obtained:

<table>
<thead>
<tr>
<th>Powder</th>
<th>Gross loading</th>
<th>V (12.5)</th>
<th>P (atmosphere)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (g)</td>
<td>(m/sec.)</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1.6</td>
<td>306</td>
<td>510</td>
</tr>
<tr>
<td>MI</td>
<td>1.9</td>
<td>310</td>
<td>490</td>
</tr>
</tbody>
</table>

This comparison demonstrates that, in spite of the reduction of the loading weight of the powder according to the invention, the powder of this invention yields the same firing values as the commercial powder which had to be used in larger quantities.

The superiority of the powder according to the present invention can clearly be seen during a test in the ballistic bomb.

**DESCRIPTION OF FIGURE**

The figure graphically illustrates the thus-obtained measuring results. On the abscissa, the proportion of combusted power mass (p/p_{end}) is plotted, and the ordinate represents the vigorousness (L) of the combustion in 100 cm² kp⁻¹ s⁻¹. The graphic representation indicates that the powder quickly develops the maximum of its efficiency during combustion, but a drop also occurs rapidly, while the powder of this invention does not have a peaked maximum, and its maximum efficiency can evolve over a longer period of time. This means that, over a longer period of time, the powder of this invention develops an almost constant gas pressure.

Suitable solvents in the manufacturing of the powder of this invention are, for the mixture of nitrocellulose with glycol dinitrate and/or glycerin trinitrate, which is called the raw material or mass hereinbelow, primarily the water-immiscible methyl-, ethyl-, or butylesters of saturated aliphatic monocarboxylic acids of 1-5 carbon atoms, preferably ethyl acetate or methyl propionate. The weight proportion of nitrocellulose in the initial mixture is from about 80 to 95%; whereas, the glycol dinitrate constitutes from 5 to 10% and glycerin trinitrate amounts to 5 to 20%; the weight ratio of glycol dinitrate to glycerin trinitrate being from 0 to 100 when both nitrates are used.

The weight ratio between solvent and raw powder material is generally between 10 : 2 and 10 : 4; a ratio of between 10 : 2.5 and 10 : 3.5 is preferably selected, so that the thus-produced lacquer forms a highly viscous solution of the raw material in the solvent.

Conventional stabilizers are added to the raw material, such as, for example, urea-derivatives, urethanes, diphenylamine or vaseline (0.5 to 2.5% by weight of the raw material) and neutralizers, e.g. lime (0.5 to 3.0% by weight of the raw material).

As the protective colloid, primarily employed are bone glue, pearl glue, or gelatin. However, it is also possible to use vegetable gum, such as gum arabic or "Schiras" gum. The amount of protective colloid added ranges between 1 and 5% by weight, preferably between 3 and 4% by weight, based on the weight of the raw material employed.

The salt is preferably added in the form of an aqueous saturated solution. Preferably, anhydrous sodium sulfate is utilized; however, the readily water-soluble sulfates, chlorides, or nitrates of other alkali or alkaline earth metals are also suitable. The amount of salt to be added considerably affects the bulk density of the thus-produced grains. When using sodium sulfate as the salt, this compound is added during the first salt addition step in an amount of 20-30% by weight and during the second salt adding step in a quantity of about 10-20% by weight, respectively based on the weight of raw material, while dissolved in water. In case other salts are used, the amounts to be added respectively must be substantially larger.

The agitation speed depends on the size and shape of the reactor vessel. The initial speed must be selected so that the raw material, dissolved in the solvent, floats on the water as a coherent lacquer. In general, decrease in volume of the reaction vessel necessitates increase of the stirring speed. The correct setting of this initial speed pertains to the state of the art and is known to any skilled person. In general, the stirring speed for preparing the lacquer amounts to between 50 and 90 revolutions per minute for reaction vessels of between 80 cm and 300 cm. of diameter and between 60 and 300 cm. of height. After the first addition of protective colloid and salt, the agitating speed is varied (i.e. decreasing by 50 to 100%) so that the lacquer segregates into small particles which, however, are allowed to coalesce again by changing the agitating speed once more (i.e. decreasing by 50 to 100%).

The first segregation of the lacquer need occur optionally only during a very short period of time, so that it is also possible to effect this process step by gradually reducing the initial agitating speed continuously. In general, the lacquer is made to flow together again by reducing the agitating speed still further past the value at which the first segregation has taken place; if desired, the agitator can also be completely deactivated.

The second segregation or flowing apart of the lacquer takes place at approximately the same agitating speed at which the first segregation was effected. As soon as the lacquer begins to separate, the agitating speed must be maintained at a constant value, so that the sphere formation can be terminated. During the sphere formation i.e. formation of the spherical particles or lacquer granules; the agitation must not be interrupted or the agitating speed must not be changed substantially—especially at the beginning of the sphere formation—since otherwise the lacquer would flow together again. The formation of the granules is terminated after about 1 to 2 hours and preferably about 1.5 hours. The finished grains are no longer altered by varying the agitating speed.

The aforementioned sphere formation process takes place at temperatures of between 50° and 90°C, but below the boiling temperature of the solvent. Preferably, the step is conducted at a temperature which is about 10°C lower than the boiling point of the solvent. The salt solution, when added, has approximately the same temperature as the solutions presented in the reactor vessel.

Subsequently to the sphere formation, the solvent is removed by distillation. After more than half of the solvent has been distilled off, the distillation is briefly interrupted, and the burn moderators are added. These are preferably dissolved in the same solvent wherein also the raw material has been dissolved. These burn moderators are added preferably at a point where about 70 - 85% of the solvent has been removed by dis-
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**tiltation.**

Suitable burn moderators are compounds which are known in the prior art for this purpose. Examples for such compounds are urea derivatives, such as, for example, diethylidiphenylurea, dimethyldiphenylurea, or urethanes, phthalic acid esters, the ester components of which alkyl groups having 2–6 carbon atoms, such as dibutyl phthalate, for example. The amount of the burn moderators to be added can be varied between 0.6 and 4% by weight, preferably between 1.0 and 2.0% by weight, based on the weight of the raw material.

After adding the burn moderators, the remainder of the solvent is distilled off — toward the end of the distillation preferably under vacuum, e.g., 50 to 100 Torr. Thereafter, the powder ball is filtered off from the water, washed repeatedly with water, screened, and dried with warm air at 60° to 85°C.

**EXAMPLE**

A reactor having a capacity of 250 liters and equipped with an agitator, a steam heating unit, and a distillation connection is charged with 12.6 kg of nitrocellulose, 2.25 kg of glycerine trinitrate, and 0.15 kg of diphenylamine. Under agitation at an agitating speed of 80 r.p.m., 48 liters of ethyl acetate is then added during the course of 5 minutes, and the temperature is brought to 68°C. After 2 hours, the agitating speed is lowered to 54 r.p.m., and 0.5 kg of pearl glue, dissolved in 10 liters of hot water (70°C), is rapidly poured into the reactor. Thereupon, a hot solution (70°C) of 3.5 kg of anhydrous sodium sulfate in 13.5 liters of water is added during the course of 5 minutes.

Following this addition of colloid and salt, the reaction mixture is stirred for another 30 minutes at the agitating speed of 54 r.p.m.; then, the agitator is shut off. The temperature is 65°C in 1 liter of mixture. During the subsequent hour, a uniform lacquer mass forms on the surface of the water.

After the end of this hour, the agitator is again set to 54 r.p.m., and 0.5 kg of pearl glue, undissolved, is added to the mixture. The pearl glue dissolves very quickly, and the lacquer begins to flow apart, i.e., segregates. After 10 minutes, a solution of 2 kg of anhydrous sodium sulfate in 9 liters of water (90°C) is added thereto, then, the agitation is continued for 3 hours at an agitating speed of 54 r.p.m.

Subsequently, the solvent is removed by distillation, the temperature being raised within one-half hour from 68°C to 78°C. After one hour, the distillation is briefly interrupted, and a solution of 0.175 kg of diethylidiphenylurea and 0.080 kg of dibutyl phthalate in 2 liters of ethyl acetate is added to the reaction mixture. After this step is finished, the temperature is brought within 90 minutes to 90°C, during which period the remainder of the ethyl acetate is distilled off. (Distillation pressure is 760 Torr.)

After cooling and repeated washing with water, the batch is discharged, screened, and dried.

While the novel principles of the invention have been described, it will be understood that various omissions, modifications, and changes in these principles may be made by one skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. A process for the preparation of spherical, multiple-base propellant powder for firearms having a low permissible maximum pressure, having a base of nitric acid esters of cellulose, which comprises utilizing a mixture of nitrocellulose and at least one nitrate selected from the group consisting of glycerin trinitrate and glycol dinitrate as propellant raw material, said mixture containing from 80 to 95 weight % nitrocellulose and from 5 to 20% of the nitrate; agitating said raw material and said stabilizer for said material dissolved in a water-immiscible first solvent under water to effect formation of a lacquer containing said raw material and said raw material and said stabilizer in said solvent within an aqueous system, the weight ratio of said mixture dissolved in said first solvent to said first solvent being from 10 : 2 to 10 : 4; segregating the thus-produced lacquer into a plurality of particles by the addition of a protective colloid and an alkaline salt; allowing the lacquer particles to flow together again by subsequently changing the agitation speed of the aqueous system and thereupon adding once more protective colloid and salt and again segregating the lacquer to form spherical particles of propellant powder by adjusting the agitating speed of the aqueous system to approximately the value at which the first segregation of the lacquer has taken place; and, after the second segregating step is finished, removing more than one-half of the solvent by distillation; adding from 0.6 to 4% by weight of burn control moderators based on the weight of said raw material dissolved in a second water-immiscible solvent to said aqueous system; and subsequently, removing the remaining portion of water-immiscible solvents from said aqueous system, said moderators being coated on said spherical particles of said propellant powder.

2. The process of claim 1, wherein from 0.5 to 2.5% by weight of said stabilizer is admixed with said raw material.

3. The process of claim 2, wherein said stabilizer is selected from the group consisting of urea derivatives, urethanes, diphenylamines and vaseline.

4. The process of claim 1, wherein in said aqueous system the amount of water employed is approximately 10 to 20 times the amount of the raw material.

5. The process of claim 1, wherein the amount of protective colloid initially added is from 1 to 5 weight % based on the weight of the raw material.

6. The process of claim 1, wherein the amount of salt initially added is from 20 to 30% by weight based on the weight of the raw material.

7. The process of claim 1, wherein the amount of salt added subsequently is from 10 to 20% by weight based on the weight of the raw material.

8. The process of claim 1, wherein segregation of said particles is conducted at temperatures from 50° to 90° which are below the boiling point of the solvents.

9. The process of claim 1, wherein distillation is effected at a temperature of from 60° to 99°C, when atmospheric pressure is applied.

10. The process of claim 1, wherein the moderators include diethylidiphenylurea, dimethyldiphenylurea, urethanes, phthalic acid esters having alkyl ester groups containing from 2 to 6 carbon atoms.

11. The process of claim 1, wherein said first solvent is a methyl, ethyl or butyl ester of saturated aliphatic monocarboxylic acid containing from 1 to 5 carbon atoms.

12. The process of claim 1, wherein said first solvent is selected from the group consisting of ethyl acetate and methylpropionate.

13. The process of claim 1, wherein the first and second solvents are the same solvent.
14. The process of claim 11, wherein the first and second solvents are the same solvent.
15. The process of claim 7, wherein the protective colloid is selected from the group consisting of bone glue, pearl white, gelatin and vegetable gum.
16. The process of claim 8, wherein said salt is selected from the group consisting of alkali metal and alkaline earth metal sulfates, chlorides and nitrates.
17. The process of claim 1, wherein said salt is added in the form of a saturated solution.

18. The process of claim 1, wherein said salt is Na₂SO₄.
19. The process of claim 1, wherein the remaining portion of the water-immiscible solvents are removed from said aqueous system by distillation under a vacuum and thereafter the resulting spherical particles are filtered off from the water, washed repeatedly with water, screened and dried with warm air at 60° to 85°C.
20. The process of claim 19, wherein the solvent is removed under a vacuum of from 50 to 100 Torr.