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MANUFACTURE OF SMOKELESS POWDERS

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This invention relates generally to the manufacture of explosives, and particularly to the manufacture of smokeless powders such as those having a nitrocellulose base.

It is among the objects of this invention to provide a process whereby deteriorated and partially unstable powder may be so treated and renovated as to render it adaptable for use in ammunition. A more specific object of the present invention is to provide a process of making smokeless powders suitable for use in small arms ammunition wherein deteriorated cannon powder having unstable regions may be employed as the raw material.

Another object is to provide a process whereby the production of grains of the desired shape and size may be controlled.

Another object is to provide a process of manufacturing smokeless powders wherein the procedure is safe and economical.

Another object is to provide a process for making smokeless powder wherein the resulting grains will be uniform as to their ignition characteristics or rate of combustion.

Other objects will become apparent to those skilled in the art when the following description of the process of this invention is read and understood. It is to be understood, however, that the embodiments hereinafter described are illustrative only of various embodiments of which this invention is susceptible. In the following description, as far as possible, an explanation will be given of what is believed to be the action taking place from a theoretical standpoint; it is to be understood, however, that in giving such explanation the theory and explanation is advanced for the purpose of facilitating an understanding from a theoretical standpoint; and it is understood that this invention is not to be limited to any advanced theory or explanation from a theoretical standpoint.

In accordance with this invention the operation may be so carried out as to produce grains which are uniform as to shape, size and ignition characteristics and the operations are susceptible of control so as to effectively vary the physical characteristics of the resultant grains within limits. Generally stated in accordance with the present invention a charge of completely gelatinized nitrocellulose in the form of fine particles, preferably fine enough to pass through a sixty-five mesh screen, may be formed into a slurry with seven or eight times its weight of water, the slurry mixed with a suitable amount of solvent for the nitrocellulose which may be substantially insoluble in water, and the whole vigorously agitated during heating to remove the solvent by evaporation.

During the removal of the solvent, such for instance as by evaporation, the tendency is for the several particles of nitrocellulose dust to coalesce or form into small clusters. The extent of this coalescence may be controlled by controlling the violence of the agitation during the removal of the solvent, and the gravimetric density of the resultant grains may be controlled by regulation of the rate of temperature increase and the period of time employed to completely remove the solvent by vaporization. Furthermore the amount of solvent employed affects not only the size, shape and surface of the resultant grains, but also the gravimetric density thereof.

The desired amount of solvent may be conviently added to the slurry of nitrocellulose dust in the form of a spray and in this manner small globules of the solvent may be readily distributed throughout the mixture. During agitation and heating the surfaces of the particles of nitrocellulose dust become softened due to the gelatinizing action of the solvent and tend to coalesce forming clusters comprising a number of dust particles. This action may be explained since it is well known that all liquid or plastic two phase systems tend to a condition of minimum surface energy which can be accomplished by coalescence. In the practice of the present invention suitable substances descriptively termed protective colloids and which may incude emulsifying and de-emulsifying agents as well as electrolytes, may, if desired, be incorporated in the mixture in order to effect modification in the granulation which will be accomplished. Among the features which contribute to the resultant physical characteristics of the resultant powder grains are the following:—Small amounts of solvent give a small rough cluster of particles as the grains while larger amounts of solvent give more spherical smoother grains. The faster and more violent the agitation, the smaller the resultant grains. While, as pointed out hereinbefore, the rate at which the temperature is raised during evaporation of the solvent affects both the granulation and density of the resultant powder. In this respect the rapidity with which certain temperatures, such for instance as the boiling point of the mixture of water and solvent, are reached has a particular effect upon the density of the powder.

After the mixture has been heated for a time

sufficient to accomplish removal of as much of the solvent as may be economically accomplished at this time the grains may be removed from the still in which the distillation has been carried out and the water removed therefrom as by centrifuging or wringing. Thereafter the grains may be given a coating for modifying the burning characteristics of the powder and rendering the same non-hygroscopic if desirable. This coating may, for instance, comprise nitroglycerine which acts as an accelerator in that it renders the powder more readily ignitable and also acts as a water proofing agent, rendering the powder non-hygroscopic. A suitable deterrent such, for instance, as dibutylphthalate may be used along with the nitroglycerine or other accelerator and water proofing agent. After this is accomplished, the grains may be dried in the usual manner and if desired, glazed and blended in accordance with the usual practice.

As an illustrative embodiment of the present invention completely gelatinized nitrocellulose powder, such, for instance, as cannon powder which may be to some extent deteriorated and contain unstable regions may be finely sub-divided in a suitable machine, such for instance as a beater, and preferably to a fineness such as will permit it to pass a sixty-five mesh screen. In accordance with the present invention the raw material employed may be, for instance, nitrocellulose powder dust which has passed through a sixty-five mesh screen and has been caught on a hundred mesh screen. Furthermore material which is passed through a hundred mesh screen is suitable for use as the raw ingredient for the process of the present invention. For certain purposes it is desirable that the raw material be of a more uniform fineness than under other conditions and accordingly under these circumstances the raw material may be caused to pass through an eighty mesh screen and caught on a hundred mesh screen. It is to be understood, however, that for some purposes the raw material may be of a larger size than sixty-five mesh.

In the case of grains containing only spots of deteriorated material, these acidic portions are likewise broken up thoroughly during the grinding operations and similarly dispersed or neutralized. Powder on which deterioration has not proceeded to such an extent that visible regions of discolored material are detectable is, nevertheless, improved in stability through the grinding operation and the contact which is afforded between the newly cut and exposed surfaces and the mild alkalinity of the water used in the grinding. The degree of stability of the resultant ground powder depends to some extent upon the degree of fineness to which the material has been ground.

Under ordinary circumstances, however, deteriorated cannon powder which may be used for this purpose will not contain so great a proportion of unstable regions of concentrated acidity that the acidity, when diffused throughout the entire mass, will be excessive. The local concentrations of acid which are responsible for the unstable character of the gelatinized nitrocellulose powder used as a raw material in the process of this invention are disposed of in this manner. Furthermore it may be said that the nitrated diphenylamines are responsible to some extent for the unstable character of the powders. Diphenylamine is a neutral compound generally employed as a stabilizer for nitrocellulose powders, but which upon nitration becomes progressively more acidic in character. Enough diphenylamine is usually present in a grain of ordinary cannon powder to produce a relatively stable mass if the nitrated and unnitrated diphenylamine were diffused throughout the mass which is accomplished in accordance with this invention. After grinding and especially if a mildly basic substance, such as calcium carbonate is added to the slurry, the resultant mass of nitrocellulose dust is not only stable but the acidity thereof is not above the allowable.

Upon completion of the grinding operation the small particles of cannon powder, which are descriptively termed dust, may be screened in order to obtain particles of the desired fineness. This may be accomplished in any suitable manner, but under ordinary conditions in accordance with the present invention, the dust which is in the form of a mud may be caused to pass a sixty-five mesh screen and be caught on a hundred mesh screen; under some circumstances, however, it will be understood that particles either above or below these limits may be employed as the raw material for the process of the present invention.

After the water of the grinding slurry has been permitted to drain from the mass of particles a charge of, for instance 325 pounds of the ground powder or dust (on a dry weight basis, it being understood that the ground product even after draining is in the form of a mud) may be placed in a still with from seven and one-half to eight times its weight of water. The mixture may be agitated in the still to form a thin slurry and during this time a suitable solvent, such for instance as ethyl acetate, may be added preferably in the form of a spray. It will be understood that the solvent which may be ethyl acetate may also contain in solution therewith suitable deterrents, stabilizers or other agents for modifying the burning characteristics or hygroscopicity of the powder. In accordance with one embodiment of the present invention the amount of solvent employed is from one and one-fourth to two times the dry weight of the raw material comprising the charge. If desired, a suitable quantity of calcium carbonate which is generally employed as a neutralizer may also be added to the still. After the solvent and other agents, if desired, have been sprayed into the still preferably at room temperature, the temperature of the still may be gradually increased until the ethyl acetate or other solvent is completely removed from the slurry in the still.

As pointed out hereinbefore, the characteristics of the resultant powders especially with regard to their granulation and density are to some extent affected by the degree of fineness of the nitrocellulose dust, the rate at which the solvent is added or sprayed into the slurry, and by the schedule of distillation, that is to say, by the manner in which the temperature is varied throughout the period of time over which the distillation extends. The distillation schedule which may be found appropriate and effective to achieve the desired grain characteristics will depend upon various other features such as, for instance, the time and amount of solvent employed. As a general rule it will be found that a shortening of the distillation schedule will have the effect of reducing the gravimetric density. This is especially true of the time period during which the solvent-water mixture is passing through its boiling point which, in the case of

ethyl acetate is 69° to 84° C. The same effect may be encountered, however, by shortening the period of time required for raising the temperature of the mixture in the still through any selected temperature bracket, but under most circumstances it is most noticeable during the period at which the solvent-water mixture is passing through its boiling point. As a suitable schedule of distillation where ethyl acetate is employed as the solvent the following is given for the purpose of illustration:

	Minutes
From room temperature to 60° C	45
From 60° to 74° C	45
From 74° to 84° C	60
From 84° to 95° C	45

In the case of ethyl acetate substantially all of the solvent will be found to be removed in accordance with the foregoing schedule of distillation when the temperature reaches 95° C. The solvent may, of course, be recovered in accordance with the usual practice.

Upon completion of the distillation just referred to the contents of the still may be withdrawn and the water removed therefrom by any suitable process, such as for instance as by centrifuging whereupon the powder will be found to exist in the form of grains, each comprising a cluster of the dust particles being substantially uniform in size and density, each of which characteristics may be controlled in the manner hereinbefore set forth.

In accordance with the present invention the contents of the still are withdrawn while a slight trace of the solvent still remains therein, and after the excess water has been removed in the manner just referred to the grains containing a small amount of solvent may be coated with suitable modifying and water proofing agent. For instance, the grains may be given a coating of a deterrent such for instance as dibutylphthalate with or without an accelerator to render the grains more readily ignitable. Nitroglycerine is a suitable accelerator since it not only renders the grains more readily ignitable but also renders the same nonhygroscopic. Furthermore nitroglycerine is a good gelatinizer for nitrocellulose, so that it operates to form a relatively impervious surface film on the grains. The nitroglycerine and dibutylphthalate may be applied as by dissolving them in alcohol with or without benzol. When the dibutylphthalate is employed alone the solvents may be dispensed with and the substance emulsified with water. This solution may then be applied to the grains which are preferably carried in a medium such, for instance, as a water slurry. Although the nitroglycerine and dibutylphthalate may be applied to the grains in the same still in which agglomeration of the dust particles has been carried out, it is preferable that these operations be carried out in separate vessels. The proportion of nitroglycerine which is added to the powder may be from 5% to 20% of the dry weight of the powder, a practical example being 10%, it being understood that the nitroglycerine is preferably handled in the form of a 20% to 30% solution of alcohol and benzol. The dibutylphthalate may be added up to 10% of the dry weight of the powder, a practical proportion being 5%. The resultant grains will be provided with a relatively impervious surface film containing the nitroglycerine which increases the ignitability and renders the powder non-hygroscopic and with it the dibutylphthalate which operates as a deterrent.

From the foregoing description it will be understood that action of the ethyl acetate is such as to cause the finely divided particles to agglomerate into clusters, forming small grains, and also to swell the grains depending upon the amount of solvent employed and the rapidity with which it is distributed throughout the water-nitrocellulose slurry. The amount of swelling which is accomplished determines the final gravimetric density of the powder produced. The agglomerating process of the present invention is admirably adapted for use where a slightly deteriorated cannon powder containing unstable regions is employed for the raw material, since it is apparent that diffusion of the nitrated and unnitrated diphenylamines and also of the acidity of the unstable regions continues during the treatment in the presence of the solvent. It is probable that the swollen condition of the nitrocellulose due to the treatment with ethyl acetate permits the ready diffusion of acid within that swollen nitrocellulose into the water with which the nitrocellulose is in intimate contact. It is obvious that, if desired, a suitable amount of neutral diphenylamine may be added to the powder, as for instance with solvent in order to render the powder more stable.

As an illustration of another embodiment of the process of this invention there may be incorporated with the nitrocellulose slurry a small quantity of a protective colloid, such, for instance, as starch. The amount of such protective colloid which may be employed may be as low as one-half to one percent relative to the weight of the water in the slurry of nitrocellulose dust and by use of such protective colloid flocculation is destricted to an extent such that the resultant grains are finer and of more uniform size.

The powder grains produced in accordance with the present invention are, therefore, small clusters of completely gelatinized particles of nitrocellulose dust. The respective particles which form the individual grains are cemented together by the action of the solvent to such an extent that, although the resultant grain may be of small size, it is of substantially spherical shape although undulations will exist in the surface thereof.

From the foregoing description it is apparent that many modifications of the process hereinbefore described will present themselves to those skilled in the art without departing from the spirit of this invention. It is to be distinctly understood, therefore, that the embodiments hereinbefore described are merely illustrative of the procedure which may be followed, but that the invention is not limited thereto. Such modifications and the use of such individual features and such subcombinations of features as do not depart from the spirit of this invention are, although not specifically described hereinbefore, contemplated by and within the scope of the appended claims.

Having thus described the invention what is claimed is:

1. In the art of making propellant powder grains, the process comprising, comminuting gelatinized nitrocellulose containing unstable regions so as to form fine particles, and treating the nitrocellulose with a solvent in the presence of a protective colloid.

2. In the art of making propellant powder grains, the process comprising, comminuting gelatinized nitrocellulose so as to form fine particles, and agitating the nitrocellulose in the presence of a solvent and a protective colloid.

3. In the art of making propellant powder grains, the process comprising, finely dividing gelatinized nitrocellulose, forming a water nitrocellulose slurry in the presence of a protective colloid, and adding to the slurry a quantity of solvent equal to 1.25 to 2 times the weight of the nitrocellulose.

4. In the art of making propellant powder grains, the process comprising, finely dividing gelatinized nitrocellulose, forming a water nitrocellulose slurry in the presence of a protective colloid, and concurrently agitating and mixing with the slurry a quantity of solvent.

5. In the art of making propellant powder grains, the process comprising, finely dividing gelatinized nitrocellulose, forming a water nitrocellulose slurry in the presence of a protective colloid, agitating the slurry, and spraying into the slurry during agitation a quantity of solvent.

6. In the art of making propellant powder grains, the process comprising, finely dividing gelatinized nitrocellulose, forming a water nitrocellulose slurry in the presence of a protective colloid, agitating the slurry, and adding a quantity of solvent sufficient to cause the particles to agglomerate.

7. In the art of making propellant powder grains, the process comprising, treating gelatinized nitrocellulose dust with a solvent in a bath and in the presence of a protective colloid.

8. In the art of making propellant powder grains, the process comprising, treating gelatinized nitrocellulose dust with a solvent in the presence of an excess of a non-solvent and a protective colloid.

9. In the art of making propellant powder grains, the process comprising, treating gelatinized nitrocellulose dust with a solvent in the presence of a protective colloid and removing the solvent after a time sufficient to soften and swell the dust particles but before the particles are completely dissolved.

10. In the art of making propellant powder grains, the process comprising, treating gelatinized nitrocellulose dust in a non-solvent with a solvent in the presence of a protective colloid, and removing the solvent before the dust particles are dissolved.

11. In the art of making propellant powder grains, the process comprising, treating dense smokeless powder particles with a solvent in a bath and collecting the particles in the presence of a protective colloid.

12. In the art of making propellant powder grains, the process comprising, treating dense smokeless powder particles with a solvent and agitating the particles in a non-solvent medium in the presence of a protective colloid.

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