GRANULAR NITROCELLULOSE MANUFACTURE

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U.S. Cl. 260—223 14 Claims

ABSTRACT OF THE DISCLOSURE

In the process for the production of granular nitrocellulose by treating flibrous nitrocellulose in a bath of water and an active solvent, the improvement comprising adding dispersant to the bath.

BACKGROUND OF THE INVENTION

Nitrocellulose or cellulose nitrate is used extensively in lacquers, plastics, and propellant compositions. Generally, nitrocellulose is supplied to the user in the form of mechanically compacted masses of fibers that are similar in physical form to the cellulose fibers from which the nitrocellulose was made. Because dry flibrous nitrocellulose is exceedingly flammable, commercial nitrocellulose is supplied to the market wet with a liquid that is a non-solvent for nitrocellulose in order to minimize fire hazards during handling, shipping, storage, and further processing. The most commonly used wetting liquids are water, the lower molecular weight alcohols such as ethanol, isopropyl, and butanol and hydrocarbons such as benzene and toluene. The solvent-wet flibrous nitrocellulose, however, is somewhat difficult to handle, since it tends to agglomerate and form slow-dissolving masses when added to an active solvent, as in the preparation of lacquers. Further, the density of the flibrous nitrocellulose, even when heavily compressed during packing, is relatively low, thereby requiring a large number of shipping containers.

Various means have been employed to overcome the handling problems associated with use of commercial liquid-wet flibrous nitrocellulose most of which involve some type of mechanical compaction of the flibrous nitrocellulose which subsequently is broken into smaller particles.

Another means of compacting flibrous nitrocellulose, disclosed in the U.S. Patent 670,346, involved changing it to a structureless coherent material by subjecting the nitrocellulose to the action of solvents diluted with a portion of non-solvent liquid. For example, acetone-water and nitrobenzene-with-alcohol were disclosed as suitable pairs of liquids for use in the process. It is known that below the compatibility point (e.g., the concentration at which nitrocellulose just becomes soluble) nitrocellulose swells, and the ratio of acetone to water imbied by the nitrocellulose is higher than that existing in the bulk liquid, in other words, the nitrocellulose selectively absorbs the active solvent. Gelatinization, but not dispersion, of flibrous nitrocellulose occurs if there is more than about 12% of water in acetone.

The phenomenon of preferential absorption by nitrocellulose of an active solvent from non-solvent liquid/solvent solution, with gelatinization of the nitrocellulose, has been used to make a free-flowing, fast-dissolving, high bulk density nitrocellulose product in a water-based system, by use of an active solvent for nitrocellulose, which solvent formed a minimum boiling azeotropic mixture with water. One such procedure for making dense particulate nitrocellulose, but without the limitation of the minimum boiling azeotropic mixture, was incorporated into a process for casting double base propellant grains described in U.S. Patent No. 2,946,673. A similar process for making hydrocarbon-wet granules of nitrocellulose is shown in U.S. Patent No. 3,284,255. These should be pointed out that from an economic viewpoint in making granules from a nitrocellulose-solvent-water slurry, it is desirable to employ slurries containing as much flibrous nitrocellulose as practicable, and the practical upper concentration limit of nitrocellulose in the slurry is governed by the ability to agitate the slurry effectively. Generally nitrocellulose-solvent slurries containing about from 5 to 20% by weight of flibrous nitrocellulose were used in these processes. A higher nitrocellulose content in the slurry is possible only by comminuting the flibrous nitrocellulose, for example, by jordaning or grinding in a ball mill before subjecting the flibrous nitrocellulose to the solvent-densification process. When such comminuted flibrous nitrocellulose is employed to make smooth, hardened, densified granules of nitrocellulose, the process is more costly to operate and is less capable of producing the larger size particles of densified nitrocellulose which are generally preferred.

A further requirement for success of these processes was to maintain vigorous agitation in the slurry from the moment that the nitrocellulose was contacted by the liquid until the softened nitrocellulose particles were hardened by removal of substantially all of the active solvent. Agitation prevented substantial agglomeration of the softened nitrocellulose particles into lumps, and had to be sufficiently vigorous at all times to keep the nitrocellulose uniformly distributed throughout the slurry.

The processes previously used frequently had to employ solvents other than acetone to obtain satisfactory results. In some cases, such as those processes requiring a minimum boiling azeotrope, acetone could not be used at all, and a higher-cost solvent such as methyl ethyl ketone was necessary.

Therefore, although the granular products produced by these processes were often satisfactory, the cost of production was increased by the higher power requirements of vigorous stirring, lower nitrocellulose/liquid ratios, and the fact that maximum efficiency could not be obtained by the use of low-cost active solvents.

SUMMARY OF THE INVENTION

The instant invention provides an improved process for the production of granular nitrocellulose characterized by greater efficiency and economy than have heretofore been obtainable. This process permits exceptionally high concentrations of flibrous nitrocellulose in the nitrocellulose/water/solvent slurry, requires substantially less vigorous stirring to satisfactorily disperse the nitrocellulose
in the aqueous medium, and operates very effectively with extremely low-cost active solvents.

Specifically, this invention provides an improvement in the process for preparing granular nitrocellulose which comprises dispersing fibrous nitrocellulose in an aqueous medium containing a volatile, water-miscible solvent for said nitrocellulose in an amount sufficient to soften but not dissolve said nitrocellulose, and distilling off said solvent, the improvement which comprises incorporating in said medium dispersant selected from the group consisting of (a) anhydrous hydroxides and (b) water-soluble salts of polybasic acids having a first dissociation constant of less than $2 \times 10^{-1}$ and more than one equivalent per mole of said acid, of said hydroxides.

DESCRIPTION OF PREFERRED EMBODIMENTS

All ingredient ratios, concentrations, percentages, and the like expressed herein are by weight unless otherwise specified.

The process of the instant invention is applicable to fibrous nitrocellulose which has been subjected to usual comminution and disintegrating treatments. The nitrogen content of the nitrocellulose can be from about 10.5% to 13.7% but usually ranges about from 10.7 to 12.7%, and the viscosity level, which varies according to the molecular weight, ranges from about 1.5 seconds for a 25% solution in a 50/25/20 mixture (by weight) of toluene/28% specially denatured alcohol/85% ethyl acetate to over 2000 seconds for a 12.2% solution in the same solvent mixture (ASTM Standard Test No. D301-33). The stabilized fibrous nitrocellulose usually is water-wet and preferably contains not more than 35% of its weight of water. While this limit on water content of the nitrocellulose is critical to the process of the instant invention, such a limit permits easy adjustment of the solvent/nitrocellulose ratio for operation of the process and, additionally, permits reuse of solvent that is recovered at about 60-65% strength by steam-stripping the solvent from the process slurry without special provision for fractional distillation during stripping of the solvent, in the manner described in the examples which follow.

The weight of water in the process slurry, including water which is introduced with the fibrous nitrocellulose, comprises about from 100 to 900 parts and preferably about from 100 to 200 parts per 100 parts of fibrous nitrocellulose.

As agents which can be used in the process of the instant invention include those organic solvents having boiling points below 100° C. or which are steam-distillable below 100° C., for example esters such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, and isopropyl isobutyrate; and ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone. Ethyl acetate, acetone, and methyl ethyl ketone are preferred active solvents, and acetone is especially preferred because of its particularly low cost and ready availability. The weight of solvent generally comprises about from 60 to 300 parts per 100 parts of fibrous nitrocellulose. The upper limit for the amount of active solvent is determined by the consideration that in no case should there be sufficient solvent to dissolve the nitrocellulose in the water-solvent mixture. The ratio by weight of active solvent/nitrocellulose preferably is maintained as low as possible to reduce the amount required to be distilled off. Operation at ratios below 1.0 is entirely practicable, ratios of about 0.6-0.8 being especially preferred. Processes previously employed used solvent/nitrocellulose ratios of about from 1.0-2.0 in order to form granules of nitrocellulose.

The optimum weights of solvent and of water used to obtain a high quality of granular nitrocellulose in the process of this invention vary according to the type of nitrocellulose and the particular active solvent. The process of this invention gives satisfactory results with slurries which initially contain about 30-35% of fibrous nitrocellulose, far greater percentages than have heretofore been possible. For example, a very satisfactory ratio of nitrocellulose to water/active solvent is considered to be one that gives a dense, granular nitrocellulose product that is substantially free of fibrous nitrocellulose and has a particle size largely in the range of 3-80 mesh (Standard Sieve series). The particle size also is affected by the grade of fibrous nitrocellulose which is being granulated, the effectiveness of the agitation, and the temperature at which the process is operated. Balancing these factors to achieve a satisfactory granular product can easily be achieved by starting with the basic formulation suggested above, and adjusting according to the particular starting components used.

Use of a dispersant in the water-solvent mixture is the essential and critical feature of the improved process of this invention. Inclusion of the dispersant provides several benefits to the process of this invention, as compared with processes of the prior art. It has been found that the use of a dispersant permits processing a slurry of fibrous nitrocellulose containing a higher nitrocellulose/liquid ratio, but which requires less power for agitation of the slurry during swelling and coalescence of the nitrocellulose and during the subsequent solvent-stripping period to obtain granulated nitrocellulose of the preferred range of particle sizes. Additionally, the presence of a dispersing agent in the liquid medium permits use of acetone as the active solvent, and in fact helps to make acetone the preferred active solvent for the process of the invention.

Dispersing agents which can be used in the instant invention include ammonium hydroxide and alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, and lithium hydroxide. Other dispersants include water-soluble salts formed by reaction of (a) polybasic acids that have a first dissociation constant of less than $2 \times 10^{-1}$, for example, azelie, borie, carbonate, citric, maleic, oxalic, ortho phosphoric, orthophthalic, pyro phosphoric, tartaric, and silicic acids; with (b) more than one equivalent, per mole of said acid, of a base selected from ammonium and alkali metal hydroxides. Representative salts of acid organic phosphates which can be used as dispersants include (1) water-soluble ammonium and alkali metal salts of acid phosphonates, such as Gafac® LO-529, PE-510, RE-610, RS-610 and RS-710; (2) water-soluble ammonium and alkali metal salts of acid alkyl phosphates, for example, Zelec® NE; and (3) water-soluble ammonium and alkali metal salts of acid fluorooxyethyl phosphates such as Zonyl® S-13. The acid organic phosphates are all derivatives of phosphoric acid in which the phosphoric acid is partially esterified by an organic OH-bearing moiety. Of the above acid phosphates, Gafac® LO-529 is supplied as a sodium salt, while the remainder are supplied as acid esters, the remaining acidic hydrogens of which are then neutralized to a pH of about 7 by ammonium or alkali metal hydroxides to form the dispersing agents indicated in (1), (2) and (3) above. Of all dispersing agents indicated above, trisodium phosphate has been found particularly effective.

The amount of dispersant used generally varies about from 0.02 to 5.0 part by weight per 100 parts of nitrocellulose, and it has been found that 0.03 to 0.5 part of dispersant per 100 parts of nitrocellulose are especially effective. Too little dispersant results in inadequate softening and coalescence of the fibrous nitrocellulose or higher power requirements for agitation, whereas use of excessive amounts of dispersant results in a densified product which contains a substantial proportion of very fine particles which pass an 80-mesh sieve. It has also been found that
somewhat less dispersant is required if higher viscosity fibrous nitrocellulose is used. Temperature is not critical to the process of the instant invention, and can vary from room temperature to the atmospheric boiling point of the slurry mixture. If the process is carried out at or near the boiling point of the slurry, a closed vessel with reflux condenser is preferably employed to contain the active solvent, and a somewhat lower solvent/nitrocellulose ratio can be used effectively. On the other hand, if the process is carried out at room temperature or somewhat above, a higher solvent/nitrocellulose ratio is required. A temperature of about 50° C. during the swelling and coalescence of the fibrous nitrocellulose is preferred, and is especially preferred if acetone is the active solvent that is used in the slurry mixture. The temperature of the slurry is increased to about 100° C. at atmospheric pressure during stripping and recovery of the solvent, while the nitrocellulose particles are being hardened. In the interest of economy of operation, the heating is continued until the slurry is substantially solvent free, after which the granular nitrocellulose is separated from the aqueous slurry.

The nitrocellulose slurry should be agitated in the process of the instant invention, but less power is required than in nitrocellulose-densification processes herebefore known which did not employ a dispersant. Agitation is maintained in the aqueous slurry from the time the fibrous nitrocellulose contacts the solvent until the particles of softened nitrocellulose have been hardened by removing the active solvent from the slurry, e.g., by distillation. Agitation is sufficiently vigorous to keep the nitrocellulose dispersed throughout the liquid at all times.

The specific details of the operation of the process are not critical to the instant invention, and can vary widely, depending on the type and grade of starting materials used and the size and quality of nitrocellulose granules desired. In general, however, it is preferred that the fibrous nitrocellulose be added to a vigorously stirred mixture of water, active solvent, and dispersant at a temperature of about 50° C. The softening and aggregation of the fibrous nitrocellulose begins almost at once and is complete within a few minutes after all the fibrous nitrocellulose has been added to the slurry. Stirring is continued while the temperature of the slurry is raised by heating the mixture, or by sparging with steam, to drive off the active solvent which is condensed and recovered, after which agitation can be stopped. The granular nitrocellulose is separated from the mixture by any suitable means such as allowing the granular nitrocellulose to drain freely, or by filtration, centrifugation, or the like. The water-wet granular material is washed with fresh water at normal temperatures and then, if desired, can be wet-screened or otherwise classified to separate any unusually large or small particles which are not desired in the product. The water-wet product easily can be packed for shipment at net weights per container considerably above those achieved by compressing the usual fibrous cellulose.

Possible alternate procedures include, for example, first agitating the fibrous nitrocellulose in water containing the dispersant, after which the active solvent is added to the slurry, and the process then carried on as before.

In another alternative, the vigorously agitated slurry of softened nitrocellulose in the mixture of water, acetone, and dispersant is diluted by gradual addition of a substantial quantity of water, whereupon the aggregates of nitrocellulose are hardened into smooth, dense particles which can be separated from the slurry, washed, and processed further, as indicated above. This procedure is generally less desirable because the active solvent is lost if the liquid is discarded after separating the granular nitrocellulose, or a much larger volume of liquid must be distilled to recover the active solvent for reuse than is the case for the preferred practice of the process of the invention.

The nitrocellulose product obtained by the process of this invention is in the form of free-floating, dense particles, generally smoothly rounded in form, though not necessarily spherical in shape and free of fibrous nitrocellulose. The particle size and density of the granular nitrocellulose will vary with the types and proportions of the solvents and nitrocellulose used in the process of the instant invention as well as the other process variables indicated above. However, in general, the nitrocellulose product will have a dry bulk density of about 33 to 51 pounds/cubic foot (0.53 – 0.82 g/ml.), and a particle size such that not more than 20% of the particles fall outside the size range represented by through 3- and on 80-mesh U.S. Standard sieves.

The following specific examples further illustrate the process of the instant invention.

EXAMPLE 1

A "½ second" lacquer grade nitrocellulose containing 11.8-12.2% nitrogen and having a viscosity of about 14 seconds (aluminum ball) at 20% concentration in the standard test solution (grade HB-14) is used in this example.

The water-wet, stabilized, fibrous nitrocellulose (100 g. dry weight) is added in agitation to a mixture containing 70 g. of acetone, 0.08 g. of Na₃PO₄, and additional water, the total water content of the combined mixture being 130 g. The temperature of the mixture is 50° C. The slurry is agitated with a twisted blade-type agitation driven by a Gast Air Motor. Uniform dispersion of the nitrocellulose is obtained at a motor speed of 850 r.p.m., using an air pressure of 20 p.s.i.g. This slurry contains 33.3% of nitrocellulose. Swelling and coalescence of the fibrous nitrocellulose begins at once. Agitation is continued while the mixture is heated by injection of live steam until the acetone is stripped from the agitated slurry. During this period of solvent stripping, the densification of the mixture is completed. The granular nitrocellulose is separated from the residual liquid by centrifugation (total volatiles content about 30%), then is washed twice by slurrying in isopropanol (2/1 isopropanol/nitrocellulose) to obtain isopropanol-wet granular nitrocellulose containing about 5 parts of water per 100 parts of dry nitrocellulose. After drying, the granular nitrocellulose all passes through a screen having 35 micron openings, is very free flowing, is free of fibrous nitrocellulose, and has a bulk density of about 45 pounds/cubic foot.

EXAMPLE 2

The procedure of Example 1 is repeated, except that the 0.08 gram of Na₃PO₄ is omitted. The motor speed required to obtain a comparable degree of dispersion is 1650 r.p.m., using an air pressure of 65 p.s.i.g.

EXAMPLE 3

The procedure of Example 1 is repeated except that no dispersant is added to the water-acetone solution before adding the nitrocellulose. The conversion of fibrous nitrocellulose to granular nitrocellulose is substantially decreased, the product consisting of 56% of granular nitrocellulose, through 3- and on 10-mesh standard sieve, and the balance (44%) remaining in the fibrous form. The mixture has a bulk density of about 29 pounds/cubic foot.

EXAMPLES 4-29

The process of Example 1 is repeated using as dispersant one or more of a variety of monocarboxylic bases and of salts of polybasic acids, which polybasic acids have a first dissociation constant of less than 2 x 10⁻⁰⁻⁰, formed by reaction of one mole of any of said acids with more than one equivalent of a base selected from ammonium hydroxide and alkali metal hydroxides. The results are shown in Table I. In all of these examples, the initial temperature of the slurry is about 50° C.
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TABLE I

<table>
<thead>
<tr>
<th>Water, total parts</th>
<th>Acetone, parts</th>
<th>Dispersant Composition</th>
<th>Parts</th>
<th>Nitrocellulose (100 parts) grade*</th>
<th>Density lb./cu. ft.</th>
<th>Particle size, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example:</td>
<td></td>
<td></td>
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<td>On ½ mesh</td>
<td>Through ½ mesh</td>
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<tr>
<td>4</td>
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<td>HB-14</td>
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<td>0</td>
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<td>43.7</td>
<td>0</td>
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<tr>
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<td>HB-14</td>
<td>43.7</td>
<td>0</td>
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<tr>
<td>7</td>
<td>130</td>
<td>70 Na&lt;sub&gt;2&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>HB-14</td>
<td>43.7</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>130</td>
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<td>0.40</td>
<td>HB-14</td>
<td>43.7</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
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<tr>
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<td>0</td>
</tr>
<tr>
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<td>HB-14</td>
<td>43.7</td>
<td>0</td>
</tr>
<tr>
<td><strong>8% N</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>On ½ mesh</td>
<td>Through ½ mesh</td>
</tr>
</tbody>
</table>

**20% NH**

*Grade HB-14 (see Example 1); Grade LC-15, low nitrogen, low viscosity grade; Grade HA-5, high nitrogen, high viscosity grade; Grade HA-100, high nitrogen, high viscosity grade; Grade F-40, 12% N, for smokeless powder.

EXEMPLARY 30

Example 1 is repeated except that 0.5 part of Gafacel<sup>®</sup> RE-610, neutralized to pH=7 by NaOH, is used in place of 0.08 part of Na<sub>2</sub>PO<sub>4</sub>. The resulting dry granular nitrocellulose has a bulk density of about 45 pounds/cubic foot and the particle size distribution, determined by screening through U.S. Standard sieves, is as follows:

- Through 3, on 10: 41
- Through 10, on 40: 48
- Through 40, on 80: 6
- Through 80: 5

EXEMPLARY 31

The procedure of Example 30 is repeated, using 100 parts of HB-14 fibrous nitrocellulose, 60 parts of methyl ethyl ketone, 125 parts of water, and 0.4 part of neutralized Gafacel<sup>®</sup> RE-610 emulsifier. The slurry contains 35.1% of nitrocellulose, the granular densified nitrocellulose produced is free of fiber, and the bulk density of about 45 pounds/cubic foot and a particle size distribution as follows:

- +3, -10 mesh: 24
- +10, -40 mesh: 58
- +40, -80 mesh: 10
- +80 mesh: 8

EXEMPLARY 32

Example 31 is repeated except that the dispersant (Gafacel<sup>®</sup> RE-610) is omitted. Granular densified nitrocellulose is not obtained, and the nitrocellulose forms a gummy mass in the agitated liquid medium.

EXEMPLARY 33

Example 31 is repeated except that the Gafacel<sup>®</sup> RE-610 is not neutralized. Granular nitrocellulose is not obtained, and the nitrocellulose forms a gummy mass in the agitated liquid medium.

EXEMPLARY 34

A mixture of 125 parts of water, 75 parts of ethyl acetate, 0.3 part of neutralized Gafacel<sup>®</sup> R-610, and 100 parts of HB-14 fibrous nitrocellulose (33.3% solids in the system) processed as in Example 1 gives granular densified nitrocellulose free of fibrous material, the bulk density about 45 pounds/cubic foot, and particle size distribution as follows:

- +3, -10 mesh: 30
- +10, -40 mesh: 55.4
- +40, -80 mesh: 37.6
- +80 mesh: 4.7

What is claimed is:

1. A process of preparing granular nitrocellulose which comprises dispersing fibrous nitrocellulose in an aqueous medium containing about from 100 to 900 parts water per 100 parts fibrous nitrocellulose and a volatile, active solvent for said nitrocellulose in an amount sufficient to soften but not dissolve said nitrocellulose, incorporating in said medium dispersant selected from the group consisting of at least one of (a) ammonium and alkali metal hydroxides and (b) water-soluble salts of polybasic acids having a first dissociation constant of less than 1x10^-3 and more than one equivalent, per mole of said acid, of said hydroxides, and distilling off said solvent.

2. A process of claim 1 wherein the dispersant comprises from about 0.02-5 parts by weight per 100 parts of nitrocellulose.

3. A process of claim 2 wherein the dispersant comprises from about 0.03-0.5 part by weight per 100 parts of nitrocellulose.

4. A process of claim 1 wherein the dispersant is ammonium hydroxide.

5. A process of claim 1 wherein the dispersant is an alkali metal hydroxide.

6. A process of claim 5 wherein the dispersant is sodium hydroxide.

7. A process of claim 5 wherein the dispersant is potassium hydroxide.

8. A process of claim 5 wherein the dispersant is lithium hydroxide.

9. A process of claim 1 wherein the dispersant is selected from water-soluble salts formed by reaction of polybasic acids that have a first dissociation constant of less than 2x10^-1 with more than one equivalent, per mole of said acid, of a base selected from ammonium and alkali metal hydroxides.

10. A process of claim 9 wherein the dispersant is selected from ammonium and alkali metal salts of acid organic phosphates.

11. A process of claim 10 wherein the dispersant is selected from water-soluble ammonium and alkali metal salts of acid polyoxyethylene monophenyl phosphates.

12. A process of claim 10 wherein the dispersant is se-
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lected from water-soluble ammonium and alkali metal salts of acid alkyl phosphates.

13. A process of claim 10 wherein the dispersant is selected from water-soluble ammonium and alkali metal salts of acid fluorooalkyl phosphates.

14. A process for the preparation of granular nitrocellulose which comprises agitating about 100 parts by weight of fibrous nitrocellulose in an aqueous bath comprising about from 100–200 parts water, about from 60–300 parts acetone and about from 0.02–5.0 parts trisodium phosphate, and continuing agitation while removing substantially all of the acetone until smooth, hardened, densified particles of nitrocellulose are obtained.

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