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3,200,092

PROCESS FOR PRODUCING SMALL PARTICLES OF NITROCELLULOSE

Richard C. Bergman, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware
No Drawing. Filed May 15, 1962, Ser. No. 194,989
4 Claims. (Cl. 260—17)

The present invention relates to a process for the manufacture of small, dense, spherical particles of nitrocellulose hereinafter called NC.

NC is of considerable interest as a polymeric binder in the formulation of solid propellants useful in rocketry, missiles and the like. Such propellant compositions currently include an oxidizer, a fuel, and a binder. In some cases, a constituent can behave in more than one manner. Thus, for example, NC can be both an oxidizer and a fuel as well as a binder. It has a relatively low energy content, however, and current propellant compositions contain oxidizers such as ammonium perchlorate along with fuels such as aluminum powder.

The present invention provides nitrocellulose particles having an average particle diameter of from about 5 microns to about 20 microns.

The process of the present invention comprises mixing water, a solvent for NC, an emulsifying agent, a protective colloid, and NC, heating the emulsion to distill off the solvent-water azeotrope while continuing agitation, and separating the spheres of NC from the remaining liquid.

The product of the present invention has an advantage over the more conventionally used 30 to 100 micron diameter NC particles, in that the propellant mix, after curing, exhibits superior tensile properties. The burning of such propellant grains is more uniform, also. The reason for these enhanced properties is probably that more intimate mixing can occur with the small diameter particles to give a more homogeneous and more thoroughly collided propellant. This advantage is surprising, nevertheless, because it would be anticipated that the smaller particles would gel much more quickly than the larger particles, thereby shortening the time during which other ingredients can be incorporated into the propellant mix to a level such that uniform mixing would be impossible.

The NC used for the process of the present invention is the type commonly known in the industry as pyro NC and has from about 12% to about 13% nitrogen. Because of the relationship of increased energy content to increased nitrogen content, the nitrogen level of the NC should be as high as is possible without detriment to the physical properties required for the finished propellant. The physical properties of the finished propellant depend considerably on the nitrogen content of the NC because higher nitrogen content NC is less soluble in those solvents used for processing propellant mixes.

The preferred NC for operating this invention is NC having from about 12.4% nitrogen to about 12.8% nitrogen. The NC of the present invention should also have a steel ball viscosity of from about 5 sec. to about 15 sec. when dissolved in a solution containing 10 g. NC, 10 g. of ethyl alcohol (denatured according to the 2B formula) and 80 g. of acetone. This viscosity is run according to procedure given in Joint Army-Navy Specification JAN-N-244 and it is a measure of the molecular weight of the cellulose and thus a measure of the tensile properties which can be expected in propellant formulations, if properly colloidized.

The protective colloid used in the practice of the process of the present invention is preferably a polyacrylic acid crosslinked with allyl sucrose (sold under the name

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of "Carbopol" 934 and described in U.S. Patent 2,798,053). In order to obtain the viscosity level necessary for the practice of this invention, the crosslinked acid is neutralized with a suitable base such as sodium hydroxide to a pH of 6.5 before it is mixed with the NC. The quantity of crosslinked acid used ranges from about 0.2 to about 0.4% by weight based on the weight of the water present during mixing.

The emulsifying agent used in the practice of this invention may be simple or complex. Emulsifying agents can be selected from anionic, nonionic or mixtures thereof. Suitable emulsifying agents include polyethenoxy carbohydrate esters such as polyoxyethylene sorbitan mono-laurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monooleate, and dialkyl sodium sulfosuccinates such as di(2-ethylhexyl) sodium sulfosuccinate and many others. The preferred emulsifying agent is a mixture of a nonionic emulsifying agent and an anionic emulsifying agent in ratios varying from 70:30 to 40:60. The emulsifying agent is present in the total amount of about 0.2% to about 0.5% based on the water present. More can be used but is wasteful. The emulsifying agents range in molecular weight from about 200 to about 2000, depending on the number of oxyethylene units present.

The solvent for NC used in the process of the present invention is an organic liquid less than 5% soluble in water. Suitable solvents are isopropyl acetate and butyl acetate. Isopropyl acetate is the preferred solvent because the isopropyl acetate-water azeotrope can be distilled from the reaction mixture at a lower temperature than the butyl acetate-water azeotrope. The ratio of the solvent to nitrocellulose can range from about 10/1 to about 20/1. Preferably, this range lies between about 15/1 to about 20/1. Using lesser quantities of solvent increases the viscosity of the emulsion so that agitation is difficult and gives larger size particles than desired with an inferior particle size distribution.

The ratio of NC to water ranges from about 1/1 to about 1/15. Preferably, this range lies between about 1/8 to about 1/12. Optionally, NC stabilizing agents can be included in the reaction mixture. These stabilizing agents are in no way required for obtaining the unique product of the present invention, but merely maintain the stability of NC in long term storage. Suitable stabilizing agents include diphenylamine, 2-nitrodiphenylamine, the centralites and many others.

Also, optionally, antifoaming agents can be included in the reaction mixture for the process of the present invention. Again, these antifoaming agents are in no way necessary to produce the unique product of the present invention, but aid in the separation of the product from the excess liquid and aid in preventing overflow of foam and other ingredients during mixing operation. By suitable choice of size of reaction vessel, however, the product of the present invention can be made without the use of the antifoaming agents. Suitable antifoaming agents are the silicone oils present from about 0.25 to about 1.0% concentration, based on the water present.

While the solvent-water azeotrope is being distilled from the mixture containing the NC spheres continuing agitation is necessary in order to prevent agglomeration of the spherical particles.

The spherical particles are separated from the liquid remaining after distillation of the solvent by conventional means such as filtration or centrifugation. Drying is also conventional and can be in a flowing heated air stream or in a static oven. Temperatures used are such as to not decompose the nitrocellulose, preferably below 60° C.

The products of the present invention are small, dense spheres of NC having an average particle diameter of about 5 microns to about 20 microns. At least 95% of

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the particles are less than 35 microns in diameter and no more than 10% of the particles are less than 3 microns in diameter. The particles have an average density of from about 1.59 g. per milliliter to about 1.65 g. per milliliter. At least 70% of the particles are spheres with most of the remainder being elongated spheres and not more than 10% being in the form of rod shaped particles. These particles are capable of being dispersed in a typical plasticizer for NC such as triethylene glycol dinitrate to give stable fluid dispersions which, when heated, gel to form solid propellant compositions. Other ingredients may be added, such as ammonium nitrate, ammonium perchlorate, aluminum powder and many other oxidizers and fuels.

The invention is more thoroughly illustrated with the aid of the following examples. Parts where given are by weight.

Example 1

Water (45,400 parts), allyl sucrose crosslinked polyacrylic acid (150 parts), and 10% aqueous sodium hydroxide (310 parts) are mixed. Polyoxyethylene sorbitan monolaurate (75 parts) and di(2-ethylhexyl)sodium sulfosuccinate (75 parts) is dissolved in isopropyl acetate (43,000 parts). This solution is added to the aqueous solution and additional isopropyl acetate (43,260 parts) and pyro grade NC (4,670 parts) are added to the combined mixture. The viscosity of the emulsion formed after mixing, as measured in a Brookfield viscosimeter, is 6,920 centipoises. The emulsion is stirred for an additional 30 minutes, and then heated to distill off the isopropyl acetate-water azeotrope at 76.6° C. The vapor temperature is allowed to rise to 100° C. to assure that all of the isopropyl acetate is removed. The solvent-free emulsion containing NC spheres is then charged while hot into a centrifuge and excess liquid is removed after which the product is dried at 55° C. The dried product consists of small, dense spheres, 50% of which have an average particle diameter of 8.3 microns or less, and 95% of which have an average particle diameter of 18.5 microns or less. The particle density of these spheres is about 1.64 g. per milliliter. Eighty-five percent of the particles are spheres, 10% are elongated spheres and 5% are rods.

Example 2

An aqueous solution is prepared of 8000 parts of water, 27.5 parts of the allyl sucrose crosslinked polyacrylic acid, and 630 parts of 10% aqueous sodium hydroxide. A solution is made consisting of 13.8 parts of polyoxyethylene sorbitan monolaurate and 13.8 parts of di(2-ethylhexyl)sodium sulfosuccinate dissolved in 3000 parts of isopropyl acetate. The two solutions are combined and 10,000 parts of isopropyl acetate and 833 parts of pyro grade NC are added. The combination is stirred for 30 minutes at room temperature. The viscosity of the combination is 5,040 centipoises as measured by a Brookfield viscosimeter. It is then heated to distill off the isopropyl acetate-water azeotrope at 76.6° C. and the vapor temperature is allowed to rise to 100° after all of the azeotrope has distilled in order to make sure of complete removal of the isopropyl acetate. The residue is then charged while hot into a centrifuge and the excess liquid removed. The product again consists of small spheres 50% of which have an average particle diameter of 10.2 microns or less, 95% of which are average particle size of 24.5 microns or less. The particle density is 1.63 g. per ml. Ninety percent of the particles are spheres, 5% are elongated spheres and 5% are rods.

Example 3, 4, 5, and 6

The procedure used in Example 1 is repeated, using a constant formulation containing different quantities of NC. The following quantities were used:

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Water, 45,400 parts; allyl sucrose-crosslinked polyacrylic acid, 150 parts; 10% aqueous sodium hydroxide, 350 parts; polyoxyethylene sorbitan monolaurate 75 parts; di-(2-ethylhexyl)sodium sulfosuccinate, 75 parts; isopropyl acetate, 86,260 parts; NC—see table below:

Example No.	3	4	5	6
Parts of NC	4,675	6,356	7,536	9,534
Avg. particle size in microns	7.6	11.2	10.0	10.4
Percent Spheres	85	85	85	85
Percent Elongated Spheres	10	10	10	10
Percent Rods	5	5	5	5
Max. particle size of 95% of particles (microns)	15.0	26	-----	31.5

Example 7

The process of Example 1 was repeated, substituting butyl acetate for the isopropyl acetate on a part for part basis. The butyl acetate water azeotrope was distilled off at 90.5° C. Otherwise, the procedure was identical. The product again consists of small, dense spheres having an average particle diameter of 10 microns.

The invention has been completely described by the foregoing. Many additional modifications will be obvious to those skilled in the art without departing from the inventive concept.

I claim:

1. A process for producing small particle nitrocellulose which comprises mixing nitrocellulose, a nitrocellulose solvent, said solvent being less than about 5% soluble in water, an emulsifying agent selected from the group consisting of anionic and non-ionic emulsifying agents and mixtures thereof, and neutralized polyacrylic acid crosslinked with allyl sucrose, distilling off the solvent-water azeotrope while continuing agitation of the mixture, and separating the small particles of nitrocellulose from the liquid present.

2. The process of claim 1 wherein the nitrocellulose contains from 12 to about 13% nitrogen.

3. A process for producing small substantially spherical particle nitrocellulose having a particle diameter within the range of from about 5 to about 20 microns which comprises

(a) mixing nitrocellulose having from about 12 to about 13% nitrogen, a nitrocellulose solvent selected from the group consisting of isopropyl acetate and butyl acetate, water, a mixture of a nonionic emulsifying agent and an anionic emulsifying agent in a ratio of from 70:30 to 40:60, and neutralized polyacrylic acid crosslinked with allyl sucrose, while continuously agitating said mixture;

(b) distilling off the solvent-water azeotrope while continuing agitation;

(c) separating small particles of nitrocellulose from the liquid present, said particles having an average diameter of from about 5 to about 20 microns.

4. The process of claim 1 wherein the nitrocellulose-solvent ratio ranges from about 1/10 to about 1/20, the nitrocellulose-water ratio ranges from about 1/5 to about 1/15, and the quantity of the polyacrylic acid crosslinked with allyl sucrose ranges from about 0.2 to about 0.4% based on the water present.

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CARL D. QUARFORTH, *Primary Examiner*.

LEON D. ROSDOL, *Examiner*.