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2,919,181

PROCESS FOR THE MANUFACTURE OF GLOBULAR NITROCELLULOSE

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This invention relates to plastics and particularly to the manufacture of minute spheres, or near-spheres, of nitrocellulose and the like.

Large quantities of globular powder grains have been manufactured in accordance with the processes disclosed in U.S. Patent Nos. 2,027,114; 2,160,626; and 2,213,255. As normally produced, such globular powder grains may range in size from .008 to .030 inch in diameter. While the practice of the processes disclosed in the aforesaid patents results in the production of a range of grain sizes (herein called "normal sizes") which are quite adequate for use as the propellant in small arms ammunition; and while such processes are susceptible of control whereby the majority of the grains in a given production batch will fall within fairly close limits (within the normal size range), such controls have definite limitations. It has not heretofore been possible to produce on a mass scale smaller sizes of well-formed globular grains, except to the extent that about 1%, or less, of a batch of normal size grains might approach a diameter of 0.002 inch.

For some years, it has been thought that the manufacture of globular powder grains having a diameter on the order of 0.001 inch, or less, would be desirable for certain purposes, and while many efforts have been made in that direction, they have been uniformly unsuccessful with the sole exception, so far as I am informed, of the process disclosed in the copending application of Eugene A. Andrew, Serial No. 470,412. While the aforesaid patents proclaim that the grain size may be controlled by varying the vigor of the agitation (the more vigorous the agitation, the smaller the globules) of the liquor in which the lacquer is suspended, or by varying the viscosity of the lacquer (the higher the viscosity, the larger the globules), the first mentioned mode of control exhibits very definite limits of operability while the last mentioned mode of control is erratic and uncertain. For example, using a typical lacquer consisting of 3 parts by weight of ethyl acetate to each part of nitrocellulose, and operating the agitator in a commercial production still at 160 r.p.m. during the graining stage of the process, results in the production of a batch of hardened grains, 60% of which will fall within the diameter limits of 0.016 to 0.025 inch, and be near-perfect spheres. If, other conditions remaining the same, the agitator speed is increased to 230 r.p.m. during the graining stage, 70% of the finished grains will be between 0.009 and 0.016 inch and be near-perfect spheres. If the agitator speed be further increased to 300 r.p.m., about 90% of the grains will be between 0.006 and 0.012 inch in diameter but the incidence of malformation is greater. Further increase in agitator speed has no appreciable influence on grain size.

Despite favorable indications which have been obtained from time to time with laboratory scale batches, the uncertainty which attends efforts of control grain size by varying the viscosity of the lacquer is well-known to those who have had the experience with the manu-

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facture of globular powder in commercial production stills. The erratic and uncertain nature of the results obtained from merely varying the viscosity of the lacquer, at the same speed of agitation, is illustrated by the following table which gives the screen analysis of the end product from four runs of the same commercial still agitated at 160 r.p.m., but at progressively increasing solvent ratio (ethyl acetate:nitrocellulose).

| Solv. Ratio | Screen Analysis | | | | | |
|-------------|-----------------|----------|----------|----------|----------|---------------|
| | on .0248 | on .0198 | on .0164 | on .0130 | on .0092 | through .0092 |
| 3.0:1 | 0.3 | 18.1 | 30.2 | 17.2 | 21.1 | 12.5 |
| 3.05:1 | 0.2 | 1.3 | 38.2 | 30.3 | 20.8 | 9.1 |
| 3.15:1 | 0.0 | 2.9 | 46.8 | 23.8 | 16.2 | 10.7 |
| 3.3:1 | 0.1 | 0.2 | 34.2 | 35.1 | 21.7 | 8.5 |

Efforts to combine high agitation speeds with low viscosity lacquers have been repeatedly made, but the trial batches made for this purpose have exhibited an apparently unconquerable tendency to coalesce, and consequently their yield of well-formed grains of the size approaching 0.002 inch in diameter has been even less than the accidental yield of such grains from normal size grain production.

It is an object of the present invention to provide a process for the mass production of near-spheres of nitrocellulose and the like, having a diameter on the order of 0.001 inch or less.

In accordance with the present invention, a lacquer of nitrocellulose, or the like, is formed and dispersed in water in accordance with the teachings of the aforesaid patents, and the size of the dispersed globules is reduced to the greatest practical extent by both decreasing the viscosity (i.e., increasing the solvent content) of the lacquer and by increasing the rate of agitation. In addition, the invention is predicated upon the discovery that further reduction in the ultimate grain size may be accomplished by emulsifying within each lacquer globule a substantial quantity, on the order of 50% by volume, of water. After the high water content lacquer globules are dispersed in the aqueous medium, they may be dewatered by the techniques disclosed in the aforesaid patent, No. 2,160,626, and then solidified by removal of solvent. Upon such dewatering and desolventization, the globules shrink to a volume of about one-fortieth of their original size. Consequently, if care be taken to reduce the globules to the smallest size feasible by the techniques of viscosity reduction and vigorous agitation, the smallest size can be further reduced by upwards of 98% by dewatering and desolventization.

More specifically, the invention contemplates that nitrocellulose, or the like, and a suitable solvent, such as ethyl acetate or a methylethyl ketone-toluene mixture, be made into a homogeneous lacquer of high fluidity containing, say, 10 parts by weight of solvent to each part of nitrocellulose. With this thin lacquer, a large quantity of water, at least equal to, and preferably in excess of, the weight of the lacquer, but containing an hydrophobic surface-active agent, is mixed. The mixture is then vigorously agitated for a time sufficient to thoroughly emulsify the water within the lacquer. Thereafter, the water-in-lacquer emulsion is dispersed in the unemulsified excess of water to which is added sufficient of an hydrophilic surface-active agent to emulsify the water-in-lacquer emulsion within the excess of water so as to produce a water in lacquer in water emulsion in which the dispersed globules of lacquer contain on the order of 50% by volume of water. Thereafter, the graining, dewatering, desolventization and hardening techniques taught by the aforesaid patents may be pro-

ceeded with. In view of the fact that the water content of the globules in accordance with the present invention is many times the water content of the globules envisioned by the aforesaid patents, the dewatering phase (as taught specifically by Patent No. 2,160,626) is necessarily more prolonged than in the practice described in said patents.

As a specific example of the process, one part by weight of nitrocellulose is formed into a lacquer with 10 parts by weight of ethyl acetate. The lacquer may, if desired, contain a small amount of a suitable stabilizer, such as 2-nitrodiphenylamine. The mixture of solvent and nitrocellulose with or without stabilizer is agitated and mixed for about thirty minutes, or until a homogeneous lacquer is produced. 25 parts of water containing 0.0125 part of an hydrophobic surface-active agent, such as diethyleneglycol monolaurate, is then vigorously agitated with the lacquer for about an hour, emulsifying at least about half the water into the lacquer. Up to this stage, the process is carried out at room temperature.

When the emulsification of water into the lacquer has been accomplished, the temperature of the batch is elevated to about 40° C., at which time there is added to the mixture a solution consisting of:

| | |
|------------------------------------|-------|
| Water ----- | 1.25 |
| Gum arabic ----- | 0.125 |
| Sodium dioctylsulfosuccinate ----- | .005 |

In lieu of the gum arabic, other protective colloids, such as Belgian gum, animal plues, or collagenous vegetable protein, may be utilized. In lieu of the sodium dioctylsulfosuccinate, other hydrophilic surface-active agents, such as sodium dihexylsulfosuccinate, or sodium tetradecyl sulfate, may be utilized.

After the introduction of the water solution of colloid and hydrophilic surface-active agent, the mixture is agitated and heated to elevate its temperature to about 50° C. over a period of one hour. During this period, some of the water previously emulsified within the lacquer reverses phase so as to become the external phase of a water-in-lacquer-in-water emulsion wherein water-in-lacquer globules are dispersed in an aqueous external phase. Agitation is continued at a rate such as to reduce the globules of lacquer (containing water) to the desired size. Agitation speeds of the character employed in a particular still for the production of normal sized globular powder grains will suffice, but where it is desired to produce the smallest possible sizes, the agitation speed should be further increased to just short of the speed, whereat malformation (due to coalescence of globules) becomes appreciable, it being noted in this connection that the maximum tolerable speed of agitation depends upon the idiosyncrasies of the particular still employed. In order to produce globular grains approaching colloidal size, however, care must be exercised that the globules of water-in-lacquer contain on the order of 50% water after such globules are emulsified as the internal phase of the emulsion.

Having produced the water-in-lacquer-in-water emulsion with globules of the smallest practicable size, but containing on the order of 50% water, the globules are dewatered in accordance with the practice taught in Patent No. 2,160,626 by the introduction of sodium sulfate, or other appropriate salt, into the aqueous external phase of the water-in-lacquer-in-water emulsion. For this purpose, 0.75 part of sodium sulfate dissolved in 1.5 parts of water may be gradually added over a period of about thirty minutes while the temperature of the mixture is maintained at 50-52° C. At the end of the salt addition, the rate of heat input to the mixture is increased over a period of two hours to bring the batch up to its solvent vaporization temperature which,

at atmospheric pressure, is around 70-72° C. During this two-hour period of temperature elevation, the water in lacquer globules are dewatered and shrunk to about 50% of their previous volume. Desolventization proceeds after the temperature of solvent vaporization is achieved, and in view of the high content of solvent within the globules, it is desirable that the removal thereof proceed slowly so that about six hours is allowed for its completion. Upon removal of the solvent from the globules, they will have shrunk to less than 10% of their dewatered volume so that when the solvent removal is completed, and the grains are hardened, the size of the globules is about 5%, or less, of their original size. The greater the amount of water emulsified within each individual globule, the smaller will be the ultimate size of that globule. In carrying out the process as just indicated, the final product consisted of well-rounded grains having a diameter under 7.5 microns.

Having thus described the invention, what is claimed and desired to be secured by Letters Patent is:

1. In the manufacture of solidified globules having a diameter of 0.001 inch or less from a lacquer whose base material is nitrocellulose, the process comprising preparing a lacquer consisting essentially of 1 part of nitrocellulose and approximately 10 parts of a water-immiscible solvent therefor, agitating said lacquer with water containing a hydrophobic surface active agent until an amount of water at least equal to the weight of the lacquer is emulsified into said lacquer as the internal phase thereof, subdividing said emulsion into fine globules and suspending said globules in an aqueous bath by vigorous agitation, and while so suspended: adding a water-soluble solute immiscible with the lacquer to the bath, maintaining the globules in suspension until substantially all of the water is removed therefrom so as to shrink said globules, and then further shrinking the globules by removing solvent therefrom.

2. A manufacture prepared by the process of claim 1 comprising solidified globules of nitrocellulose lacquer having a diameter of 0.001 inch or less.

3. The process of claim 1 wherein the water content of the fine globules is approximately fifty percent.

4. In the manufacture of solidified nitrocellulose globules having a diameter of 0.001 inch or less, the process comprising preparing a lacquer of 1 part of nitrocellulose and about 10 parts of a water immiscible solvent selected from the group consisting of ethyl acetate and a methyl ethyl ketone-toluene mixture, agitating said lacquer with water containing a hydrophobic surface active agent until an amount of water at least equal to the weight of the lacquer is emulsified into said lacquer as the internal phase thereof, subdividing the lacquer into globules and suspending them in an aqueous bath by vigorous agitation of the bath, dissolving a water-soluble solute immiscible with the lacquer in the bath, dewatering the suspended lacquer globules by maintaining the suspension of the globules in the bath containing the solute and removing the solvent from the dewatered lacquer globules.

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