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METHOD OF PRODUCING CELLULOSE  
PELLETS

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This invention relates to cellulose, and more particularly to the method of producing regenerated cellulose pellets in substantially spherical form.

Cellulose pellets have a variety of uses, for example, as a raw material for nitration in the formation of a propellant powder, as a gas evolving material in electrical protective devices, as heat insulation, as dielectric material, and as a mild abrasive. It has been proposed heretofore to form cellulose pellets by treating bleached wood pulp with sodium hydroxide and carbon disulfide to form a paste, extruding the paste through a die to form strings, cutting the strings up into pellets and then regenerating the cellulose in the pellets by treatment with acid or other suitable regenerating agent. Such a method, however, does not lend itself to manufacture of spherical or spheroidal particles. Regenerated cellulose pellets of spherical shape provide the advantages, among other things, of being free-flowing and permitting uniform packing with a much wider utility than pellets of non-spherical shape.

An object of the invention is to provide a novel method for producing pellets of regenerated cellulose. Another object is to provide a novel and efficient method for the formation of spheres of regenerated cellulose. Other objects and advantages will become apparent from the following detail description of the invention.

The foregoing objects are advantageously accomplished in accordance with this invention by forming a solution of cellulose, passing drops of the cellulosic solution through a liquid inert thereto wherein they acquire sphericity and then through a liquid interface into a contiguous coagulating bath immiscible with the inert bath wherein the cellulose in at least the surface of the spheres is precipitated to preserve their globular shape.

In carrying out the process the force of gravity is utilized to effect travel of the drops of cellulose solution through the inert or shaping bath into the coagulating bath by formulating the compositions of the cellulose solution, inert bath, and coagulating bath in such manner that they each have a suitable specific gravity. If it is desired that the drops travel upward through the treating baths then the compositions should be so formulated that the cellulose solution has a lower specific gravity than the coagulating bath and so that the coagulating bath likewise has a lower specific gravity than the inert bath. On the other hand, if it is desired that the drops of cellulose solution travel downward through the

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treating baths then the compositions should be so formulated that the cellulose solution has a higher specific gravity than the coagulating bath and so that the coagulating bath has a higher specific gravity than the inert bath. In either event it is, of course, necessary that the inert and the coagulating baths be immiscible with each other so that a plurality of treating layers are formed.

Any of the usual cellulose solution processes may be employed, for example the viscose or cuprammonium processes. The regenerated cellulose resulting from such processes has been variously described as "cellulose" and "cellulose hydrate" and it should be understood that the term "regenerated cellulose" as used herein includes the materials so described.

The shaping bath may be formed of any suitable liquid which is immiscible with and does not otherwise react with the cellulose solution and is thus inert thereto and has the proper specific gravity. For instance, a liquid hydrocarbon of low specific gravity and carbon tetrachloride which has a relatively high specific gravity may be mixed in such proportions as to give an inert or shaping bath of proper specific gravity.

The coagulants may be those usually employed with the particular solution process, and the concentration of coagulant may be so adjusted as to give the coagulating solution the necessary specific gravity. For instance, solutions of ammonium salts, or solutions of sodium sulfate, or solutions of sodium sulfate in dilute sulfuric acid are suitable as coagulants for viscose solutions and caustic soda may be employed for coagulating cuprammonium solution. When viscose solution is utilized, it has been found that neutral aqueous substantially saturated solutions of sodium sulphate, i. e., about 10% to about 19% at temperatures in the range of 20° C. to 100° C., are particularly suited as coagulants in the manufacture of smooth-surfaced cellulose pellets and other relatively thick regenerated cellulose articles having at least one dimension of about 0.040 inch to 0.100 inch. The time required for complete coagulation of the viscose solution in such thick shapes may be somewhat shortened by maintaining the concentration of sodium sulphate and temperature as high as possible in the ranges of 10%–19% and 20°–100° C., respectively, while maintaining uniform coagulation.

Complete coagulation may be effected in just one coagulating bath, or, if desired, coagulation may be carried out in a plurality of stages so that only partial coagulation sufficient to fix the



cellulose in globular form may be effected in the first coagulating bath and the spheres may then be removed to one or more coagulating baths to complete the coagulation. After coagulation, the spheres may be subjected to acid or other usual treatment to effect complete regeneration of the cellulose and may be washed, dried, screened, sized, and otherwise handled in a manner customary with the solution process and such particulate material.

It has been found that a small amount of a suitable wetting agent incorporated in the coagulating bath facilitates passage of the globules without deformation through the inert liquid-coagulating solution interface. Since the coagulation proceeds slowly, care must be taken to keep the globules in motion in the coagulating bath until they have become sufficiently hardened to resist deformation. In order to avoid insufficient coagulation the specific gravity of the coagulating solution may be so controlled as to cause the globules to pass only slowly through it, and a deep coagulating bath may be employed, or a mild agitation may be utilized which is positive enough to maintain the spheres in free motion within the bath but which is not sufficiently violent to deform the spheres or deleteriously disturb the interface between the liquid layers.

In order to further explain and clarify this invention, following is a typical embodiment thereof in which the preparation of regenerated cellulose spheres utilizing the viscose process is illustrated in detail. In the following example, the globules of cellulose solution are passed downwardly through the treating bath.

Bleached wood pulp having an alpha cellulose content of 94%, of the type employed in the manufacture of rayon, in sheet form was passed through a hammer mill to defiber the sheet. Two pounds of the resulting ground pulp were steeped in 20 pounds of 18% sodium hydroxide solution for 30 minutes at 20° C. The resulting soda cellulose was then transferred to a press and pressed until a ratio of 2 parts caustic to one part cellulose resulted. The pressed cake was then broken up and fluffed uniformly to provide crumbs of alkali cellulose which were then aged at a temperature of  $20 \pm 1^\circ$  C. for 72 hours.

After the aging period, 2.1 pounds of carbon disulphide were continuously mixed with 8 pounds of cellulose in the form of such alkali cellulose crumbs for a period of 20 minutes. One and four tenths pounds more of carbon disulphide were then continuously mixed with the ingredients for a period of 130 minutes. The temperature during the mixing with carbon disulphide was maintained at  $20 \pm 1^\circ$  C.

The excess carbon disulphide was removed from the resulting cellulose xanthate by subjecting the mixture to a vacuum of 10 inches of mercury for 20 minutes and subsequently passing a small stream of air over the cellulose xanthate for 10 minutes.

The cellulose xanthate was then dissolved in 87 pounds of 5.1% sodium hydroxide (sp. gr. 1.056). The resulting viscose solution was then filtered to remove any insoluble matter present and was aged under a vacuum of 3 inches of mercury for 18 hours at 20° C. The viscose solution was then allowed to stand and ripen for 8 days at temperatures from 20–30° C.

The aged cellulose solution had a specific gravity of 1.115 at 20° C., a relative viscosity of 11560 centipoises, an age of 7.8 ml. of 10% ammonium

chloride (Hottonroth test), and contained 6.01% cellulose, 5.95% caustic soda, and 1.54% sulphur in combination.

The coagulating bath was composed of an aqueous solution of 12% sodium sulphate and 0.045% of the wetting agent, isopropyl naphthalene sodium sulfonate. The coagulating bath had a specific gravity of 1.110 at 27° C. The shaping bath or upper layer of liquid, inert to or unreactive with the cellulose solution, was composed of 68.5% benzene and 31.5% carbon tetrachloride and had a specific gravity of 1.104 at 25° C. The height of this shaping bath or upper liquid layer was 10 inches and the height of the coagulating bath or bottom layer of liquid was 72 inches.

The treatment of the cellulose solution in the baths was carried out at a temperature of approximately 25° C.

The cellulose pellets were then formed by causing drops of the solution to fall from an orifice 0.118 inch in diameter 18 inches through the air into the shaping bath, which drops assumed a spherical shape while passing through this shaping bath through the action of surface tension. As the drops fell from the shaping bath through the liquid interface into the coagulating bath, chemical reaction occurred between the salt solution and cellulose solution resulting in a precipitation or coagulation of the cellulose in the spheres. The layer of coagulating solution was subjected to mild agitation insufficient to disturb the liquid interface between the coagulating solution and the shaping bath and insufficient to deform the globules, in order to prevent the globules from settling on the bottom of the coagulating bath before they were sufficiently hardened to resist deformation. The coagulating or hardening treatment in the coagulating bath was continued for approximately 2 hours and the hardened globules were then removed and placed in a second aqueous coagulating bath which contained 16% sodium sulphate. The globules were suspended in this bath with continuous agitation for 1 hour at 90° C. In order to insure complete coagulation throughout each pellet they were placed in a third bath 16% sodium sulfate for ½ hour at 90° C. The pellets were then washed for 32 hours in water at a temperature of 70–80° C. in order to reduce the ash content to .125%. The pellets were then dried in hot air drier at a temperature of 50° C. for 8 hours and at a temperature of 75° C. for an additional 2 hours with intermittent stirring of the pellets. The pellets were then classified and screened to remove any irregular shaped pellets.

The resulting regenerated cellulose pellets had an average diameter of 88.1 mils with the ratio of major to minor diameters being 1.034 and less, a specific gravity of 1.50 at 23° C., a bulk density of .890, a number per pound of 50,000, and had a smooth surface, like color, and free-flowing characteristics.

Somewhat larger spheres may be formed employing an orifice of the same diameter for the cellulose solution as that employed in the foregoing example, if the orifice is under the surface of the liquid of the shaping bath so that the drop is formed in the shaping bath, instead of being dropped through the column of air. The size of cellulose sphere can be varied also by changing the concentration of cellulose in the solution and by otherwise introducing larger or smaller globules of cellulose solution into the shaping bath, for instance with orifices of different size. When it is desired that the cellu-



lose solution travel downwardly through the treating bath it is preferred that the shaping and coagulating layers have a specific gravity respectively about 0.016 and about 0.006 less than that of the cellulose solution at operating temperature, although lesser or greater differences are operable. When it is desired that the cellulose solution travel upwardly through the treating bath it is preferred that the coagulating and shaping baths have specific gravities respectively about 0.016 and about 0.006 greater than the cellulose solution at operating temperature, although lesser or greater differences are operable. In order to preserve a proper ratio of specific gravity between the cellulose solution, coagulating solution, and shaping baths, it is desirable to carry out the treatment in a vessel equipped with suitable heating and cooling means to provide a relatively constant temperature in the coagulating and shaping layers during the process.

Solid spherical pellets of regenerated cellulose having a specific gravity of 1.45 to 1.6 and a ratio of major to minor diameters of less than 1.05 are readily formed in accordance with this invention.

Although the use of a viscose solution is described in the foregoing specific example, it is to be understood that cuprammonium cellulose solutions and other cellulose solutions may be employed to secure the advantages of this invention and that various changes may be made in the specific details as set forth therein without departing from the spirit and scope of this invention.

Having now described the invention what is claimed as new and desired to be secured by Letters Patent is:

1. In the manufacture of cellulose pellets, the process which comprises introducing drops of cellulose solution into a coagulating bath through an intermediate layer of liquid inert to said cellulose solution, and maintaining the drops of cellulose solution in said coagulating bath at least until the cellulose in the drops is sufficiently coagulated to retain its shape in subsequent handling.

2. In the manufacture of cellulose pellets, the process which comprises forming a solution of cellulose, causing drops of said solution to move freely through a layer of liquid inert to the cellulose solution into a coagulating bath immiscible with said inert liquid and maintaining the resulting globules of cellulose solution in said coagulating bath until the cellulose in said glob-

ules is sufficiently coagulated to retain sphericity in subsequent treating and drying operations.

3. In the manufacture of cellulose pellets, the process which comprises introducing drops of viscose solution into a coagulating salt bath containing a wetting agent through an intermediate layer of benzene-carbon tetrachloride mixture, and agitating the resulting globules of viscose solution in said salt bath until the cellulose in the globules is sufficiently coagulated to retain sphericity in subsequent treating operations.

4. A method for the manufacture of regenerated cellulose pellets which comprises forming a solution of cellulose, passing drops of said solution through a liquid inert to said cellulose solution wherein said drops are converted to globules, passing said globules through a liquid interface into a contiguous coagulating bath immiscible with said inert bath, and maintaining said globules in said coagulating bath until the cellulose in the globules is sufficiently coagulated to retain sphericity in subsequent treating and drying operations.

5. A method for the manufacture of regenerated cellulose pellets which comprises forming a solution of cellulose, forming a treating bath having a layer of liquid inert to said cellulose solution and an aqueous layer immiscible with said inert layer containing coagulants for said cellulose solution, with the specific gravity of said layers being so adjusted that a drop of said cellulose solution in said inert layer will move by gravitational force into said coagulating layer, passing drops of said cellulose solution through said inert layer into said coagulating layer, and maintaining the resulting globules of cellulose solution in said coagulating solution until the cellulose therein is sufficiently coagulated to retain sphericity in subsequent handling.

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