(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 153 182**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **85301079.1**

(22) Date of filing: **19.02.85**

(51) Int. Cl.⁴: **D 21 B 1/36**

(30) Priority: **20.02.84 JP 29937/84**

(43) Date of publication of application: **28.08.85**
Bulletin 85/35

(84) Designated Contracting States: **DE FR GB**

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(54) Process for producing finely divided cellulose particles.

(57) Finely divided cellulose particles of uniform size can be produced in high yield by applying pressure and heat to cellulose fibers in a hydrous condition and then discharging them explosively into a receiver tank at atmospheric pressure. The size of the finely divided cellulose particles can be controlled by varying the conditions under which pressure and heat are applied to the cellulose fibers.

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PROCESS FOR PRODUCING FINELY DIVIDED CELLULOSE PARTICLES

BACKGROUND OF THE INVENTION

This invention relates to a process for producing finely divided cellulose particles in which substantially lignin-free cellulose fibers are chemically and physically reduced to fine particles by the partial hydrolysis with activated water and by the utilization of the force resulting from instantaneous vaporization of water.

Finely divided cellulose particles have a large specific surface area and have excellent characteristics of adsorptivity, colloidal disperisibility and reactivity. Accordingly, they are widely used as absorbents, thickeners, excipients, adsorbents and other industrial materials and as dietary food materials in the field of pharmaceutical industry, food industry and other manufacturing industries.

DESCRIPTION OF THE PRIOR ART

The microstructure of cellulose fibers is believed to be such that microcrystals having molecular

chains of cellulose highly oriented by means of hydrogen bonds and amorphous regions having a low degree of orientation are alternately arranged in the lengthwise direction to form elementary fibrils, a plurality of elementary fibrils are joined to constitute a fibril, and such fibrils are further combined to form a higher order of fibrous structure.

Conventionally, in order to disintegrate cellulose fibers having the above-described fibrous structure and thereby obtain finely divided cellulose particles, there have been proposed a variety of methods which are based on mechanical techniques, chemical techniques or combinations thereof [see, for example, FRANKLIN W. HERRICK et al., J. of Applied Polymer Science, Applied Polymer Symposium, 37, 797-813(1983); ALBIN F. TURBAK et al., J of Applied Polymer Science, Applied Polymer Symposium, 37, 815-827(1983); U.S. Pat. No. 2,978,446 (ORLANDO A. BATTISTA et al.); Japanese Patent Publication No. 12496/'64; and Japanese Patent Publication No. 26274/'65].

The size, polymerization degree, crystallinity and shape of finely divided cellulose particles produced by these conventional methods vary according to the particular process employed.

For example, mechanical processes are simple

in operation and, in particular, dry processes are characterized in that the microstructure of cellulose fibers is disintegrated by the action of direct impact to yield a powder having low crystallinity and polymerization degree. However, where a vibration mill is used according to common practice, the size of the resulting particles is limited to as large as several tens of microns and their size reduction requires much energy. Well-known wet processes include the beating process commonly used in the making of paper pulp and the process in which cellulose fibers are broken by passing them through an orifice under high pressure to effect rapid deceleration. However, the finely divided cellulose particles produced by these processes have the disadvantage that they consist of extremely fibrillated fiber particles varying in shape and having very high water retention properties and the fibrous structure has not been disintegrated down to the level of microcrystals. In addition, the cellulose fibers in the form of a suspension need to be agitated or transferred at high speed, resulting in a large consumption of energy.

On the other hand, chemical processes are ones in which cellulose fibers are subjected to hydrolysis or oxidative decomposition in a heterogeneous system so as to disintegrate their morphological

structure. In order to obtain finely divided cellulose particles having an especially high degree of purification, it is common practice to employ a process comprising a combination of acid hydrolysis at high temperature and a mechanical treatment as described above. This combined process is based on the principle that the acid hydrolysis at the glucoside linkages of the molecular chains of cellulose takes place in the amorphous regions of the cellulose fibers more preferentially than in the crystalline regions. Thus, the amorphous regions of the cellulose fibers are attacked to loosen and disintegrate their fibrous structure. Subsequently, the cellulose fibers so treated are reduced to fine particles by subjecting them to the mechanical treatment. In this combined process, however, the amorphous regions of the cellulose fibers are decomposed and dissolved away, resulting in a low yield of the finely divided cellulose particles. (For example, where fine particles of the order of several microns in size are produced by using wood-derived dissolving pulp as the starting material, the yield is of the order of 30 to 50% based on the starting material). Moreover, since the aforesaid chemical treatment involves the use of an acid, the cellulose itself is liable to deterioration during the treatment and, in addition, the equipment should indispensably

be made of a material having acid resistance at high temperatures.

SUMMARY OF THE INVENTION

In the course of investigation on a process for producing finely divided cellulose particles which can overcome the disadvantages encountered in the above-described conventional processes, the present inventors paid attention to the structure of cellulose fibers in which the bonds between fibrils, between microfibrils, and in amorphous regions are relatively weak and discovered that, if the force resulting from quick depressurization and vaporization of high-temperature water placed under high pressure is focused on such portions having relatively low bond strength, the aforesaid bonds can be properly broken without causing deterioration of the cellulose itself. The present invention has been completed on the basis of this discovery.

Accordingly, it is the primary object of the present invention to provide a process for producing finely divided cellulose particles of small size in high yield which comprises enclosing cellulose fibers in a pressure vessel, applying pressure and heat to them in a hydrous condition, and then discharging them explosively into a receiver tank at atmospheric pressure,

whereby finely divided cellulose particles can be produced without causing deterioration of the cellulose and without requiring much energy.

Other objects of the present invention will become apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION

The cellulose fibers used as the starting material in the process of the present invention are substantially lignin-free cellulose fibers which are obtained by subjecting a cellulosic material such as wood fibers (e.g., wood chips), bast fibers or seed fibers (e.g., linters) to a treatment for the removal of lignin.

In this connection, the present inventors have previously reported that, when water-containing wood chips are held under high-temperature and high-pressure conditions and then depressurized quickly, the wood tissue is easily disintegrated and defibrated to yield pulp and, at the same time, finely divided cellulose particles [Kobunshi Kako, Vol. 32, No. 12, 39-47(1983)]. However, the cellulose particles obtained by treating wood chips as described above are extremely non-uniform in size and colored, so that a highly purified product cannot be obtained. Moreover, their yield is low.

This means that, in the disintegration and defibration of wood chips, it is necessary to destroy the middle lamellae consisting of lignin and hemicellulose contained in wood. For this purpose, the aforesaid treating conditions must be made severe. However, this not only causes partial deterioration of the cellulose, but also undesirable coloring due to adsorption of the condensates of lignin and hemicellulose as well as resin and pigments.

For the above-described reasons, the process of the present invention uses, as the starting material, cellulose fibers which have been made substantially lignin-free by subjecting a raw cellulosic material to a treatment for the removal of lignin.

Examples of such cellulose fibers include commercial products of chemical pulp for paper-making use, chemical pulp for dissolving use, and the like. However, pulp comprising highly purified cellulose should preferably be used to enhance the yield of the resulting finely divided cellulose particles. In the case of chemical pulp for paper-mkaing use having a high hemicellulose content, the hemicellulose tends to undergo hydrolysis and dissolve out during the application of high pressure and high temperature, resulting in a reduced yield of the product.

Moreover, the cellulose fibers used as the

starting material should preferably have a water content of 10% or greater. However, since the application of pressure and heat to the cellulose fibers is carried out by blowing in saturated steam, the drain resulting from condensation of the saturated steam brings the whole cellulose fibers into a hydrous condition. Accordingly, the cellulose fibers may be used as they are, unless they are in an excessively dry condition.

Prior to the application of pressure and heat to the cellulose fibers, mineral acids such as sulfuric acid, hydrochloric acid, sulfurous acid, etc., organic acids such as acetic acid, formic acid, etc., or alkalis such as sodium hydroxide, magnesium hydroxide, calcium hydroxide, etc. may be added to the cellulose fibers for the purpose of promoting the disintegration thereof. However, if such acids or alkalis are added, it is likely that the cellulose fibers are hydrolyzed during the application of pressure and heat thereto and the resulting finely divided cellulose particles are reduced in yield. Thus, care must be taken not to use these acids or alkalis in excessively large amounts.

In the process of the present invention, the application of pressure and heat to the cellulose fibers is carried out by placing the cellulose fibers

in a pressure vessel having a jacket, introducing low-pressure steam having a gauge pressure of about 1 to 2 kg/cm^2 into the vessel to expel the air contained therein, and then heating the entire vessel and simultaneously blowing saturated steam into the vessel up to a predetermined pressure so as to bring the cellulose fibers into a hydrous condition.

As a result of the above-described application of pressure and heat to the cellulose fibers, the amorphous regions of the cellulose fibers is partially hydrolyzed by activated water, resulting in a reduction in the degree of polymerization of cellulose. In this case, however, its decomposition to lower-molecular-weight compounds can hardly proceed in contrast to the case of conventional acid hydrolysis in a heterogeneous system. Rather, the hot water promotes the rearrangement of molecular chains in the amorphous regions and thereby enhances the degree of crystallinity.

However, it should be noted that, if the above-described application of pressure and heat is continued for a long period of time, the cellulose may undergo partial decomposition. Accordingly, in the process of the present invention, the application of pressure and heat may be carried out for a very short period of time which is of the order of minutes.

In the process of the present invention, the hydrous cellulose fibers obtained by the above-described application of pressure and heat are instantaneously and explosively discharged through a small tube into a receiver tank at atmospheric pressure. In order to discharge the hydrous cellulose fibers instantaneously and explosively into a receiver tank at atmospheric pressure, it is preferable to use a device having excellent sealability (e.g., a ball valve or a rotary valve) as the on-off valve. When the hydrous cellulose fibers obtained by the application of pressure and heat are discharged in the manner described above, finely divided cellulose particles in homogeneous and hydrous form are produced by the synergistic action of the force resulting from quick vaporization of high-temperature water placed under high pressure and the mechanical shock and/or friction between the fibers themselves or between the fibers and the tube wall resulting from the passage of the hydrous cellulose fibers through the small tube.

The resulting finely divided cellulose particles in hydrous form are suspended in water to form a thick slurry. If desired, this slurry may be subjected to a simple bleaching treatment using a chlorine-containing bleaching compound (such as sodium

hypochlorite, calcium hypoclorite or chlorine dioxide), hydrogen peroxide or ozone. Then, the slurry is filtered, washed and, if necessary, sieved to obtain a product. Furthermore, this product may be dried according to such techniques as heating, spray drying, freeze-drying and the like.

Inherently, cellulose has a very strong affinity for water because it possesses hydroxyl groups in the molecular chain. Accordingly, when cellulose fibers are exposed to water, the water penetrates into higher order tissues such as cell walls, cell cavities (lumen), etc. and, further, into their microstructure. However, the water becomes adsorbed by the amorphous regions having randomly oriented hydroxyl groups and on the surfaces of the crystals, and does not penetrate into the crystals, so that the force resulting from vaporization of the water acts effectively on the cellulose fibers and thereby reduces them to fine particles. More specifically, when the uniformly hydrous cellulose fibers placed under high-temperature and high-pressure conditions are depressurized quickly, the water contained in the cellulose fibers and the water adsorbed in the cell walls and cell cavities, between fibrils, between microfibrils, by the amorphous regions and on the crystal surfaces vaporize instantaneously. The strong

expansion force so generated acts uniformly, efficiently and concentratedly on the weak portions of the fibrous structure to loosen and break the bonds present in the fibrous structure and thereby disintegrate the fibrous structure.

According to the present invention, the degree of disintegration of the fibrous structure can be arbitrarily controlled by varying the conditions under which pressure and heat are applied to the cellulose fibers in the above-described manner. For example, in order to obtain finely divided cellulose particles consisting of fibril aggregates whose lengths are of the order of several tens microns, it is preferable to use saturated steam having a gauge pressure of 5 kg/cm^2 or higher. In order to obtain finely divided cellulose particles comprising microfibrils several microns or less in length and, further, microcrystals, it is preferable to use saturated steam having a gauge pressure of 25 to 30 kg/cm^2.

When the cellulose fibers are treated by the application of a relatively low pressure, the resulting cellulose particles consist of small fiber pieces or fibril aggregates in which the bonds between fibrils, between microfibrils, in the microcrystalline regions, and in the non-crystalline regions have not been fully broken as yet. However, since the fibrous structure

is loosened, the aforesaid cellulose particles can be reduced to fine particles of smaller size by subjecting them to a post-treatment selected from relatively simple mechanical treatment such as beating, defibration and the like.

As described above, the present invention permits finely divided cellulose particles having a relatively wide range of sizes and consisting of highly purified, homogeneous cellulose to be economically produced according to a relatively simple procedure and by use of equipment including a discharge device composed of an ordinary pressure vessel and a small tube.

Moreover, as previously stated, the finely divided cellulose particles obtained according to the present invention have been disintegrated down to the level of microfibrils or amorphous regions by the action of the force resulting from vaporization of pressurized water. Therefore, they are excellent in such properties as adsorptivity, colloidal dispersibility and reactivity, as compared with the finely divided cellulose particles produced by conventional chemical processes based on acid hydrolysis in a heterogeneous system or by conventional mechanical processes based on wet grinding.

The present invention is further illustrated

by the following examples. However, these examples are not to be construed to limit the scope of the invention.

Example 1

According to the conventional sulfate pulping process, domestic mixed hardwood chips were pulped. The resulting pulp was treated in six stages with chlorine, caustic soda, chlorine, caustic soda, sodium hypochlorite and chlorine dioxide to prepare fully bleached pulp having a brightness of 88.3%. This bleached kraft hardwood pulp was hand made into a sheet, which was air-dried to obtain a sheet consisting of substantially lignin-free cellulose fibers and having a water content of 12.5%. This sheet was manually torn to pieces measuring several centimeters square. About 200 g of the above pulp pieces were enclosed in a pressure vessel (with a maximum working pressure of 40 kg/cm^2 and a volume of 2 liters) having a steam inlet tube and an air outlet tube at the top and a discharge tube with ball valve at the bottom. This discharge tube connected with a receiver tank fitted with a silencer. Then, the air outlet tube was opened and saturated steam having a gauge pressure of 2 kg/cm^2 was blown in for 2-3 seconds to expel the air. This procedure was repeated two more times.

After purging with steam, the air outlet tube was closed and saturated steam having a gauge pressure of 12 kg/cm^2 was passed through the pressure vessel and the jacket to increase the temperature and pressure rapidly. The internal temperature of the pressure vessel reached a maximum value of about 190°C. As soon as the maximum temperature of 190°C was reached, the passage of saturated steam was stopped and the vessel was allowed to stand for 2 minutes. Thereafter, the ball valve at the bottom was opened to cause the contents of the vessel to be discharged into the receiver tank in a very short period of time. The time required for all the contents to be discharged was almost instantaneous. By washing the interior of the receiver tank with water, the finely divided cellulose particles discharged thereinto were collected in the form of a thick suspension.

When the resulting suspension of finely divided cellulose particles was observed under a microscope, most of the particles consisted of fibril aggregates partially separated into microfibrils and having lengths of 50-100 microns. The yield of the fibril aggregates based on the dry weight of the starting material was 96.5%.

Example 2

An aqueous suspension of second-cut crude linters was prepared, passed through a screen to remove any dust, and then dewatered. To the resulting wet material was added an aqueous solution of sodium hydroxide. After being stirred well, the mixture was placed in an autoclave and steam was blown thereinto to cook the linters at 160°C for 2 hours. The cooked linters were washed with water, dewatered and then treated in one stage with sodium hydrochlorite to obtain bleached linter pulp having a brightness of 85.2%. This bleached linter pulp was dewatered by means of a centrifuge to obtain hydrous pulp consisting of substantially lignin-free cellulose fibers and having a water content of 71.8%. This hydrous pulp was suitably broken into pieces, which were enclosed in the same pressure vessel as used in Example 1. Using saturated steam having a gauge pressure of 20 kg/cm^2 and following the same procedure as described in Example 1, the application of pressure and heat to the pulp was carried out under such conditions that a maximum temperature of about 200°C was held for 3 minutes.

When the resulting thick slurry of finely divided cellulose particles was observed under a microscope, most of the particles consisted of

microfibril aggregates having lengths of 50 microns or less. The yield based on the refined linter pulp was as high as 97.1%.

Example 3

Domestic mixed hardwood chips were cooked according to the calcium base sulfite process. Thus, unbleached pulp having an cuoxam relative viscosity of 7.6 and a Permanganate number of 5.8 was obtained in a 42.5% yield based on the chips. This unbleached pulp was treated in five stages with chlorine, caustic soda, chlorine, caustic sold and sodium hypochlorite to obtain bleached dissolving grade pulp. This bleached pulp was hand made into a sheet, which was air-dried to obtain a dry sheet consisting of substantially lignin-free cellulose fibers and having a water content of 10.5%. This sheet was cut into pieces measuring 5 cm x 5 cm and enclosed in the same apparatus as used in Example 1. Using saturated steam having a gauge pressure of 28 kg/cm^2 and following the same procedure as described in Example 1, the pieces were treated under such conditions that a maximum temperature of about 230°C was held for 16 minutes. Thus, there was obtained a thick slurry of finely divided cellulose particles having a light-brown color.

When the resulting suspension of finely divided cellulose particles was observed under a microscope, most of the particles consisted of microcrystals and microfibril aggregates having lengths of 2 microns or less. The yield based on the charged pulp was 91%.

Example 4

A slurry of bleached dissolving grade pulp was prepared according to the same procedure as described in Example 3, and adjusted to pH 2.5 by the addition of dilute sulfuric acid. This slurry was dewatered by compression and the resulting cake was crushed to obtain granules having a water content of 57.0%. Using saturated steam having a gauge pressure of 18 kg/cm^2 and following the same procedure as described in Example 1, these granules were treated under such conditions that a maximum temperature of about 202°C was held for 10 minutes. Thus, there was obtained a slurry of finely divided cellulose particles having a pale-yellow color. This slurry was formed into an aqueous suspension having a solid content of 10%. Sodium hypochlorite was added thereto in an amount of 1.2% (as available chlorine) based on the cellulose. Using an initial pH of 12, the suspension was bleached at 50°C for 2 hours. Thereafter, the

suspension was filtered and then washed with water which had been adjusted to pH 4.0 with sulfurous acid. This procedure was repeated several times. When the resulting finely divided cellulose particles were observed under a microscope, most of them consisted of fibril aggregates having lengths of 100 microns or less. The yield based on the charged pulp was 90%.

Then, these finely divided cellulose particles were formed into an aqueous suspension having a solid content of 12%. This suspension was treated in a spray dryer (Model L-12; Oogawara Kakoki Co.) to obtain finely divided cellulose particles in dry form. The conditions under which this spray drying was carried out included a feed rate of 10 kg/hour, an atomizer speed of 25,700 rpm, an inlet gas temperature of 150°C and an exhaust gas temperature of 90°C. Some properties of the resulting finely divided cellulose particles in dry form are shown in the following table.

Table

Degree of polymerization	200	
Copper number	13.3	
Water content	50%	
Ash content	0.04%	According to the testing methods for "Crystalline Cellulose" described in the Japanese Pharmacopoeia.
Water-soluble matter	1.5 mg/5 g	
Apparent volume	2.5 cc/g	
100-mesh residue	4.5%	

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CLAIMS:

1. A process for producing finely divided cellulose particles which comprises the steps of enclosing substantially lignin-free cellulose fibers in a pressure vessel, applying pressure and heat to said cellulose fibers in a hydrous condition, and then discharging said cellulose fibers explosively into a receiver tank at atmospheric pressure and thereby reducing said cellulose fibers to fine particles.

2. A process as claimed in claim 1 wherein said substantially lignin-free cellulose fibers comprise chemical pulp for paper-making use, chemical pulp for dissolving use, or cotton fibers, these materials being obtained by subjecting a fibrous material selected from the group consisting of wood fibers, bast fibers and seed fibers to a treatment for the removal of lignin.

3. A process as claimed in claim 1 wherein said step of applying pressure and heat to said cellulose fibers in a hydrous condition is carried out using pressurized saturated steam.

4. A process as claimed in claim 3 wherein said pressurized saturated steam has a gauge pressure of 5 to 30 kg/cm^2.