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(54) Title:
MICROCRYSTALLINE CELLULOSE MANUFACTURE

(57) Abstract:
The present invention relates to a new method for producing microcrystalline cellulose using never-dried pulp as the cellulose source.


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MICROCRYSTALLINE CELLULOSE MANUFACTURE

FIELD OF INVENTION

This invention generally relates to a method for producing microcrystalline cellulose (or MCC) from a cellulose source material, and more particularly, to the production of MCC using never-dried pulp as the cellulose source.

BACKGROUND OF INVENTION

Microcrystalline cellulose is a well-known material that has a wide variety of commercial applications, for example in food, pharmaceutical and cosmetic preparations.

The traditional and preferred method of producing MCC from cellulosic materials includes the steps of acid hydrolysis of the cellulosic material, acid neutralization typically with ammonium hydroxide, filtering, washing and drying to yield MCC. In the acid hydrolysis step, the acid removes amorphous cellulose material leaving a substantially insoluble residue comprising microcrystals of cellulose, also called cellulose crystalline aggregates and commonly referred to in the art as MCC, or in earlier publications as level of degree of polymerization (“LODP”) cellulose. O.A. Battista “Hydrolysis and Crystallization of Cellulose,” *Industrial and Engineering Chemistry*, 42, pp. 502-507 (1950). The MCC can be further processed by attrition or other means to produce colloidal particles or to produce a form suited for a particular end use.

Many different cellulosic materials have been effectively used in MCC manufacture, with the most common being wood pulp. Wood pulp has traditionally been available in sheet form, having been formed into sheets and dried for ease of storage and transport. When used to manufacture MCC, such wood pulp sheets must be shredded or broken apart and rewetted in a mineral acid solution (hydrolysis) in order to reconstitute a pulp slurry, which is then used in the MCC producing process. Thus, the traditional process requires the steps of forming a pulp sheet, drying the pulp sheet, breaking the pulp sheet apart and
re-wetting the pulp sheet.

U.S. patents 3,141,875, 3,146,168, 3,251,824, 3,278,519 and 3,357,845 to Battista disclose various articles, structures and pharmaceutical compositions made from cellulosic materials. The cellulosic material is produced through hydrolysis of a cellulose ether or a cellulose ester of an organic acid with hydrochloric acid, followed by mechanical disintegration of the resulting hydrolyzed, water insoluble crystals in an aqueous medium which can be neutral or alkaline, to form colloid-forming particles.

U.S. patent 2,978,446 to Battista discloses a method for making MCC which includes hydrolyzing a purified cellulose source with hydrochloric acid, filtering to remove the hydrolyzed amorphous cellulose from the crystalline cellulose, mechanically disintegrating the crystals in an aqueous acidic medium, neutralizing the acid and washing the resulting cellulose crystals.

It is known in the art to utilize never-dried pulp as the starting material in MCC manufacture via enzymatic hydrolysis with cellulase. U.S. patent 5,346,589 to Braunstein discloses a method of making MCC wherein the cellulose source is never-dried pulp. However, the never-dried pulp is hydrolyzed with a cellulase enzyme rather than acid.

The use of fibrillated never-dried pulp as the starting material in the manufacture of MCC is also known. U.S. patent 4,391,973 to Cruz, Jr. discloses a method for making what is referred to as “a new physical form of cellulose” with properties that are clearly different than those of MCC. The starting material is preferably fibrillated never dried pulp and the process is similar to the known process for MCC manufacture as taught in the aforementioned '446 patent to Battista, except that the pulp, is “fibrillated" prior to hydrolysis. This fibrillation, or milling, of the pulp replaces the mechanical disintegration of the isolated cellulose crystals as taught in the '446 patent, otherwise the process is identical: the pulp is
added to water and hydrochloric acid and heated to 104-106°C for 14-15 minutes, then is washed, filtered, neutralized and dried.

U.S. patent 4,427,778 to Zabriskie discloses a method of making MCC wherein the cellulose source is hydrolyzed with a cellulase enzyme. U.S. patent 5,175,275 to Dobashi discloses a method for preparing powdery crystalline cellulose by treating a cellulosic source material with a cellulase, subjecting the enzyme-treated cellulose material to mild acid hydrolysis, followed by mechanical disintegration of the hydrolyzed cellulose material. U.S. patent 6,037,380 to Venables discloses a method for the manufacture of colloidal MCC from MCC wherein the MCC is wet-ground with an attriting aid under high shear high solids mixing conditions.

None of the related art provides for a traditional method of producing MCC using never-dried pulp as the cellulose source material. It is known that drying causes irreversible changes to the pulp fibers and reduces the ability of acid to penetrate the cellulose. (The Effect of Drying Conditions on the Swelling and Bonding Properties of Bleached Kraft, 2000, Thad C. Maloney and Hannu Paulapuro, Helsinki University of Technology, PO Box 6300, FIN-02015 HUT, Finland; Cellulose Cocrystallization in Hornification of Kraft Pulp, 1996, Roger Newman and Jacqueline A. Hemmingson, Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand). Since the method of the present invention utilizes never-dried pulp, said method reduces the time and cost of producing MCC. Further, because the fiber is never dried and is not made into sheets, the resulting fiber pulp has reduced fiber damage.

**SUMMARY OF THE INVENTION**

It is therefore an object of the present invention to provide a method of producing MCC from cellulosic materials, wherein the cellulose material is never-dried pulp.
Another object of the present invention is to provide a method of producing MCC from never-dried pulp, which method includes the traditional means of hydrolyzing a cellulose source with a mineral acid.

Another object of the present invention is to provide a method of producing MCC from never-dried pulp, wherein the never-dried pulp is any wood pulp, including but not limited to prehydrolyzed kraft hardwood, prehydrolyzed kraft softwood, hardwood sulfite, softwood sulfite, paper-grade softwood or paper-grade hardwood.

Another object of the present invention is to provide a method of producing MCC from never-dried pulp, which method includes the traditional means of hydrolyzing a cellulose source with a mineral acid, wherein the mineral acid is hydrochloric acid, sulfuric acid, phosphoric acid, or nitric acid.

A further object of the present invention is to provide a method of producing MCC from fibers that have not been subjected to heat or thermal energy for drying, thereby reducing the fiber damage produced through fiber handling in the process of sheet making and drying.

Another object of the present invention to reduce production time and cost by eliminating thermal drying, rolling/baling and shredding stages from the process of producing MCC.

Another object of this invention is to provide a method for producing MCC products which products are comparable in quality and functionality to existing MCC products and can be adapted for a variety of uses, including the use of MCC in the manufacture of various articles.

Other objects, features and advantages of the present invention will be apparent when the detailed description of the preferred embodiments of the
invention is considered which should be construed in an illustrative and not limiting sense as follows.

DISCLOSURE OF THE INVENTION

In accordance with a preferred embodiment of the invention, MCC is produced by subjecting never-dried pulp to acid hydrolysis and neutralizing the residue of the acid. The recovered cellulose is then subjected to various treatments in order to form microcrystalline cellulose. For instance, the pulp is then washed and dried to form MCC. Since the use of never-dried pulp eliminates the steps of drying the fiber, forming sheets and then rewetting the sheets to form a pulp slurry, this method reduces the time and cost of traditional MCC producing processes. Furthermore, since thermal drying of the wood pulp causes a collapse of lumen in the natural wood fibers (fiber hornification), which could lead to poor accessibility by acid during MCC manufacture, the never-dried pulp has higher acid accessibility, resulting in reduced processing time and cost.

The expression "never-dried" is intended to refer to a cellulose material that has not been dried using heat or other thermal energy during or following any type of preliminary processing after having been harvested. In this case, cellulose material subjected to mechanical dewatering or pressing that removes free liquid without the use of heat is considered to be never-dried pulp. The material may contain lignin and hemicelluloses. Such materials may include waste fiber or recycled fiber that is not thermally dried after the de-inking process.

Traditionally, a very high purity dissolving pulp (with a low hemicellulose content (<2.0%) and a high R-10 (up to 98%) is used as the starting material for MCC. In the present invention wherein never-dried pulp is used in the MCC producing process any type of wood pulp, regardless of purity may be used.
In a preferred method of the present invention, the never-dried pulp fibers may be any dissolving pulp grade including but not limited to prehydrolyzed kraft hardwood, prehydrolyzed kraft softwood, hardwood sulfite, softwood sulfite, paper-grade softwood or hardwood. Examples of prehydrolyzed kraft hardwood include ESTERCELL™, TYRCELL™, and VISCOCCELL™, all of which are commercially available from International Paper, Chemical Cellulose Business, 61 Carthage Point Road, Natchez, MS 39120.

Hydrolysis may be effected by various specific methods, including the use of various mineral acids. Examples of mineral acids include hydrochloric acid, sulfuric acid, nitric acid and phosphoric acid. Acid hydrolysis is carried out under traditional conditions. For instance, never-dried fiber can be subjected to hydrolysis at an acid concentration of 0.1 to 2.5 normal, a temperature of about 100°C to 125°C for about 5 to 25 minutes. Hydrolysis achieves substantially complete removal the amorphous form of the cellulose starting material and yields highly crystalline particulate cellulose.

The recovered cellulose consists essentially of aggregates of the so-called crystalline cellulose. This cellulose is separated by filtration and washed free of acid using methods well known in the art. Preferably, the wash may contain a small amount, about 1%, of ammonium hydroxide to insure the removal of the acid. The recovered cellulose is then dried according to methods well known in the art, for example flash drying or spray drying to form microcrystalline cellulose.

The following examples describe the manner and process of making and using the present invention and set forth the best mode contemplated by the inventors for carrying out the invention, but are not to be construed as limiting the invention.
Example 1:

Ten (10) grams (OD) of never-dried ESTERCELL™ fibers were placed in a three-necked flask fitted with a mechanical stirrer and positioned in a heating mantel. Deionised water was added to the flask to make a slurry having total water content in the reaction vessel of 634 ml. The slurry was stirred and heated to about 100°C. While stirring, hydrochloric acid (165.6 ml) was added to the slurry such that the final concentration of the hydrochloric acid was 2.5N. The temperature of the stirred slurry was raised to about 106°C. After 15 minutes the heating mantel was switched off and deionised water (100 ml) was added to the reaction vessel. The fiber suspension was filtered through a sintered funnel containing two pre-wetted Whatman #541 filter papers, washed with deionised water. The cellulose was then transferred to a 500ml beaker and approximately 300ml of deionised water was added to the beaker. The solution was then neutralized to pH 7 with ammonium hydroxide (1%). Using a sintered funnel, the cellulose was rewashed with deionised water (500ml). The final slurry was freeze-dried.

Example 2:

Example 1 was repeated but the time period for hydrolysis at about 106°C was 10 and 20 minutes, respectively.

Example 3:

In this example, machine dried ESTERCELL™ fibers were used instead of the never-dried fibers. A pulp slurry of the machine-dried ESTERCELL™ in water was prepared before adding the acid. All other processing steps remained the same.

Example 4:

A three-necked flask fitted with a stirrer and positioned in a heating mantel was filled with 800ml of 2.5N hydrochloric acid and heated up to about 106°C. Then, 10 grams (OD) machine-dried ESTERCELL™ fiber was added to
the flask to form an acid slurry. The slurry was stirred and the temperature of the stirred slurry was maintained at about 106°C for 15 minutes. Then, 100 ml of deionised water was added to the reaction vessel to form a fiber suspension. The fiber suspension was then filtered through a sintered funnel having two pre-wetted Whatman #541 filter papers and washed with deionised water. The cellulose was then transferred to a 500 ml beaker and deionised water was added to approximately 300 ml. The solution was then neutralized to pH 7 with ammonium hydroxide (1%) and the cellulose was rewashed with deionised water (500 ml) using the sintered funnel. The final slurry was freeze-dried.

Example 5:

In this Example, never-dried SOLVEKRAFT™ fibers were used. All processing steps are the same as Example 1. SOLVEKRAFT™ is commercially available from International Paper, Chemical Cellulose Business, 61 Carthage Point Road, Natchez, MS 39120.

Example 6:

In this Example, machine-dried SOLVEKRAFT™ pulp was used instead of never-dried SOLVEKRAFT™ fibers. All processing steps were the same as in Example 4.

The hydrolysis time, and leveling-off degree of polymerization (LODP) of the MCC powders produced in Examples 1-6 are shown in Table 1. LODP is a property of MCC that is commonly measured and can indicate product performance. LODP is a measurement of the number of glucose molecules in the cellulose chain.

The LODP value is dependent primarily upon the starting cellulosic material and to a lesser extent upon the severity of the hydrolyzing conditions. In general, the LODP of native cellulose fibers is in the range of between 200 and 300, whereas that derived from regenerated cellulose lies in the range of
from 25 to about 60. Table 1 shows that for the same hydrolysis conditions, the LODP is higher for never-dried pulps. This provides the manufacturer of MCC with the added advantage of being able to modify the processing conditions, for example, decreasing hydrolysis time or acid concentration for a given temperature to produce the same LODP for a dried pulp.

<table>
<thead>
<tr>
<th>EXAMPLE 1</th>
<th>CELLULOSE MATERIAL</th>
<th>HYDROLYSIS TIME</th>
<th>LODP</th>
<th>REMARKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ESTERCCELL™</td>
<td>15 minutes</td>
<td>158</td>
<td>Never-dried Pulp</td>
</tr>
<tr>
<td>EXAMPLE 2</td>
<td>ESTERCCELL™</td>
<td>10 minutes</td>
<td>160</td>
<td>Never-dried Pulp</td>
</tr>
<tr>
<td></td>
<td>ESTERCCELL™</td>
<td>20 minutes</td>
<td>156</td>
<td>Never-dried Pulp</td>
</tr>
<tr>
<td>EXAMPLE 3</td>
<td>ESTERCCELL™</td>
<td>15 minutes</td>
<td>154</td>
<td>Machine-Dried Pulp</td>
</tr>
<tr>
<td>EXAMPLE 4</td>
<td>ESTERCCELL™</td>
<td>15 minutes</td>
<td>152</td>
<td>Machine-Dried Pulp</td>
</tr>
<tr>
<td>EXAMPLE 5</td>
<td>SOLVEKRAFT™</td>
<td>15 minutes</td>
<td>167</td>
<td>Never-dried Pulp</td>
</tr>
<tr>
<td>EXAMPLE 6</td>
<td>SOLVEKRAFT™</td>
<td>15 minutes</td>
<td>150</td>
<td>Machine Dried Pulp</td>
</tr>
</tbody>
</table>

Although the invention has been described with reference to preferred embodiments, which should be construed in an illustrative and not limiting sense, it will be appreciated by one of ordinary skill in the art that numerous modifications are possible in light of the above disclosure. For example, different acid strengths or different acids may be used. There is potential that a weaker acid is required
to hydrolyze amorphous cellulose of never-dried fibers as compared to machine-dried fibers. Further the current pulp making process may be modified to further reduce production time, chemical cost saving and yield improvements. All such variations and modifications are intended to be within the scope and spirit of the invention.
We claim:

1. A method of producing microcrystalline cellulose comprising selecting as a starting material, a never-dried cellulosic material.

2. The method of claim 1 wherein the cellulosic material is prehydrolyzed kraft hardwood.

3. The method of claim 1 wherein the cellulosic material is prehydrolyzed kraft softwood.

4. The method of claim 1 wherein the cellulosic material is hardwood sulfite.

5. The method of claim 1 wherein the cellulosic material is softwood sulfite.

6. The method of claim 1 wherein the cellulosic material is paper-grade softwood.

7. The method of claim 1 wherein the cellulosic material is paper-grade hardwood.

8. The method of claim 2 wherein the prehydrolyzed kraft hardwood is ESTERCELL™.

9. The method of claim 2 wherein the prehydrolyzed kraft hardwood is TYRCELL™.

10. The method of claim 2 wherein the prehydrolyzed kraft hardwood is VISCOCELL™.

11. A method of producing microcrystalline cellulose comprising:
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(a) selecting as a starting material, a never-dried cellulosic material;
(b) subjecting the cellulosic material to acid hydrolysis;
(c) neutralizing the acid,
(d) washing; and
(e) drying to form microcrystalline cellulose.

12. The method of claim 11 wherein the cellulosic material is prehydrolyzed kraft hardwood.

13. The method of claim 11 wherein the cellulosic material is prehydrolyzed kraft softwood.

14. The method of claim 11 wherein the cellulosic material is hardwood sulfite.

15. The method of claim 11 wherein the cellulosic material is softwood sulfite.

16. The method of claim 11 wherein the cellulosic material is paper-grade softwood.

17. The method of claim 11 wherein the cellulosic material is paper-grade hardwood.

18. The method of claim 12 wherein the prehydrolyzed kraft hardwood is ESTERCELL™.

19. The method of claim 12 wherein the prehydrolyzed kraft hardwood is TYRCELL™.

20. The method of claim 12 wherein the prehydrolyzed kraft hardwood is
21. The method of claim 11 wherein the acid hydrolysis step is carried out with dilute sulphuric acid.

22. The method of claim 11 wherein the acid hydrolysis step is carried out with dilute hydrochloric acid.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

- IPC(7) : D01C 3/00
- US CL. : 169/9, 19, 25

According to International Patent Classification (IPC) or to both national classification and IPC.

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

- U.S. : 169/9, 19, 25

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>US 5,345,229 A (BRAUNSTEIN et al) 13 September 1994, see col. 3, lines 21-33.</td>
<td>1, 2, 11, 12, 21, 22</td>
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<td>3-10, 13-20</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

- * Special categories of cited documents:
  - ′A′ document defining the general state of the art which is not considered to be of particular relevance
  - ′E′ earlier document on or after the international filing date
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