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CONVERTING FIBROUS CELLULOSE INTO AN EASILY POWDERABLE FORM

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This invention relates to the treatment of cellulose and to its conversion into cellulose derivatives, especially cellulose ethers and esters.

As is well-known cellulose in its naturally occurring forms is almost always fibrous in structure and appearance. The fibres may be long, as in the seed hairs of cotton and in bast fibres such as flax, jute and ramie; or they may be quite short as in some forms of wood pulp, notably pulps obtained from hardwoods, and also some types of cotton linters. As a consequence raw cellulose is supplied in commerce either as a baled and compressed fibrous mass or in the form of compressed fibrous sheets. It is however often desirable to have the cellulose in the form of small particles. Various methods are available for converting compressed baled or sheet cellulose into such a form; the most common method is probably shredding, which converts the compressed cellulose mass of high density into a loose fluffy material of low packing density. In all the known industrial methods the ultimate particles are in the main the original fibres of which the compressed cellulose mass was made up, and it has heretofore been very difficult, if not impossible, to convert fibrous cellulose into a form having a high packing density, as for example a substantially non-fibrous powder.

The present invention provides a method whereby cellulose, for example cotton linters or wood pulp cellulose, can be converted into a flake or powder form of high packing density, showing little or nothing of the original fibrous structure.

We have found that fibrous cellulose can be converted into a form which is easily flaked or powdered by subjecting it to heat and mechanical pressure such that in appearance it partly sinters, but does not char. (While it is necessary that the product shall appear to be partly sintered, the possibility that actual sintering takes place is not excluded.) Preferably the cellulose is at the same time subjected to a shearing action. It is advantageous that the greater part or all of the heat required should be generated within the cellulose by the mechanical deformation to which it is subjected.

In the preferred method of carrying out the invention, the cellulose, for example in the form of a compressed sheet such as a sheet of the type in which wood pulp is commonly supplied and transported, is passed through the nip of one or more pairs of closely set hard-surfaced rolls, the treatment being repeated as may be necessary at least until the cellulose appears to have lost its fibrous form and is in the form of a brittle sheet.

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This brittle sheet may then be subjected to further treatment on the rolls until it is broken down to flakes or powder of the desired degree of fineness, or it may be broken down in some other way, for example in a hammer mill.

The rolls may, for example, be made of or surfaced with steel and are preferably provided with means for cooling or heating them and with means for varying the width of the nip and the relative peripheral speeds of the rolls; thus, rolls of the type frequently used for working rubber may be used with very good results in the present process. The rolls may be kept at or even below room temperature, or they may be heated, e. g. to a temperature between about 50° and 100° C. and especially to about 60°–80° C. Temperatures above about 150° C. are preferably not used. The rolls may be run at the same or different peripheral speeds; preferably the ratio of the peripheral speeds is between about 1.0 and 1.5 or 2.0 and especially about 1.25. The clearance at the nip is preferably less than 0.05 in. and especially less than 0.025 in., a clearance of 0.01 to 0.025 in. usually giving the best results.

The cellulose to be treated need not be given any special treatment before it is passed through the rolls. Thus it may be in a normal air-dry condition. We have, however, found that when the cellulose contains a substantial proportion of moisture, especially above 8%, the product has a somewhat higher molecular weight than when moisture-free cellulose or cellulose containing considerably less than 8% of moisture is treated. Thus before being passed through the rolls the cellulose may be conditioned by steaming, or a fine spray of water may be directed on to the cellulose before it reaches the rolls. If desired, a small proportion of an anti-oxidant, e. g. hydroquinone, may be applied to the cellulose before it enters the rolls, in order still further to conserve the original molecular weight. For example, if the cellulose is sprayed as described above, the spray may contain an anti-oxidant in solution.

The number of passages through the rolls required to convert the cellulose into an easily powderable form will depend partly on the moisture content of the cellulose entering the rolls. As a rule, the lower this moisture content, the more rapidly is the cellulose converted, while with moisture contents above 8%, e. g. 11% or higher, a rather longer treatment is required. Similarly, when dry cellulose or cellulose of low moisture content is treated, it can usually be broken down all the way to a fine powder on the rolls, but when cellulose of a higher moisture content is treated,

it is often found to be better to convert the brittle mass first formed into flake or powdered form by means of a separate treatment, for example in a hammer mill or like device.

Cellulose of high packing density produced in accordance with the invention may be converted into alkali cellulose, for example for further conversion into cellulose ethers or viscose, or it may be acetylated, propionylated or otherwise esterified, or it may be converted into other derivatives. Alkali cellulose may, for example, be made by mixing powder or flake cellulose with powder or flake caustic soda, or with a highly concentrated caustic soda solution, for example as described in United States applications S. Nos. 51,655 and 51,656, both filed September 28, 1948, of the present applicants and M. H. Wilcox; or it may be made by mixing the powder or flake cellulose (preferably the former), with aqueous caustic soda of less high concentration, especially concentration between about 18% and 50% or 65%. When fibrous cellulose, for example a sheet of wood pulp cellulose or the loose fluffy cellulose of low packing density obtained by shredding such a sheet, is treated with an alkali solution of concentration between about 18% and 60%, it is usually necessary, if a uniform product is to be obtained, to employ much more alkali solution than corresponds to the amount of alkali it is desired to introduce into the cellulose, and then to remove the excess solution by pressing or other means. When on the other hand the cellulose is in the form of a powder or flake of high packing density, as is produced in accordance with the present invention, we have found it sufficient to employ only as much solution as corresponds to the amount of alkali required in the alkali cellulose, so avoiding the necessity for pressing out excess solution. For example, if an alkali cellulose is desired containing two moles of caustic soda for each mole of cellulose (reckoned as one anhydro-glucose unit), the powder or flake cellulose may be stirred with a 20-65% caustic soda solution containing the desired amount of caustic soda until the solution has been substantially completely absorbed by the cellulose.

Alkali cellulose made from the cellulose of high packing density has itself a high packing density. While it may be used for any of the purposes for which alkali cellulose in general is employed, for example for viscose production, it is particularly useful when it is desired to react the alkali cellulose with a solid in the substantial absence of solvent or diluent. Examples of such processes are the production of carboxymethyl cellulose by reaction of alkali cellulose and sodium chloroacetate or chloroacetic acid, and the production of sulpho-ethyl cellulose by reaction between alkali cellulose and sodium 2-chloro-ethyl sulphionate. Thus carboxymethyl cellulose (in the form of its sodium salt) is ordinarily made by mixing alkali cellulose and chloroacetic acid or its sodium salt in a Werner Pfeleiderer mixer, very vigorous and thorough mixing throughout the time needed for the greater part of the reagents to react being necessary if a product of good and uniform properties is to be obtained. If the alkali cellulose is in powder or flake form of high packing density, a very much shorter time of vigorous mixing is necessary and the reaction may then be completed by allowing the mixture of reagents to stand in bins, or by simply tumbling it; moreover the Werner Pfeleiderer mixer may be replaced by less efficient but

cheaper devices. A similar procedure may be adopted in the production of sulpho-ethyl cellulose.

The alkali cellulose of high packing density can also be used with advantage in processes wherein the alkali cellulose is reacted with a liquid. For example, when making ethyl or methyl cellulose by reaction between alkali cellulose and the appropriate alkyl chloride in the liquid phase, it is usually necessary to use a large excess of the alkyl chloride, proportions of 20-30 moles for each mole of alkali cellulose being frequently specified. If in such case cellulose of high packing density is employed, the proportion of alkyl chloride can be reduced, for example by a half or more. Furthermore, it is found that when the alkali cellulose of high packing density is employed, it is often possible to perform the reaction without stirring and yet obtain a product having uniform properties.

As already stated, the powder or flake cellulose of high packing density is also suitable for esterification, e. g. acetylation. The usual methods may be employed. It is advisable as a rule to give an activating pretreatment, as it is with the forms of cellulose used heretofore; for example, the cellulose may be pretreated with acetic acid which preferably contains a little water, say 2-7%, especially when the cellulose has not had time to regain its equilibrium water content after the treatment on the rolls. Owing to the ease and rapidity with which the powder or flake cellulose mixes with and is wetted by the various reagents, as compared with the various fibrous forms of cellulose, it is particularly suitable for use in continuous processes.

The following examples illustrate the invention:

Example 1

An air-dry sheet of a purified wood pulp (a so-called rayon pulp) was passed a number of times through the nip of a pair of steel rolls heated to about 60° C., set to a clearance of 0.015 in., and running at the same peripheral speed, until a brittle, semi-transparent sheet was obtained in which the original fibrous structure was no longer obvious. This sheet was then broken up in a hammer mill to form a mixture of small flakes and fine powder. The powder was separated by screening the mixture on a 40-mesh sieve, and the flakes were then screened on a 15-mesh sieve. The density of the original sheet was 29.5 lb./cu. ft.; the packing density of the 15-mesh flakes was 28.5 lb./cu. ft. and that of the 40-mesh powder was above 30 lb./cu. ft. For comparison, it may be stated that the packing density of shredded wood pulp is usually in the neighbourhood of 5 or 6 lb./cu. ft.

These and other packing densities given in the present specification were determined by the following method: A 100 cc. measuring cylinder is filled with the cellulose, and is then dropped twenty times through 3 inches onto rubber; the final volume occupied by the cellulose is then noted and the cellulose is weighed.

Example 2

An air-dry sheet of purified wood pulp was passed repeatedly through a pair of steel rolls heated to 65° C. and set to a clearance of 0.015 in., the peripheral speeds of the rolls being in the ratio of 5:4, until the greater part of the cellulose had been reduced to a fine powder. The cellulose was then screened on a 40-mesh sieve,

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and the residue on the sieve was again passed through the rolls until it, too, had been powdered. The two powders were mixed, and the blend had a packing density of about 35 lb./cu. ft.

Example 3

A sheet of purified wood pulp was conditioned to a moisture content of 11.6% and then was passed several times through a pair of unheated rolls set to a clearance of 0.02 in. A hard horn-like sheet was formed which could not easily be reduced to a powder by further treatment on the rolls, but which on being broken up in a bridge Banbury mill gave a powder of packing density above 30 lb./cu. ft.

Example 4

Air-dry cotton linters were passed several times through rolls heated to 65°-80° C. A flake was formed which could easily be powdered, either by further treatment on the rolls or by means of a hammer mill, to give a product of packing density about 35 lb./cu. ft.

Example 5

Carboxymethyl cellulose in a useful powder form was made by the following method from a powdered cellulose of packing density of about 35 lb./cu. ft. obtained as described in Example 2.

17 parts by weight of the powdered cellulose (1 mole) and 32 parts by weight of a 25% aqueous caustic soda solution (2 moles caustic soda) were well mixed in a Werner Pfeiderer mixer. 7 parts by weight of chloroacetic acid (0.75 mole) was then added and mixing continued for 10 minutes; the resulting composition was then allowed to stand with occasional mixing for 4 hours and without any mixing for a further 16 hours. The product was washed with 80% methanol and was then obtained as a white freely flowing powder, completely soluble in hot and cold water, and consisting of 97.15% sodium carboxymethyl cellulose and 2.85% sodium carbonate. Its 2% aqueous solution had a viscosity of 192 cps. and a clarity of 28%.

Example 6

Air-dry powdered cellulose (1 mole) obtained as described in Example 2 was milled for a few minutes in a Werner Pfeiderer mixer with 2.4 moles of caustic soda in 31.5% aqueous solution. 0.7 mole of sodium 2-chloroethane sulphonate was added and mixing was continued for 5 to 10 minutes. During the next 3 hours the mixture was allowed to stand with two 5 minute periods of mixing. It was then transferred to a substantially air-tight container in which it was kept at 50° C. for 27 hours, and at room temperature for another 15 hours. The reaction was conducted under nitrogen throughout. The sulphoethyl cellulose formed was washed with ethanol. It was completely soluble in water and gave a colourless solution of good clarity.

Example 7

Air-dry powdered cellulose (1 mole) obtained as described in Example 2 was introduced into an autoclave at a charging density of 0.08 kgm./litre of reaction space, and stirred for 3 hours with about 4 times its weight of a 60% caustic soda solution at 60° C. under nitrogen. The reactor was then evacuated and about 10 moles of ethyl chloride admitted. The mixture was heated to 125°-130° C. for about 8 hours, stirring all the time. After being cooled the ethyl cellulose formed was still largely in the form of a powder,

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and although it showed some tendency to agglomerate and form lumps, these lumps were very friable and easily reconverted into powder. The ethyl cellulose was washed free from alkali with water. It gave a smooth solution in 80/20 benzene/ethanol, and its ethoxyl content was about 44%.

Example 8

Air-dry powdered cellulose obtained in accordance with Example 2 was introduced into an autoclave at a charging density of 0.05 kgm./litre of reaction space, and stirred for 2 hrs. with 1.4 times its weight of a 41.5% caustic soda solution at 25° C. under nitrogen. The reactor was then evacuated and about 16 moles of methyl chloride admitted. The mixture was heated to 70°-95° C. for 2 hours, stirring all the time. The methyl cellulose formed was washed with water at 90° C. until free from salts and then dried at 110° C. It could very easily be broken down into a powder by passing it through a hammer mill. Its methoxyl content was 23.5% and it gave a 2% aqueous solution of good clarity, viscosity 229 cps. at 20° C., and coagulation temperature about 70° C.

Example 9

A powdered cellulose of packing density about 35 lb./cu. ft. produced from cotton linters as described in Example 4 was mixed with half its weight of 93% aqueous acetic acid and allowed to stand for 4 hours at 25° C. It was then fed into an acetylation mixture which had been precooled to 0° C. and which consisted of 3 parts by weight each of acetic acid and acetic anhydride and 14% of sulphuric acid, all based on the weight of the powdered cellulose. After 1¼ hours a clear solution was obtained, the peak temperature reached being 42° C. The solution was then ripened at 25° C. for 48 hours, and the cellulose acetate precipitated by means of dilute acetic acid. It had an acetyl value of 53.3%.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for the treatment of cellulose which is in a visibly fibrous form to render it more easily powdered, which comprises subjecting the visibly fibrous cellulose to the simultaneous action of mechanical pressure and shearing forces applied quickly to the cellulose by the combined forwarding and crushing action of two opposing rotating hard cylindrical surfaces having a temperature below 150° C. and a clearance at the nip less than 0.05 inch, whereby there is generated in the cellulose sufficient heat to raise it to an elevated temperature below its charring temperature, and the visibly fibrous cellulose is changed into a brittle form no longer possessing a fibrous appearance.

2. Process for the treatment of cellulose which is in a visibly fibrous form to render it more easily powdered, which comprises subjecting the visibly fibrous cellulose to the simultaneous action of mechanical pressure and shearing forces applied quickly to the cellulose by the combined forwarding and crushing action of two opposing rotating hard cylindrical surfaces having a temperature below 150° C. and a clearance at the nip less than 0.05 inch, the ratio of the speeds of the said surfaces being between 1:1 and 1:1.5, whereby there is generated in the cellulose sufficient heat to raise it to an elevated temperature below its charring temperature, and the visibly fibrous cellulose is changed into a brittle form no longer possessing a fibrous appearance.

3. Process according to claim 2, wherein the

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visibly fibrous cellulose is treated as a compact sheet of fibres.

4. Process according to claim 2, wherein the visibly fibrous cellulose is treated as a mass of loose fibres.

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5. Process for the treatment of cellulose which is in a visibly fibrous form to render it more easily powered, which comprises moistening the visibly fibrous cellulose with water and subjecting the moistened cellulose to the simultaneous action of mechanical pressure and shearing forces applied quickly to the cellulose by the combined forwarding and crushing action of two opposing rotating hard cylindrical surfaces having a temperature below 150° C. and a clearance at the nip less than 0.05 inch, the ratio of the speeds of the said surfaces being between 1:1 and 1:1.5, whereby there is generated in the cellulose sufficient heat to raise it to an elevated temperature below its charring temperature, and the visibly fibrous cellulose is changed into a brittle form no longer possessing a fibrous appearance.

6. Process according to claim 5, wherein the visibly fibrous cellulose is treated as a compact sheet of fibres.

7. Process according to claim 5, wherein the

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visibly fibrous cellulose is treated as a mass of loose fibres.

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