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(54) Title: TREATMENT OF A MIXTURE CONTAINING CELLULOSE WITH A REDUCING AGENT

(57) Abstract: The present invention relates to a method for treating a mixture containing cellulose, comprising at least one step of adding at least one agent capable of reducing carbonyl groups. The invention further relates to a specialty cellulose pulp, obtained by a method comprising said treatment. Furthermore, the invention relates to the use of the specialty cellulose pulp according to the invention or the specialty cellulose pulp obtained by a method according to the invention for the production of cellulose derivatives or materials containing cellulose molecules, including but not limited to, cellulose ethers or cellulose esters. Cellulose derivatives obtained from the specialty cellulose pulp according to the invention display increased viscosity and/or improved brightness over cellulose derivatives obtained from specialty cellulose pulp not subjected to the inventive treatment.

TREATMENT OF A MIXTURE CONTAINING CELLULOSE WITH A REDUCING AGENT

Field of the Invention

The present invention relates to a method for treating a mixture containing cellulose, comprising at least one step of adding at least one agent capable of reducing carbonyl groups. The invention further relates to a specialty cellulose pulp, obtained by a method comprising said treatment. Furthermore, the invention relates to the use of the specialty cellulose pulp according to the invention or the specialty cellulose pulp obtained by a method according to the invention for the production of cellulose derivatives or materials containing cellulose molecules as a raw material, including but not limited to, cellulose ethers or cellulose esters. Cellulose derivatives obtained from the specialty cellulose pulp according to the invention display increased viscosity and/or improved brightness over cellulose derivatives obtained from specialty cellulose pulp not subjected to the inventive treatment.

Background of the Invention

Although the method according to the invention can be employed for any mixture containing cellulose, by way of example, the treatment of mixtures containing

cellulose leading to specialty cellulose pulp is used to illustrate the particular embodiments. However, this shall not be construed to mean that the method as claimed is only applicable to specialty cellulose pulp. For the purpose of the present invention, wherever applicable, the term "specialty cellulose pulp" is synonymous to the general term "pulp".

Specialty cellulose pulp is used to manufacture a number of products that require physical and chemical properties not provided by the pulp used for the manufacture of standard paper, linerboard or cardboard. Specialty cellulose pulp therefore differs from the major portion of cellulose pulp produced in the world today.

Any treatment that a mixture containing cellulose is subjected to, in particular if it is to be used as specialty cellulose pulp, has to be performed as to maintain the properties important to the end use, in particular the integrity of the cellulose molecules themselves. One of the most important steps of treatment of a mixture containing cellulose, typically obtained from pulping wood, is a step of bleaching, or, in most applications, a multi-stage bleaching process. Bleaching is commonly achieved by treating a pulp slurry with chemicals that either remove colored compounds such as lignin, or alter the structure of colored compounds so that they are no longer colored. The extent to which a specialty cellulose is bleached depends on the requirements for the end-product manufactured from the specialty cellulose pulp.

The expert in the field typically understands a bleaching process as one that increases the ISO brightness of a mixture containing cellulose. Futhermore, the expert in the field typically understands that bleaching is achieved primarily by oxidation processes, i.e. bleaching of any mixture containing cellulose according to the prior art typically involves the application of an oxidizing agent. For environmental reasons, common elemental chlorine bleaching using chlorine and/or hypochlorite is successively replaced by elemental chlorine free bleaching (ECF) processes, wherein chlorine dioxide replaces chlorine and/or hypochlorite. Totally

chlorine free (TCF) bleaching uses chlorine-free bleaching agents such as oxygen or peroxides. A method for the non-chlorine bleaching of cellulose pulp using oxygen gas in sophisticated treatment stages is described in, for example, US 6 126 782. Other oxidizing agents are ozone or enzymes. JP-A 0 6 033 390 for example discloses a method for using ozone to bleach pulp. A main concern is to limit the oxidizing agent exposure time in order to limit damage to the cellulose molecules.

In summary, bleaching techniques known to the expert in the field typically involve oxidizing agents. The degree of ISO brightness achievable by these methods of bleaching is limited to the extent that strong oxidizing agents (or highly concentrated oxidizing agents) which would result in a high degree of ISO brightness also tend to damage the cellulose molecules. In particular, strong or highly concentrated oxidizing agents tend to reduce the degree of polymerization (DP) of the cellulose.

A process known as "reductive bleaching" is used commonly for brightening virgin mechanical pulps or pulp from recycled newsprint. In this process, a reducing agent, typically sodium borohydride, is used to generate sodium hydrosulfite in situ from primary chemicals, i.e. the reducing agent is not used to reduce carbonyl-groups in the pulp but to generate a bleaching agent. This process is disclosed, e.g. on pages 502 through 504 of "Pulp Bleaching; Principles and Practice", Dence and Reeve (Eds.), TAPPI Press, 1996.

The use of reducing agents is also known in the context of late stages of the treatment of cellulose pulps. For example, US 5 501 711 discloses the use of borohydrides to treat cellulose fabric that already had been subjected to a bleaching treatment. Here, the application of reducing agents improves the dyeability of said cellulosic fibers. The US 6 217 621 relates to stripping textile fibers, including cellulose acetates and other products obtained from specialty cellulose pulp, of their dyes by using reducing agents such as borohydrides.

Another process involving the use of reducing agents in the context of the treatment of cellulose pulp is disclosed in US 5 035 772. Said process involves treating a cellulose pulp that had already been bleached with one or more reducing agents in order to reduce carbonyl groups on the lignin contained in the cellulose pulp. The process includes adding a complexing agent together with the reducing agent and processing the mixture at a temperature not greater than 40^0C. This treatment is followed by at least one further step: either a treatment with a chemical that will block the phenolic hydroxyl groups of the lignin and/or a treatment to convert short-wave light quanta to long wave light quanta. The object of the process according to the US 5 035 772 is to prevent the yellowing with age of lignin contained in (high yield) cellulose pulps. The process is to be used with groundwood pulp, refiner pulp, thermo-mechanical and chemical-mechanical pulp for paper manufacture. Therefore, the US 5 035 772 does not relate at all to the treatment of specialty cellulose pulp.

Finally, the possible use of borohydrides has been discussed in "Pulp Bleaching; Principles and Practice", Dence and Reeve (Eds.), TAPPI Press, 1996, pages 297, wherein a borohydride is mentioned as a possible additive to eliminate some of the loss in strength of paper induced by the alkaline extraction.

The object of the present invention was to provide a method of treating a mixture containing cellulose, preferably a mixture containing cellulose leading to specialty cellulose pulp, so that the degree of brightness or the viscosity of cellulose derivatives obtained therefrom, or both, is/are increased over the prior art. In addition, as a result, a specialty cellulose pulp as such, leading to cellulose derivatives with increased viscosity and/or brightness was to be provided.

Summary of the Invention

Surprisingly, it was found that this object could be achieved by treating a mixture containing cellulose with at least one step of adding at least one agent capable of reducing carbonyl groups. This treatment can be performed at any stage of processing a mixture containing cellulose into specialty cellulose pulp once a mixture containing cellulose has been obtained from (i) chemically pulping wood (="cooking"), (ii) chemically and mechanically pulping wood or (iii) unpulped cotton or (iv) any combination of (i) to (iii). The inventive treatment is either the sole step of the entire process or is performed prior to bleaching and/or after bleaching or is performed as at least one step of a multi-stage bleaching process.

The solution according to the invention is particularly surprising since the prior art does not teach that treating a mixture containing cellulose, i.e. treating a pulp, leads to cellulose derivatives obtainable from the treated pulp with improved viscosity and/or brightness in comparison to a similar cellulose derivative obtained by the same process but excluding the inventive step of adding at least on agent capable of reducing carbonyl groups.

The present invention therefore relates to a method for treating a mixture containing cellulose, comprising at least one step of adding at least one agent capable of reducing carbonyl groups. The invention further relates to a specialty cellulose pulp, obtained by a method comprising said treatment. Furthermore, the invention relates to the use of the specialty cellulose pulp according to the invention or the specialty cellulose pulp obtained by a method according to the invention for the production of cellulose derivatives or materials containing cellulose molecules as a raw material, including but not limited to, cellulose ethers or cellulose esters. Cellulose derivatives obtained from the specialty cellulose pulp according to the invention display increased viscosity and/or improved brightness over cellulose derivatives obtained from specialty cellulose pulp not subjected to the inventive treatment.

Brief Description of the Figures

In FIG 1, the viscosity of the (derivative) end product obtained via estherification/etherification from the inventive specialty cellulose pulp, CMC, (vertical axis; units: mPa s) is shown as a function of the limiting viscosity number of the specialty cellulose pulp as defined in the standard "SCAN-CM 15:99" (horizontal axis, units: dm^3/kg).

In FIG 2, the brightness of CMC powder (vertical axis, units: % brightness) is shown as a function of the intrinsic brightness of the specialty cellulose pulp from which the CMC powder has been obtained by means of etherification (horizontal axis; units: % brightness)

FIG 3 shows a typical particle size distribution of a CMC powder after grinding in the Fritsch Pulvarisette 19 knife mill as used in Examples 1, 2 and 3. The horizontal x-axis represents the particle diameter in µm. while the vertical y-axis represents the volume of the corresponding particles in %.

Detailed Description of the Invention

A "mixture containing cellulose" according to the invention is any mixture that contains the glucose polymer of cellulose. No principal limitations exist as to the state of the cellulose source, i.e. it may be solid, liquid, a suspension, slurry, paste or powder. Furthermore, no limits exist as to the origin of the cellulose. In a preferred embodiment, the mixture containing cellulose is derived from cotton linters and/or wood. In a particularly preferred embodiment, the mixture containing cellulose is derived from wood. Other cellulose sources, in particular annual plants and/or biomass, (micro)biologically produced and/or derived cellulose, or cellulose from all types of cell walls are included as well.

Furthermore, no limitations exist with respect to the degree of polymerization of the mixture containing cellulose, as well as of any product, such as specialty cellulose pulp and/or derivatives thereof, obtained from said mixture containing cellulose.

According to the invention, the mixture containing cellulose may be derived from raw materials that need to be pulped. In general, the term "pulping" refers to any process that separates the cellulose from the at least one component that holds the cellulose together in the raw material. For example, in wood, the cellulose is held together by lignin and hemicellulose in fibers. The pulping process is meant to separate, at least partly, the lignin from the carbohydrate moieties of these fibers.

As to pulping processes, three different methods are commonly discerned: (i) chemical pulping (or "cooking"), (ii) mechanical (or "groundwood") pulping and (iii) semi-chemical or chemical-mechanical pulping. In (i), the raw material, typically wood, is cooked in a "digester" at elevated temperatures with chemicals suited to break the bonds between the cellulose molecules and the lignin. In (ii), the raw material is typically pressed against a grinder which physically separates the fibers. The process (iii) refers to any combination of (i) and (ii). In the context of the present invention, no principal limitations exist as to how the pulping is to be performed, so long as the pulping results in a mixture containing cellulose that can be subjected to the treatment according to the invention.

"Pulping" may not be necessary for all raw materials. For example, if cotton linters are used as the mixture containing cellulose, no chemical or mechanical pulping is necessary prior to any subsequent treatment, including the inventive treatment and/or bleaching.

A mixture containing cellulose that has been pulped as described above, is commonly referred to as "pulp". In the context of the present invention, the term "pulp" is to be seen as more general than the term "mixture containing cellulose", since the term "pulp" is meant to refer to the mixture containing cellulose before the inventive treatment *as well as* to the treated mixture, for example the specialty cellulose pulp as obtained after the inventive treatment. By contrast, the term "mixture containing cellulose" is only meant to describe the pulp *before* the treatment according to the invention.

Although the inventive method of treating a mixture containing cellulose with the objective to obtain specialty cellulose pulp can be, in principle, performed with any mixture containing cellulose, the method according to the invention is particularly effective, and therefore preferred, when applied to a mixture containing cellulose derived from wood. It is further preferred to pulp the wood chemically prior to the inventive treatment.

As far as wood as a source for the mixture containing cellulose is concerned, both hardwood and softwood tree species may be used. Examples of softwoods include but are not limited to: pines, in particular Southern pine, White pine, Caribbean pine; Western hemlock; spruces, in particular Norway Spruce, Sitka Spruce; Douglas fir or the like. Examples of hardwoods include, but are not limited to: gum, maple, oak, eucalyptus, poplar, beech, or aspen. Mixtures of two or more types of soft and/or hard wood are included as well.

Prior to the at least one step of adding at least one agent capable of reducing carbonyl groups and/or prior and/or during and/or after any step of pulping, the mixture containing cellulose may be optionally subjected to any type of pretreatment. Such types of pretreatment include but are not limited to enzyme treatments, mechanical refining, addition of additives, addition of complexing agents, treatment

with delignification and other catalysts, the removal of fines as well as any combination of the aforementioned steps.

After the mixture containing cellulose has been prepared and/or obtained and/or pretreated and/or treated with at least one agent capable of reducing carbonyl groups (i.e. the inventive treatment), the mixture may be subjected to a bleaching process. The term "bleaching" as used in the context of the present invention refers to any treatment of the mixture containing cellulose in which the degree of brightness after the bleaching is increased over the degree of brightness before bleaching. The term "ISO brightness" as used in the context of the present invention is defined in "ISO 2470-1999 - paper, boards and pulp - measurements of the diffuse blue reflectance factor (ISO brightness)" and refers to the brightness of the pulp. It is important to discriminate this term from the term "brightness" as used in the context of the present invention, which refers to the brightness of the end product, i.e. the derivative of the specialty cellulose pulp. A standard for measuring said brightness according to the invention is given in Example 6. In principle, bleaching can be performed with any agent capable of achieving the above mentioned objective.

At at least one stage of the processing of the mixture containing cellulose, obtained after pulping as has been described above, at least one agent capable of reducing carbonyl groups (= reducing agent) is added to the mixture containing cellulose. As a reducing agent in the context of the present invention, every compound or mixture of compounds can be used that results in at least the partial reduction of at least a part of the carbonyl groups in at least one of the components contained within the pulp.

Carbonyl groups form a part of the molecular structure of the main compounds in any mixture containing cellulose. As compounds are to be named, by way of example, cellulose, hemicellulose, lignin and resins. The carbonyl groups according to the invention that are, at least partially, reduced in the inventive step of adding

a reducing agent, may either be naturally present in the raw-material structures or may be generated during processing or both. This is particularly true of the mixtures containing cellulose used for the manufacture of specialty cellulose pulps derived from wood but is also the case, to a lesser extent, for pulp derived from other raw materials, such as pulp derived from cotton linters.

In principle, any agent that at least partially reduces at least a part of the carbonyl-groups present in the mixture containing cellulose can be used. Borohydrides are particularly preferred, while water-compatible borohydride salts are further preferred. Such salts include but are not limited to sodium borohydride, potassium borohydride, lithium borohydride, sodium cyanoborohydride, sodium triacetoxyborohydride, sodium trimethoxyborohydride, tetramethylammonium borohydride, tetramethylammonium triacetoxyborohydride, tetraethylammonium borohydride, tetrabutylammonium borohydride, tetrabutylammonium cyanoborohydride, cetyltrimethylammonium borohydride, benzyltriethylammonium borohydride, Bis(triphenyl-phosphine) copper(I) borohydride, lithium aluminium hydride, dimethylamineborane (DMAB) and mixtures of at least two of these. Preferably, said reducing agents used should be water-soluble.

The reducing agent can be used by itself, in combination with other reducing agents and/or in combination with stabilizers such as calcium hydroxide, magnesium bicarbonate or other mildly basic salts. Further additional substances with other purposes may be added as well.

The reducing agents and/or additional substances may be added as a solid, a powder, a dispersion, suspension, emulsion or as a solution. In a preferred embodiment, if borohydrides are used, they are used in powder form or in the form of a standard solution, e.g. sodium borohydride, which can be purchased as a 12 wt% solution in 40 wt% aqueous sodium hydroxide (e.g. Borol® from Rohm and Haas, Hydrafin™ from Finnish Chemicals (Nokia) Ltd). All commercially available

forms of these chemicals, as well as any chemical of this kind prepared in a laboratory, may be used to carry out the treatment of a mixture containing cellulose as disclosed here.

As has been mentioned above, the reducing agent may be added at any stage of the processing of the mixture containing cellulose. In a preferred embodiment, the reducing agent is added in at least one step during a multi-stage bleaching process.

In a particularly preferred embodiment, the at least one reducing agent is added, i.e. the inventive treatment is performed, at least as the last stage or after the last stage of a multi-stage bleaching process.

The content of reducing agent added in at least one step may vary from 0.01 to 500g, preferably from 0.1 g·mol/ton mixture containing cellulose (dry basis) to 2000 g·mol/ton mixture containing cellulose, depending on the chemical additives and the specific composition of the mixture containing cellulose. In a preferred embodiment of the invention, wherein sodium borohydride is added as the carbonyl-reducing agent and the sole purpose of the at least one step of the treatment is the chemical reduction of carbonyl groups, the charge is between 0.3 and 100 g·mol/ton mixture containing cellulose (on a dry basis).

In a further preferred embodiment, where sodium borohydride is added as the carbonyl-reducing agent and an additional purpose of the at least one step of the treatment is the delignification of the mixture containing cellulose, the charge is from 0.1 and 500 g·mol/ton mixture containing cellulose (on a dry basis), preferably from 0.1 to 80 g mol/ton.

In a preferred embodiment, the reducing agent is added as the at least one agent in at least one stage of a multi-stage bleaching process and/or is added as at least one of at least two agents in at least one stages of a multi-stage bleaching process. In particular, the reducing agents can be added simultaneously during the addition of one or more oxidizing agents, known to the expert in the field as the traditional bleaching agents, at one or more stages during a multi-stage bleaching process. It is also conceivable, that adding reducing and oxidizing agents occur as alternating or subsequent steps, optionally separated by steps of washing or otherwise treating the specialty cellulose pulp.

The reducing agent may be added together with any other agent or substance, so long as the at least one additional agent does not prevent the reducing agent to at least partly reduce at least a part of the carbonyl groups. In a preferred embodiment, the pH achieved in the pulp upon adding the at least one reducing agent is below 12.

As far as the at least one oxidizing agent that may be added in a multi-stage bleaching process is concerned, any agent(s) known to the expert in the field may be used. Examples of such oxidizing agents may be selected from but are not limited the following group: chlorine, chlorine dioxide, hypochlorite, chlorite, oxygen, per-compounds such as peroxide, and ozone, as well as mixtures of two or more of the aforementioned substances.

Another agent that is commonly used during the bleaching process of a specialty cellulose pulp, namely sodium hydroxide, may be added before and/or during and/or after any of the at least one step of bleaching as mentioned above. The main purpose of adding sodium hydroxide is the extraction of at least a part of the hemicellulose portion of the pulp, as well as, to some extent, regulation of the pH

value. The amount and/or conditions under which the sodium hydroxide is to be added are known to the expert in the art.

The aforementioned treatment of the mixture containing cellulose, can be carried out in any reaction device known to the expert in the field in the context of pulp bleaching processes, for example in a bleaching tower, so long as the device is adapted to comply with health and safety issues related to the use of the specific reducing agent(s) and/or any other agent used. There are no limitations as to the design and/or function of the reaction device. For example, it may be a vessel or a tube, operated in batch mode or continuously.

In a preferred embodiment, said reaction device will be a steel tower of the type known to the expert for commercial-scale cellulose pulp bleaching processes. In a further preferred embodiment, the device will be of dimensions such that cellulose retention time under reaction conditions ranges from up to 6 hours. Preferably, the device is of sufficient dimensions so that the reaction time ranges up to 3.5 hours. The actual size of the reaction device is, inter alia, determined by the pulp production rate in a continuous process and, correspondingly, by the batch volume in a batch process. Preferably, the reaction device is fitted with a fan capable of maintaining a level of hydrogen gas well below the explosion limit since hydrogen gas may be generated during treatment with a borohydride. Any other method capable of keeping the amount of hydrogen in the reaction device below the explosion limit, such as hydrogen scavengers, controlled reactions of hydrogen or purging the reaction device with inert gases or mixtures containing inert gases may be used as well.

The mixture containing cellulose that is to be subjected to the at least one step of the treatment according to the invention is pumped into the aforementioned reaction device. Preferably, it is pumped in the device in the form of an aqueous

slurry, having a content ranging from 0.1 to 40 wt% of pulp based on dry mass of the mixture containing cellulose, preferably a content ranging from 1 to 25wt%, further preferred ranging from 5 to 15 wt%. The mixing of the slurry with the reducing agents may take place either inside or outside the reaction device, by means of a chemical mixer or any other means that produces homogeneous mixing. Any other chemicals added to the reactor device (e.g. for pH adjustment, bleaching purposes, hemicellulose extraction purposes or as chemical aids to the main chemical functions in the process stage) may also be mixed into the slurry inside or outside the reaction device. Preferably, any mixing takes place outside of the reactor device, as this facilitates the formation of an homogeneous reaction slurry.

As far as the temperature at which the at least one reducing agent is added to the mixture containing cellulose, is concerned, any temperature is conceivable at which the at least one reducing agent at least partly reduces carbonyl groups contained in the mixture. In case of an integrated method comprising several process stages, in particular several stages of bleaching, the process temperature may be chosen to be suitable for all stages. In a preferred embodiment, the temperature will be set as to optimize the integrated process, or, if necessary, regulated as to optimize each stage individually. In a further preferred embodiment, the multi-stage bleaching process is carried out at a temperature ranging from ambient temperature to 140°C.

In a further preferred embodiment and in particular if the chemical reduction of carbonyl groups in the pulp is the primary object, the temperature for the bleaching process ranges from ambient temperature to 80°C, further preferred from 35°C to 75°C and yet further preferred from 50°C to 60°C. Furthermore, if the function of the inventive treatment also relates to delignification or to any form of bleaching, in addition to chemical reduction of carbonyl groups, the temperature of the reaction device is set to a value that allows the best combination of bleach-

ing action and chemical reduction of carbonyl groups. In a process stage of the process in which common bleaching chemicals known to the expert in the field are used, temperatures should preferably range from ambient temperature to 80°C, further preferred from 30°C to 70°C.

The heating of the reactor device is effected using heaters or heat-exchangers of the type known to the expert in the field.

The pH-value of the pulp slurry containing the previously described active chemical agents should be between 5 and 14. As for the case of temperature, the pH of a preferred embodiment of the invention depends on the full process function of the process stage in question.

Most preferably, especially if sodium borohydride is used as the carbonyl-reducing chemical, the pH should be maintained between 6 and 14, in a preferred embodiment between 10 and 13 as to minimize decomposition of the borohydride moiety and subsequent hydrogen gas release. A pH between 11 and 12 is particularly preferred. For the same reason, it is preferable to adjust the pH of the pulp slurry to a sufficiently high pH prior to the addition of sodium borohydride. This can be achieved by adding sodium hydroxide to the slurry at a point between the previous process stage and the addition of sodium borohydride. The amount of sodium hydroxide added depends on the pH of the mixture containing cellulose that is fed from the previous process stage.

Should the process stage where the invention is applied have the additional function of delignification or other bleaching action using common bleaching chemicals, the pH of the slurry in the reactor device should preferably be set at a value from pH 8 to 14, wherein the specific value chosen should best suit the optimal combination of bleaching and chemical reduction of carbonyl groups in the pulp.

As a result of the treatment of the mixture containing cellulose described above, in particular after treating said mixture in a bleaching process comprising at least one stage of adding a reducing agent, a treated mixture containing cellulose is obtained. In the context of the present invention, this mixture is referred to as (treated) "specialty cellulose pulp", i.e. as a pulp that has been treated and can now be further processed to obtain specialty cellulose products. By way of example, one class of products obtainable from specialty cellulose pulp are cellulose ethers.

Said cellulose ethers, for example sodium carboxymethylcellulose, methylcellulose, methylhydroxyethylcellulose, methylhydroxypropylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, ethylcellulose, and mixtures of at least two components thereof, are used as additives in a large range of household and industrial products. The main purpose of adding said cellulose ethers to other materials lies in the possibility of controlling the rheological properties of said materials. The viscosity of the cellulose ether solution (henceforth termed cellulose ether viscosity), which is strongly related to the degree of polymerisation (DP) of the cellulose in the pulp feedstock, is therefore one of the most important properties of cellulose ethers.

The upper limit of cellulose ether viscosity that can be obtained is per se limited by the upper limit of the cellulose DP in the specialty cellulose pulp from which the cellulose ether is derived, as well as by the DP of the cellulose ether molecule following etherification.

Furthermore, in a large proportion of products containing cellulose ethers, the appearance of the product is of high importance. Value is often attached to a cellulose ether solid that is as white as possible, and to a cellulose ether solution that

is as transparent as possible. The upper limit of brightness of cellulose ether that may be achieved is principally limited by the upper limit of the ISO brightness of the specialty cellulose pulp from which it is derived.

The brightness achievable for commercial cellulose ether products is also indirectly limited by the viscosity of the specialty cellulose pulp feed-stock. This is because of a tradeoff in the production of specialty cellulose pulp between high ISO brightness and high cellulose DP in the specialty cellulose pulp.

The specialty cellulose pulp as obtained after the inventive treatment with at least one agent capable of reducing carbonyl group and after any other optional treatment, in particular after bleaching in a multi-stage bleaching process, can now be subjected to any step of post-treatment.

Of particular importance in this context is the removal of water from the specialty cellulose pulp. This can be achieved by filtering, pressing, drying at temperatures above room temperature, applying a pressure that is below the partial pressure of water etc. Examples of other post-bleaching steps, that may be applied either prior to, during, or after water removal, are, but are not limited to, removal of fines, enzyme treatments, and the addition of or treatments with chemical agents to improve pulp processability characteristics. In a preferred embodiment, the specialty cellulose is present in the form of a solid sheet or powder, preferably obtained after at least one step of post-treatment.

The specialty cellulose pulp obtained as described above can be subjected to any step of further processing and/or derivatization. Of particular interest in the context of the present invention is any process of forming cellulose derivatives. Cellulose ethers and/or cellulose esters are of particular importance in this context. Following bleaching and post-treatment (including a possible stage of drying), the specialty cellulose sheets are packed in a roll or sheets of a given configuration

determined by the cellulose derivative producer and transported to the cellulose derivative producer. There, the sheets are typically cut up or ground to a powder. In the case of cellulose ethers, the pulp pieces or powder is typically pre-treated with sodium hydroxide at below room temperature and reacted with the desired etherifying agents in an oxygen-free environment at temperatures between 60 and 100^{0}C. The cellulose ether product is washed free of salts, dried and often ground to become the final product.

The viscosity of a cellulose ether as obtained from the specialty cellulose pulp as described above can be improved by at least 8-50% using the treatment as disclosed in this invention compared to the same product not subjected to the at least one step of adding of at least one reducing agent during the processing of the specialty cellulose pulp. Characteristic advantages of the method according to the invention over the prior art for etherification products obtained from the specialty cellulose pulp (in a substantially oxygen-free environment) are illustrated in FIG 1 and FIG 2.

In FIG 1, the effect of the method according to the invention as applied to a mixture containing cellulose from wood pulp is shown. The viscosity of a sodium carboxymethyl cellulose (CMC), i.e. a cellulose derivative obtained via etherification from the specialty cellulose pulp according to the invention, is shown in FIG 1. Here the viscosity of the end product, CMC, (vertical axis; units: mPa s) is shown as a function of the limiting viscosity number of the specialty cellulose pulp as defined in the standard "SCAN-CM 15:99" (horizontal axis, units: dm^3/kg).

It can be seen that across a broad range of specialty cellulose degree of polymerization (as represented by its limiting viscosity number values), the corresponding viscosity of a 1% aqueous solution of CMC varies linearly, irrespective of whether the mixture containing cellulose is treated according to the invention

(open squares; solid line indicates least square fit) or if the mixture had not been treated with at least one reducing agent (open triangles). The data clearly show two distinct linear relationships for treated and untreated pulps. However, the viscosity of the CMC resulting form the treated specialty cellulose pulp is constantly about 200 mPa s higher than the viscosity of the untreated, but otherwise same, mixture. These data provide clear evidence that specialty cellulose pulp that had not been treated according to the invention does not reach its fullest degree of polymerization (DP) during etherification, as evidenced by a significantly lower viscosity of the end product.

According to the present invention, specialty cellulose pulp that has been obtained from chemically and/or mechanically pulping wood can be obtained, for the first time, with a viscosity of 1700 dm^3/kg as measured according to the standard "SCAN-CM 15:99". In a preferred embodiment, said viscosity is higher than 1750 dm^3/kg, with more than 1800 dm^3/kg being particularly preferred. In a further preferred embodiment the viscosity of said product ranges from 1650 dm^3/kg s to 2000 dm^3/kg.

The large effect of the at least partial reduction of carbonyl groups in a specialty cellulose pulp on the brightness of its cellulose ether derivative was particularly unexpected. It has been found that the brightness could be improved from 5% to 80%. This effect is shown in FIG 2, where the brightness of CMC powder (vertical axis, units: % brightness) is shown as a function of the intrinsic ISO brightness of the specialty cellulose pulp from which the CMC powder has been obtained by means of etherification (horizontal axis; units: % brightness). It can be clearly seen that the brightness of the treated specialty cellulose pulp (open squares) results in a brightness that is from 5 to 20% higher than the corresponding brightness of the powder resulting from the untreated specialty cellulose pulp (open triangles).

The present invention also relates to the product of the inventive process, i.e. to a treated specialty cellulose pulp obtainable by a process comprising the treatment of a mixture containing cellulose, wherein the treatment comprises at least one step of adding at least one agent capable of reducing carbonyl groups. In particular, an integrated process may be employed. This process comprises at least the following steps:

(I) Chemical or chemical and mechanical pulping of a raw material containing cellulose resulting in a mixture (I) containing cellulose;

(II) treating an unpulped mixture containing cellulose or treating a mixture (I) containing cellulose, wherein the treatment comprises at least one step of adding at least one agent capable of reducing carbonyl groups, resulting in a treated specialty cellulose pulp (II) ;

(III) at least one step of post-processing of the specialty cellulose pulp (II);

wherein the steps (I) and (III) are optional.

In a preferred embodiment, step (II) is performed as part of a multi-stage bleaching process. In a further preferred embodiment, the step (III) of post-processing comprises at least one step of removing water and/or of drying at temperatures above room temperature.

The specialty cellulose pulp as claimed in this invention can be used for any application for which specialty cellulose pulp is better suited than regular pulp used for the manufacture of paper or cardboard. In particular, all applications in which cellulose molecules alone or in combination with other materials can be used, are included.

By way of example but without the intent to limit the scope of the invention, the following areas of use are mentioned: manufacture of cellulose derivatives, in particular of cellulose ethers or cellulose esters; textile fibers, in particular viscose or high tenacity rayon yarn, non-woven fabrics; micro-crystalline cellulose, for-

mulations for food, in particular as edible diet food, pharmaceutical or cosmetics applications, technical filters, absorbing materials, fluff fibers, photographic papers, as an additive during plastic molding, the use of said fibers in graft copolymerisation, as a component in composite materials, applications in packaging, paints, inks, thickeners, LCD screens, high value specialty papers, laminates, battery separators, electrical circuits and the like.

Examples

In the following, working examples are used to illustrate the present invention. Theses examples, however are not meant to limit the scope of the invention as described above.

Example 1: Production of specialty cellulose pulp according to the invention and subsequent carboxymethylation

Norway spruce was cooked in batch using the acid sulfite process. Once cooking was complete, the pulp had a mean kappa number (SCAN method C 1:77) of 46. This pulp was transferred to a bleach plant typical of the design found in other bleach plants used in the manufacture of specialty and other cellulose pulps.

In this first example the pulp bleaching process consists of four distinct, industrial scale stages, working continuously and in series, followed in series by a one stage, industrial-scale embodiment of the inventive treatment. All these stages, with the exception of the inventive treatments, are variations on bleach treatments common in the specialty cellulose and other cellulose pulp industries, and are well known to one skilled in the art.

The main treatment at each of the five stages comprising this example is carried out in stainless steel reactors commonly known as bleach towers, some of which are lined inside with chemically resistant materials, typical of those commonly used in the specialty cellulose and other cellulose pulp industries. Some additional but important procedures, such as washing, dilution, filtration, and chemical dosing, are carried out either prior to the pulp entering, or after the pulp leaving the towers. Details of the conditions inside each of the five towers and the bleaching, extraction chemical, and reducing agent dosages used in this example of the invention can be found in Table 1.

Treatment stage	**Parameter**	**Units**	**Level**
E_0	NaOH	Kg/ton pulp (dry)	57
	Temperature	^0C	95
	Residence time	Minutes	132
	Consistency	%	11.5
	Borol Solution®	Kg/ton pulp (dry)	5
D_0	pH	-	2
	Temperature	^0C	15
	Residence time	Minutes	43
	Consistency	%	3.5
	ClO_2	Kg/ton pulp (dry)	8.2
P_0	pH	-	11
	Temperature	^0C	35
	Residence time	Minutes	126
	Consistency	%	10
	H_2O_2	Kg/ton pulp (dry)	2
D_1	pH	-	2.5

	Temperature	^0C	45
	Residence time	Minutes	148
	Consistency	%	10
	ClO_2	Kg/ton pulp (dry)	10
P_1	pH	-	11.6
	Temperature	^0C	29
	Residence time	Minutes	163
	Consistency	%	10
	H_2O_2	Kg/ton pulp (dry)	2.5
B	pH	-	11.6
	Temperature	^0C	53
	Residence time	Minutes	163
	Consistency	%	10
	Borol Solution®	Kg/ton pulp (dry)	5

Table 1: Details of the conditions inside the towers at each stage of processing in Example 1.

The term "consistency" as used in the context of the present invention refers to the dry mass of pulp in weight percent with respect to the total mass of pulp.

The first stage of this example of the invention, the stage (E_0), is an alkaline extraction. In this stage, in addition to the main component NaOH, a borohydride is added in the form of Borol Solution® (a 12 wt% solution of sodium borohydride in 40 wt% aqueous sodium hydroxide purchased from Rohm and Haas). The dosage of Borol Solution® was 5 kg/ ton pulp (dry basis) which amounts to 15.9 g moles of sodium borohydride per ton dry pulp. This dosage was carried out immediately prior to the pulp entering the tower. Prior to the dosage of sodium borohydride, the pulp was twice washed with deionized water, passed over a filter

and press dewatered. Following pressing and prior to the sodium borohydride dosage, 58 kg/ ton pulp (dry basis) of sodium hydroxide was dosed. Immediately prior to the pulp entering the E_0 tower, the consistency of the pulp slurry was 11.5%. In the E_0 bleach tower, the temperature was maintained at 95°C. The residence time of the pulp slurry at the base of the E_0 tower was 132 minutes. The alkaline extraction stage serves the purpose of hemicelluose removal and the borohydride serves as an additive to eliminate some of the loss in strength of paper induced by the alkaline extraction.

The second stage, namely the stage (D_0), is a chlorine dioxide treatment. Prior to entering the D_0 tower, the pulp slurry was pressed and washed with deionized water, then washed a second time over a filter. Prior to the pulp entering the D_0 tower, the pH was adjusted to 1.9, and 8.2 kg/ ton pulp (dry basis) of chlorine dioxide was dosed. Following this chemical dosage, the consistency of the pulp slurry was 3.5%. In the D_0 tower, the temperature was maintained at 15°C. The residence time of the pulp slurry in the D_0 tower was 43 minutes.

The third stage, namely the stage (P_0), is an oxidative bleaching stage using hydrogen peroxide. Prior to entering the P_0 tower, the pulp-slurry was washed with deionized water over a filter. The pH of the pulp slurry was then adjusted to 10.9 using sodium hydroxide, and 2.0 kg/ton pulp (dry basis) hydrogen peroxide was added. The consistency of the pulp slurry was then 10%. In the P_0 tower, the temperature was maintained at 35°C. The residence time of the pulp slurry in the P_0 bleach tower was 125 minutes.

The fourth stage, namely the stage (D_1), is a chlorine dioxide treatment. Prior to entering the D_1 tower, the pulp was washed with deionized water over a filter. The pH of the pulp slurry was then adjusted to 2.5 using sulphur dioxide, and 10 kg/ ton pulp (dry basis) of chlorine dioxide was dosed. In the D_1 tower, the tempera-

ture was maintained at 45°C. The residence time of the pulp slurry in the D_1 tower was 148 minutes.

The fifth stage of this example of the invention, namely the stage (B), has the sole purpose of effecting chemical reduction of the carbonyl groups in the pulp, and is therefore the inventive borohydride treatment. Sodium borohydride was dosed in the form of Borol Solution®. The dosage of Borol Solution® was 5 kg/ ton pulp (dry basis), which amounts to 15.9 g moles of sodium borohydride per ton dry pulp. This dosage was carried out immediately prior to the pulp entering the B tower. Prior to the dosage of sodium borohydride, the pulp was washed with de-ionized water over a filter and the pH of the slurry adjusted to 11.5 using sodium hydroxide. Immediately prior to the slurry entering the B tower, its consistency was 10%. In the B tower, the temperature was maintained at 55°C. The residence time of the pulp slurry in the B tower was 163 minutes.

After leaving the B tower, the pulp slurry was washed with deionized water over a filter and the pH adjusted to 4. The pulp was then transported to the drying section of the specialty cellulose manufacturing process, where it was screened, washed in deionized water, and dried to a moisture content of 7%. The dried pulp was packed in a form (approx. 20 ton rolls) typical of finished product specialty cellulose that is ready for sale to other parties wishing to use this as raw material for a cellulose derivatization.

The properties of the finished specialty cellulose product can be found in Table 2.

Brightness (ISO 2470-1999) (%)	82.00
Limiting viscosity number (SCAN-CM 15:99) (ml/.g)	1532
S18 (SCAN-C2:61) (alkali solubility of pulp; in %)	7.02

Table 2: Selected properties of specialty cellulose pulp produced according to Example 1.

A 50 g sample of the specialty cellulose pulp manufactured using the inventive treatment described above and with properties as found in Table 2 was subjected to etherification yielding sodium carboxymethyl cellulose (CMC).

The aforementioned specialty cellulose pulp sample was first ground using a knife mill (Fritsch pulvarisette 19). The resulting specialty cellulose pulp powder had a mean particle size of 200 µm as measured by a Coulter LS 200 particle analyzer. 35 g of powder (weighed on a dry basis) and was subsequently etherified to carboxymethyl cellulose according to the carboxymethylation procedure described in Example 4. The 1 wt% solution viscosity and powder brightness of the resultant carboxymethyl cellulose product was measured. The corresponding values can be found in Table 3.

Viscosity of 1 wt% aqueous solution (mPa s)	1840
Powder brightness (%)	71.1

Table 3: Selected properties of CMC made from specialty cellulose pulp produced as per Example 1. The degree of substitution of the CMC was 1.05.

Details of the procedures used for viscosity and brightness measurements of CMC can be found in Example 4.

Example 2: Production of specialty cellulose pulp and subsequent carboxymethylation without the inventive treatment (comparative example)

In this example, exactly the same processing conditions as described in Example 1 (within the repeatability limits for an industrial scale process) were used in the stages E_0, D_0, P_0 and D_1. However, no inventive treatment stage was applied in the form of the addition of sodium borohydride or any other agent capable of reducing carbonyl groups at stage B. In this comparative Example 2, an oxidative

bleaching stage using hydrogen peroxide (P_1) was directly substituted for the inventive stage B that had been applied in Example 1. Therefore, in this case, the pulp bleaching process consisted of five distinct, industrial scale stages, working continuously and in series. Details of the conditions inside each of the five towers and the bleaching and extraction chemical dosages used in this example of the invention can be found in Table 4.

Treatment stage	**Parameter**	**Units**	**Level**
E_0	NaOH	Kg/ton pulp (dry)	58
	Temperature	^{0}C	95
	Residence time	Minutes	134.
	Consistency	%	11.5
	Borol Solution®	Kg/ton pulp (dry)	5.
D_0	pH	-	1.9
	Temperature	^{0}C	15
	Residence time	Minutes	43
	Consistency	%	3.5
	ClO_2	Kg/ton pulp (dry)	8.9
P_0	pH	-	11
	Temperature	^{0}C	35
	Residence time	Minutes	126
	Consistency	%	10
	H_2O_2	Kg/ton pulp (dry)	2
D_1	pH	-	2.5
	Temperature	^{0}C	45

	Residence time	Minutes	148
	Consistency	%	10
	ClO_2	Kg/ton pulp (dry)	10
P_1	pH	-	11.6
	Temperature	^0C	29
	Residence time	Minutes	163
	Consistency	%	10
	H_2O_2	Kg/ton pulp (dry)	2.5

Table 4: Details of the conditions inside the towers at each stage of processing in Example 2.

The stage P_1, being the 5th treatment stage during the bleaching of the specialty cellulose pulp in this example, was a hydrogen peroxide treatment. The chemical reactor (bleach tower) used for this treatment was the same tower used as stage B in Example 1. Prior to entering the P_1 tower, the pulp was washed with deionized water over a filter and 2.5 kg/ ton pulp (dry basis) was then dosed simultaneous to the pH of the slurry being adjusted to 11.8 using sodium hydroxide. Immediately prior to the slurry entering the P_1 tower, its consistency was 10%. In the P_1 tower, the temperature was maintained at 29°C. The residence time of the pulp slurry in the P_1 tower was 163 minutes.

The properties of the finished specialty cellulose product can be found in Table 5.

Brightness (ISO 2470-1999) (%)	85.80
Limiting viscosity number (SCAN-CM 15:99) (dm^3/kg)	1574
S18 (SCAN-C2:61) (alkali solubility of pulp; in %)	7.00

Table 5: Selected properties of specialty cellulose pulp produced according to Example 2.

A 50 g sample of the specialty cellulose pulp manufactured using the treatment described above and with properties as found in Table 5 was subjected to etherification to sodium carboxymethyl cellulose (CMC).

The aforementioned specialty cellulose pulp sample was first ground using a knife mill (Fritsch pulvarisette 19). The resultant specialty cellulose pulp powder had a mean particle size of 200 μm as measured by a Coulter LS 200 particle analyzer. 35 g of powder (weighed on a dry basis) was subsequently etherified to carboxymethyl cellulose according to the carboxymethylation procedure described in Example 4. Relevant properties of the resultant carboxymethyl cellulose product were measured, and their values are found in Table 6.

Viscosity of 1 wt% aqueous solution (mpa.s)	1530
Powder brightness (%)	70.6

Table 6: Selected propertied of CMC made from specialty cellulose pulp produced as per Example 2. The degree of substitution of the CMC was 1.05.

A comparison of the 1 wt% solution viscosity of the CMC obtained from specialty cellulose pulp obtained from Example 1 (Table 3) with that from Example 2 (Table 6), reveals a substantially superior CMC viscosity of the CMC derived from pulp from Example 1 (20% higher). This is despite the limiting viscosity number of the pulp from Example 1 being 42 units lower than the pulp from Example 2.

Furthermore, despite the ISO pulp brightness of the specialty cellulose pulp from Example 1 being 3 units lower than the pulp from Example 2, the CMC powder brightness is of the same magnitude. These improvements in CMC viscosity per unit pulp viscosity, and CMC brightness per unit pulp brightness, are indicative of the effect of the inventive treatment disclosed here.

Details of the procedures used for viscosity and brightness measurements of CMC can be found in Examples 5 and 6.

Example 3: Post-bleaching processing of specialty cellulose pulp using the inventive treatment and subsequent carboxymethylation

In this example, a 50 g sample of the specialty cellulose pulp manufactured using the treatment described in Example 2 and with properties as found in Table 4 was treated as per an embodiment of the inventive treatment.

The 50 g pulp sample was partitioned into two equal halves of 25 g each. These samples were separately wet and torn into strips in 2.5 L of deionized water. The pulp suspension was then homogenized using a desintegrator (a steel rotor blade of 6 cm diameter rotating at 600 RPM for 30 seconds). Both pulp suspensions were transferred into the same sealable plastic container. Into the pulp suspension was added 0.233 g of Borol Solution®, amounting to 5 kg of Borol Solution®/ton pulp (dry basis), or 15.9 g moles of sodium borohydride per ton pulp (dry basis). The pH was then adjusted to 11.2 using sodium hydroxide.

The container containing the pulp suspension was sealed and shaken, and set in a water bath at a temperature of 55°C for 180 minutes. The pulp suspension was then washed twice with 5 l of deionized water and dried to a moisture content of 7%. The limiting viscosity number and the ISO brightness of the pulp following the inventive treatment were found to be unchanged from those of the pulp prior to applying the inventive treatment. The pulp properties are therefore the ones found in Table 5.

This specialty cellulose pulp sample was then ground using a knife mill (Fritsch pulvarisette 19). The resultant specialty cellulose pulp powder had a mean particle size of 200 μm as measured by a Coulter LS 200 particle analyzer. 35 g of powder (weighed on a dry basis) was subsequently etherified to carboxymethyl cellulose according to the carboxymethylation procedure described in Example 4. Relevant

properties of the resultant carboxymethyl cellulose product were measured, and their values are found in Table 7.

Viscosity of 1 wt% aqueous solution (mpa.s)	1870
Powder brightness (%)	75.6

Table 7: Selected propertied of CMC made from specialty cellulose pulp produced as per Example 7. The degree of substitution of the CMC was 1.05.

A comparison of the 1 wt% solution viscosity of the CMC obtained from specialty cellulose pulp obtained from Example 3 (Table 7) with that from Example 2 (Table 6), reveals a substantially superior CMC viscosity of the CMC derived from pulp from Example 2 (22% higher). This is despite having the same limiting viscosity number of the pulp.

Furthermore, the CMC powder brightness of the CMC obtained from specialty cellulose pulp obtained from Example 3 is 5 units, or 7%, higher than the CMC from example 2. This is despite the two pulps having the same ISO brightness values. These improvements in CMC viscosity per unit pulp viscosity, and CMC brightness per unit pulp ISO brightness, are indicative of the effect of the inventive treatment disclosed here.

Example 4:Carboxymethylation procedure (as used in Examples 1 through 3)

Chemicals: Specialty Cellulose pulp, treated as per invention (Borregaard ChemCell, Sarpsborg, Norway); iso-propanol (87 wt-% in H_2O and 100 wt-%, ρ_{iso} = 0.780 g ml^{-1}); N_2 (g); sodium hydroxide (s); sodium monochloroacetate, 99% pure (s); acetic acid; phenolphthalein; methanol (70 wt-%, ρ_{meth} = 0.891 g ml^{-1}); silver nitrate solution (0.1 M); deionized water.

Equipment: Refrigerator; analytical balance accurate to 1/100th of gram; Parr-reactor complete with stirring (cooled), external heating-element, internal cooling element, N_2 feed and temperature control; knife mill (Fritsch Pulverisette 19); measuring cylinders (100 ml, 500 ml); glass beaker; plastic beakers (100 ml, 2 liter); graduated pipette (2-10 ml); glass mixing rod; vacuum flask; ceramic vacuum funnel; black band filter paper; watch glass (25 cm diameter); vacuum dryer.

The purpose of this example is to illustrate the process leading from the specialty cellulose pulp according to the invention to the derivative end product, in this case an etherified derivative. However, any other derivatization would be conceivable in this context, in particular any process of esterification.

35 g (dry basis) of specialty cellulose pulp ground in the knife mill was introduced into the Parr-reactor. Immediately following this, precooled (5°C) iso-propanol solution (448 ml 100 % iso-propanol + 40.7 ml deionized water) was then poured in to the reactor. The heating jacket was fixed in place and the reactor sealed. The stirrer arm its cooler were then connected. The nitrogen gas feed was turned on and the flow-rate regulated to 100 ml/min. The cooling water feeding both the stirrer and reactor cooling coil was turned on.

Stirring was set to 250 rpm and the temperature controller program (0°C for 15 mins; 5°C per min for 2 mins to 10°C for 60 mins; 1°C per minute for 50 mins to 60°C for 60 minutes; 5°C per minute for 6 mins to 20°C for 30 mins) was initiated.

After 15 minutes at 0°C, 22.0 g NaOH (NaOH-to-cellulose molar ratio is 2.5) in 20.4 ml deionized water was introduced to the reactor. This is done rapidly to avoid oxygen entering the reactor. Immediately afterwards, 78 ml iso-propanol (100 %) was rapidly introduced. The stirring speed was then increased to. 500 rpm for a few seconds to attain a uniform mixture. then decreased again to 250 rpm and the reactor was left for 60 minutes at 10°C.

51.3 g sodium monochloroacetate (MCA) (MCA-to-cellulose molar ratio is 2.0) was mixed with 44 ml of iso-propanol (87 %) and rapidly introduced to the reactor. The remaining, undissolved MCA residue was washed into the reactor with a further 44 ml of 87% iso-propanol. The stirring speed was then set at 500 rpm for a few seconds, then set back to 250 rpm. The temperature program then ensured the reactor contents were heated to 60°C over 50 minutes and remained at this temperature for 60 minutes. The total reaction time (with MCA) was therefore 120 minutes.

At the completion of 60 minutes at 6o°C, the reactor contents were neutralised (phenolphthalein indicator) using an acetic acid solution (5 g acetic acid in 10 ml 87 % iso-propanol). The reactor contents were vacuum-filtered and the product was first washed with 700 ml of iso-propanol (87 %), then four times with 700ml of methanol (70 %). After the 5^{th} and final wash, the filtrate methanol was checked for being chloride free using a few drops of $AgNO_3$. No precipitation of AgCl was observed meaning the product was sufficiently chloride free.

The washed product was dried in a vacuum drying cabinet at 60°C over night. The product was weighed to $1/100^{th}$ of a gram and its moisture content determined. The product was then ground to a powder of mean particle size of 119 µm and a particle size distribution as shown in Figure A1, in the knife mill.

Example 5: Procedure for measurement of the viscosity of a CMC solution.

2.00 g of CMC powder (dry basis) was dissolved in 200 ml of deionized water using a mechanical stirrer arm rotating at 200 rpm over the course of 1 hour at room temperature. The 1 wt% CMC solution was then transferred to a constant temperature water bath set at 20°C.

An Anton Paar Physica UDS 200 was used to perform the viscosity measurement. The temperature bath on the instrument was first set to 20°C, and the spindle (MK 25/8) was mounted. The measurement program was initiated and 5.5 ml of 1 wt% CMC solution is placed in the receptor below the spindle. The spindle was set in the "measuring position" and surplus sample was removed. Measurement was initiated and the dynamic viscosity in mPa.s was read as that reported from the machine measurement at a shear rate of 11.3 s^{-1} as the spindle is on the way up.

Example 6: Procedure for measurement of the brightness of a CMC powder

CMC powder was placed into a stainless steel receptor fitted with a threaded press and a glass plate that ensured a pressed, smooth powder surface. After the CMC powder was placed on the glass plate, the press was screwed into place, and the device was turned upside down and disassembled. The powder then lay on the circular glass plate with the smoothed powder surface facing upwards. The plate and powder sample was then placed in a Minolta CM-3630 apparatus, and the CMC powder brightness read at a wavelength of 457 nm. Each sample was prepared twice and the average of brightness readings is reported.

It should be noted that in order to obtain complete reproducibility of this procedure, any CMC powder analyzed must have the same or a very similar mean particle size and a particle size distribution as that described in FIG 3. FIG 3 shows a typical particle size distribution of a CMC powder after grinding in the Fritsch Pulvarisette 19 knife mill as used in Examples 1, 2 and 3. The horizontal x-axis represents the particle diameter in µm while the vertical y-axis represents the volume of the corresponding particles in %.

Claims

1. A method for treating a mixture containing cellulose that has not been pulped or that has been pulped chemically or chemically and mechanically, characterized in that the treatment comprises at least one step of adding at least one agent capable of reducing carbonyl groups.

2. A method according to claim 1, characterized in that the at least one agent capable of reducing carbonyl groups is added during at least one step of a multi-stage bleaching process.

3. A method according to claim 2, characterized in that the at least one agent capable of reducing carbonyl groups is added after or as the last stage of a multi-stage bleaching process.

4. A method according to any of the preceding claims, characterized in that the mixture containing cellulose is obtained from (i) chemically or chemically and mechanically pulping wood or is obtained from (ii) unpulped cotton linters or from any combination of (i) and (ii).

5. A method according to any of the preceding claims, characterized in that the mixture containing cellulose is an aqueous slurry of cellulose leading to a specialty cellulose pulp.

6. A method according to claim 5, characterized in that the cellulose content in the aqueous slurry is from 1 to 40 % by weight, with respect to the total weight.

7. A method according to any of the preceding claims, characterized in that the at least one agent capable of reducing carbonyl groups is selected from the group of borohydrides, DMAB, LiAlH and mixtures thereof.

8. A method according to any of the preceding claims, characterized in that the overall content of agent capable of reducing carbonyl groups added to the mixture containing cellulose is from 0.1 to 200 g·moles per ton of the dry mixture containing cellulose.

9. A method according to any of the preceding claims, characterized in that the step of adding at least one agent capable of reducing carbonyl groups is performed at temperatures from ambient temperature to 90°C.

10. A method according to any of the preceding claims characterized in that the step of adding at least one agent capable of reducing carbonyl groups is performed at a pH value from 8 to 14.

11. An integrated method for producing specialty cellulose pulp comprising at least the following steps:

(I) Chemical or chemical and mechanical pulping of a raw material containing cellulose resulting in a mixture (I) containing cellulose;

(II) treating an unpulped mixture containing cellulose or treating a mixture (I) containing cellulose wherein the treatment comprises at least one step of adding at least one agent capable of reducing carbonyl groups, resulting in a treated specialty cellulose pulp (II) ;

(III) at least one step of post-processing of the specialty cellulose

pulp (II);

wherein the steps (I) and (III) are optional.

12. An integrated method according to claim 11, characterized in that the at least one step of post-processing is a step of drying.

13. Specialty cellulose pulp, obtainable by a process comprising at least one step of treating a mixture containing cellulose that has not been pulped or that has been pulped chemically or chemically and mechanically, characterized in that the treatment comprises at least one step of adding at least one agent capable of reducing carbonyl.

14. Specialty cellulose pulp according to claim 13, characterized in that the viscosity or the brightness, or both, of cellulose derivatives obtained from said specialty cellulose pulp are increased over the viscosity or the ISO brightness, or both, obtained from a specialty cellulose pulp that has not been treated with the at least one step of adding at least one agent capable of reducing carbonyl groups.

15. Specialty cellulose pulp according to claim 13, characterized in that the viscosity of the specialty cellulose pulp, as measured according to the standard "SCAN-CM 15:99", is increased by at least 50 dm^3/kg over the viscosity obtained from a specialty cellulose pulp that has not been treated with the at least one step of adding at least one agent capable of reducing carbonyl groups.

16. Specialty cellulose pulp that has been obtained from chemically and mechanically pulping wood or from chemically or mechanically pulping wood, characterized in that it has a viscosity of at least 1700 dm^3/kg as measured according to the standard "SCAN-CM 15:99".

17. Use of the specialty cellulose pulp according to any of the claims 13 to 16 or of the specialty cellulose pulp produced according to any of the claims 1 to 10 or of the specialty pulp produced according to claims 11 or 12, for the production of cellulose derivatives, including cellulose ethers or cellulose esters.

18. Use of the pulp according to any of claims 13 to 16 or of the specialty cellulose pulp produced according to any of the claims 1 to 10 or of the specialty pulp produced according to claim 11 or 12 for the production of viscose, composite materials, micro-crystalline cellulose formulations for food, cosmetics and pharmaceutical applications, technical filters, special photographic paper, as an additive during plastic molding, high-tenacity rayon yarn for tires and industrial hoses, paints, printing inks, LCD screens, high value specialty paper applications, battery separators, circuit boards and non-woven fabrics.

AMENDED CLAIMS
[received by the International Bureau on 15 December 2003 (15.12.03);
original claims 1-18 replaced by new claims 1-14)

Claims further to the International Search Report from October 21, 2003

(clean copy)

1. A method for treating a mixture containing cellulose that has not been pulped or that has been pulped chemically or chemically and mechanically, characterized in that

   (i) the treatment comprises at least one step of adding at least one agent capable of reducing carbonyl groups after or as the last stage of a multi-stage bleaching process and

   (ii) that the mixture containing cellulose is an aqueous slurry of cellulose leading to a specialty cellulose pulp.

2. A method according to claim 1, characterized in that the mixture containing cellulose is obtained from (i) chemically or chemically and mechanically pulping wood or is obtained from (ii) unpulped cotton linters or from any combination of (i) and (ii).

3. A method according to claim 1 or 2, characterized in that the cellulose content in the aqueous slurry is from 1 to 40 % by weight, with respect to the total weight.

4. A method according to any of the preceding claims, characterized in that the at least one agent capable of reducing carbonyl groups is selected from the group of borohydrides, DMAB, LiAlH and mixtures thereof.

5. A method according to any of the preceding claims, characterized in that the overall content of agent capable of reducing carbonyl groups added to the mixture containing cellulose is from 0.1 to 200 g·moles per ton of the dry mixture containing cellulose.

6. A method according to any of the preceding claims, characterized in that the step of adding at least one agent capable of reducing carbonyl groups is performed at temperatures from ambient temperature to 90°C.

7. A method according to any of the preceding claims characterized in that the step of adding at least one agent capable of reducing carbonyl groups is performed at a pH value from 8 to 14.

8. An integrated method for producing specialty cellulose pulp comprising at least the following steps:

(I) Chemical or chemical and mechanical pulping of a raw material containing cellulose resulting in a mixture (I) containing an aqueous slurry of cellulose leading to a specialty cellulose pulp;

(II) treating an unpulped mixture containing cellulose or treating a mixture (I) containing cellulose wherein the treatment comprises at least one step of adding at least one agent capable of reducing

carbonyl groups after or as the last stage of a multi-stage bleaching process resulting in a treated specialty cellulose pulp (II) ;

(III) at least one step of post-processing of the specialty cellulose pulp (II);

wherein step (III) is optional.

9. An integrated method according to claim 8, characterized in that the at least one step of post-processing is a step of drying.

10. Specialty cellulose pulp, obtainable by a process comprising at least one step of treating a mixture containing cellulose that has not been pulped or that has been pulped chemically or chemically and mechanically, characterized in that the treatment comprises at least one step of adding at least one agent capable of reducing carbonyl after or as the last stage of a multi-stage bleaching process.

11. Specialty cellulose pulp according to claim 10, characterized in that the viscosity of the specialty cellulose pulp, as measured according to the standard "SCAN-CM 15:99", is increased by at least 50 dm^3/kg over the viscosity obtained from a specialty cellulose pulp that has not been treated with the at least one step of adding at least one agent capable of reducing carbonyl groups.

12. Specialty cellulose pulp that has been obtained from chemically and mechanically pulping wood or from chemically or mechanically pulping wood, characterized in that it has a viscosity of at least 1700 dm^3/kg as measured according to the standard "SCAN-CM 15:99".

13. Use of the specialty cellulose pulp according to any of the claims 10 to 12 or of the specialty cellulose pulp produced according to any of the claims 1 to 7 or of the specialty pulp produced according to claims 8 or 9, for the production of cellulose derivatives, including cellulose ethers or cellulose esters.

14. Use of the pulp according to any of claims 10 to 12 or of the specialty cellulose pulp produced according to any of the claims 1 to 7 or of the specialty pulp produced according to claim 8 or 9 for the production of viscose, composite materials, micro-crystalline cellulose formulations for food, cosmetics and pharmaceutical applications, technical filters, special photographic paper, as an additive during plastic molding, high-tenacity rayon yarn for tires and industrial hoses, paints, printing inks, LCD screens, high value specialty paper applications, battery separators, circuit boards and non-woven fabrics.

Figure 1

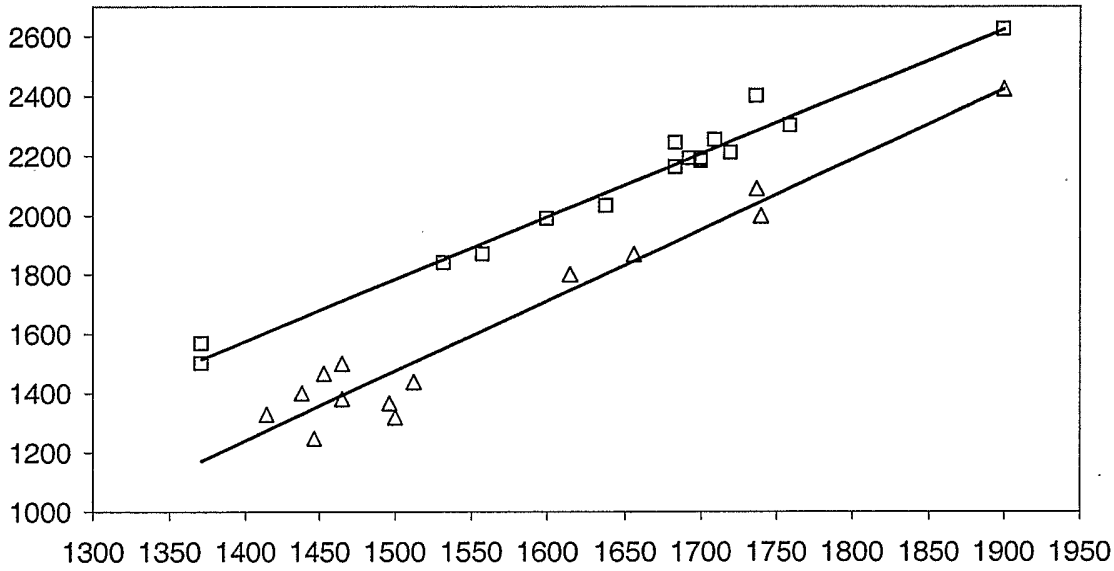

2600
2400
2200
2000
1800
1600
1400
1200
1000
1300 1350 1400 1450 1500 1550 1600 1650 1700 1750 1800 1850 1900 1950

Figure 2

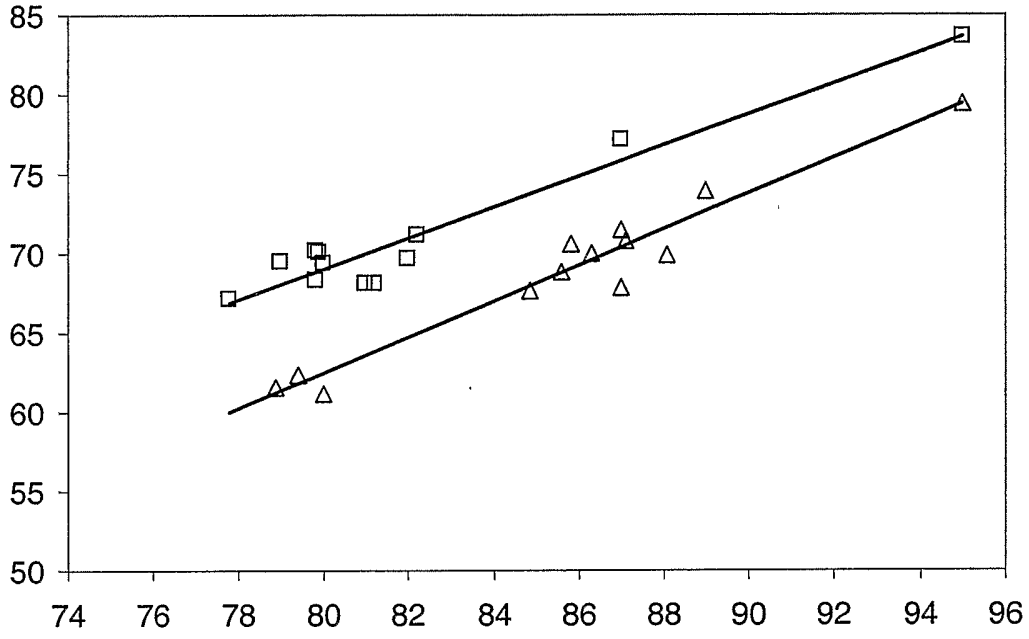
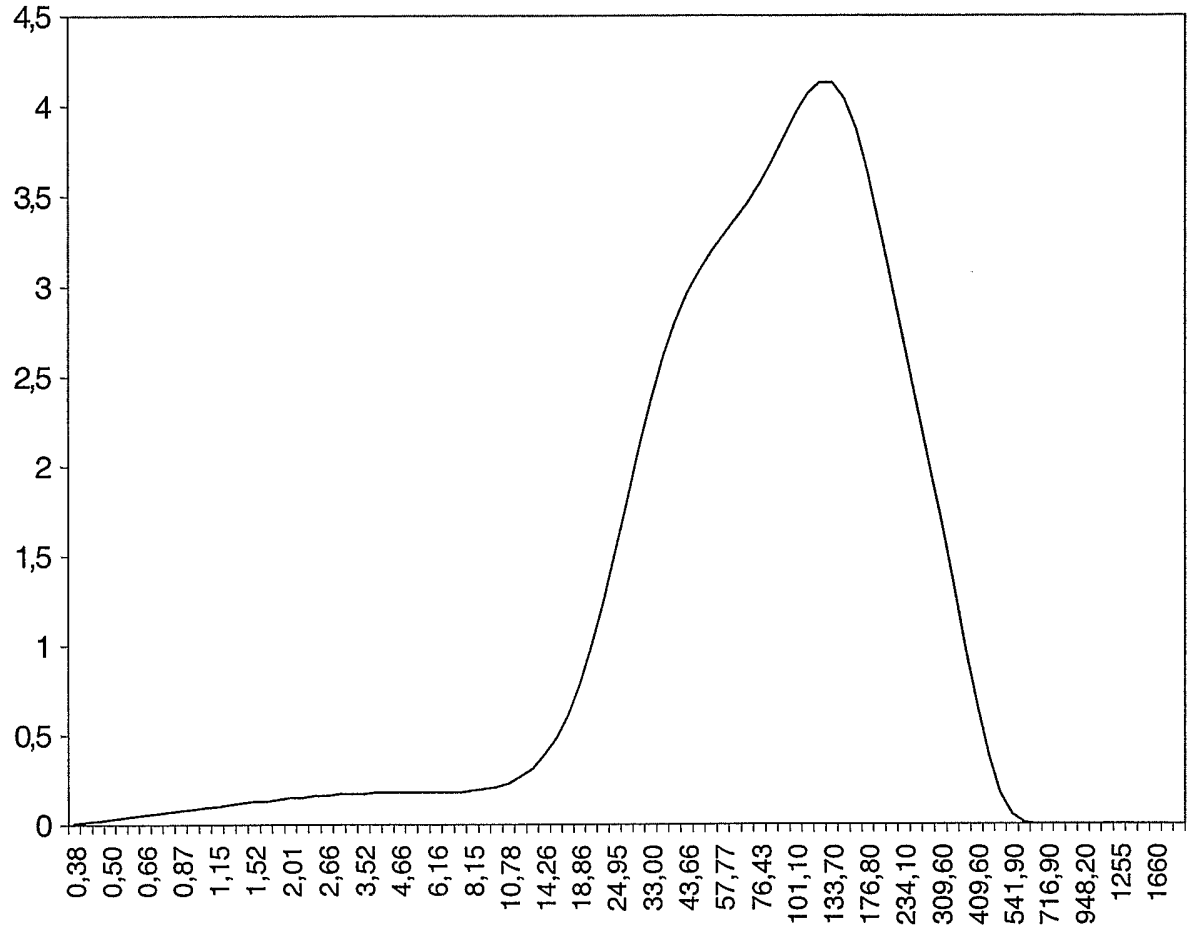


Figure 3


4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
0,38
0,50
0,66
0,87
1,15
1,52
2,01
2,66
3,52
4,66
6,16
8,15
10,78
14,26
18,86
24,95
33,00
43,66
57,77
76,43
101,10
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716,90
948,20
1255
1660

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/06652

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21C9/00 C08B1/00

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)
IPC 7 D21C C08B D21H

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 practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 610 655 A (WILLIAM H. RAPSON) 13 December 1960 (1960-12-13) page 1, column 1, line 35 - line 63 page 1, column 2, line 22 - line 45 page 2 -page 3 ---	1-18
X	US 2 898 333 A (INGVAR JULLANDER ELOF) 4 August 1959 (1959-08-04) column 1, line 15 - line 35 column 2, line 37 -column 3, line 25; claim 5 ---	1-18
X	US 6 325 892 B1 (VAN HEININGEN ADRIAAN R P ET AL) 4 December 2001 (2001-12-04) column 2, line 4 -column 3, line 39 --- -/--	1-16

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 September 2003	21 OCT 2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	MARIANNE BRATSBERG/ELY

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/06652

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 035 772 A (AGNEMO ROLAND A ET AL) 30 July 1991 (1991-07-30) column 3, line 24 - line 33 -----	1-14

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Information on patent family members

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