(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
29 November 2012 (29.11.2012)

WIPO | PCT

(10) **International Publication Number**
WO 2012/160363 A1

(51) **International Patent Classification**:
C08J 3/28 (2006.01) ***A24D 3/10*** (2006.01)
C08J 3/09 (2006.01) ***D01F 2/00*** (2006.01)
C08J 5/18 (2006.01)

(21) **International Application Number**:
PCT/GB2012/051140

(22) **International Filing Date**:
18 May 2012 (18.05.2012)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
1108530.5 20 May 2011 (20.05.2011) GB

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,

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(54) Title: PROCESS

(57) **Abstract**: Disclosed herein is a method of producing cellulose shaped articles comprising the steps of exposing non-dissolving cellulose-containing pulp to electron beam radiation originating from a plurality of locations, forming a solution or dope comprising the cellulose-containing pulp, and casting a cellulose shaped article from the solution. Products of the method and systems for implementing the method are also disclosed.

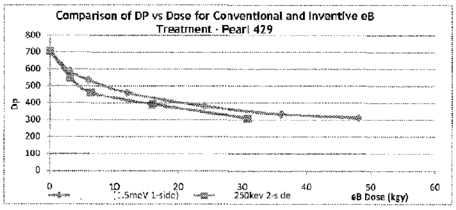

Figure 1A

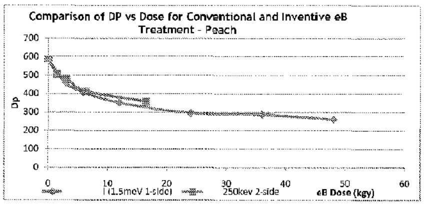

Figure 1B

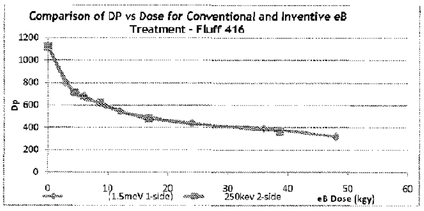

Figure 1C

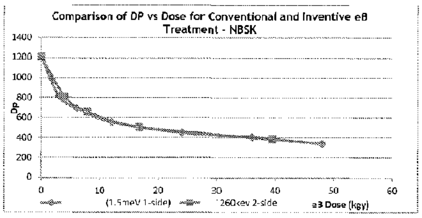

Figure 1D

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CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

PROCESS

The present invention provides a method of processing cellulose in which a non-dissolving cellulose-containing pulp is treated to render it suitable for the preparation of cellulose shaped articles, such as fibres. Also provided are systems for implementing such methods.

In addition to its utility in the industrial production of paper, cellulose-containing pulp has a number of other applications, including the industrial manufacture of cellulose shaped articles, such as fibres.

There are numerous sources of cellulose-containing pulps, for example wood, (especially softwood), cotton, flax, hemp and bamboo. Pulp is generally prepared from those raw materials by treatment to separate out and remove lignin and hemicellulose, so as to maximise the cellulose content of the pulp.

There are two general pulping techniques known to those skilled in the art. Firstly, pulp can be prepared mechanically, by milling or grinding the raw material to physically separate cellulose fibres from hemi-cellulose and lignin.

Alternatively, the raw material can be chemically treated to dissolve lignin and hemicellulose, ideally without disrupting the cellulose fibres native to the raw material. Examples of chemical pulping processes include the Kraft process and the Sulphite process.

There are also a number of hybrid pulping processes where chemical processing steps are employed in a mechanical pulping process, or vice versa. Examples of such processes include thermomechanical processes, where, in addition to mechanical comminution, wood chips or other raw materials are also exposed to heat, and chemithermomechanical processes, where wood chips are firstly exposed to chemicals used in chemical pulping processes before comminution and exposure to heat.

For those skilled in the art of cellulose regeneration, there are two classes of pulp obtained from chemical pulping processes. Firstly, there are ‘dissolving pulps’ or ‘dissolving grade pulps’, which are used as feedstocks in the viscose process. Dissolving pulps are characterised by a high cellulose content, around 90% or higher. As their name suggests, they are soluble in solvents or dopes used in commercial cellulose regeneration processes.

The other class of pulps are ‘non-dissolving pulps’, examples of which include ‘market pulps’ or ‘fluff pulps’. These have limited utility in the viscose process and in other processes for producing cellulose shaped products because, as their name suggests, they are not soluble in conventionally used processing solutions or dopes. Accordingly, they are principally used in applications other than cellulose regeneration. For example, over 80% of all fluff pulp manufactured is used in the production of baby diapers.

Owing to the lower cost of non-dissolving pulps, as compared to dissolving pulps, there have been attempts made previously to employ non-dissolving pulps in the viscose process. However, as a result of their deleterious effects on the properties of the resulting viscose solutions, they can only be used in low proportions, as filler materials, making up no more than about 5 to 10% of the total pulp used.

Examples of commercially available non-dissolving pulps include Pearl 429 (Weyerhauser), Peach (Weyerhauser), Fluff 416 (Weyerhauser), Port Wentworth SBSK (Weyerhauser) and Bleached Eucalyptus pulps available from Fibria, UPM and ENCE.

In addition to their dissolution properties, non-dissolving pulps differ from dissolving pulps in a number of ways. For example, they generally have a higher hemi-cellulose content, a lower alpha-cellulose content, are less refined, have higher degrees of polymerisation (DP) and / or have lower quality control than dissolving pulps.

As those skilled in the art will be aware, the viscose process as generally practiced includes the steps of dissolving or slurrying a pulp in caustic soda, steeping it in the caustic solution, xanthating the cellulose with carbon disulphide, and re-dissolving it in an aqueous caustic solution to form viscose.

Viscose is typically filtered and refiltered in order to maximise the purity of the material to improve product quality. It is then formed into a desired shape using techniques known to those in the art, for example by extruding it through a spinnerette to form a fibrous material, which is then contacted with an acidic casting solution to regenerate the cellulose from viscose.

In certain applications, between the steeping and xanthation steps, the steeped cellulose slurry or solution may be subjected to mercerisation, where a portion of the caustic liquid is removed, for example by pressing, to achieve an alkali cellulose having a target cellulose and soda content. The purpose of this step is to improve the properties of the cellulose, notably by reducing its degree of polymerisation (DP).

If a non-dissolving pulp is subjected to these steps as conventionally practiced, the resulting viscose solution will have unacceptably low filterability for shape forming applications. It is this adverse effect on the filterability of viscose solutions which has prevented non-dissolving pulps being used in the viscose process in proportions greater than about 5% to 10% by weight of the total pulp.

Dissolving pulps, on the other hand, which are optimised for use in the viscose process can be used to produce viscose liquids exhibiting a high level of filterability.

Filterability can be measured using a number of different testing methods. The clog constant (Rv) is calculated by taking the slope of the curve generated by plotting the weight of viscose passed through a filter cloth in five minute intervals.

TVW is a measure of the total amount of viscose filtered within a thirty minute period.

Typically, the higher the Rv and the TVW values, the higher quality the viscose as it does not clog or block the filter cloth.

Ball fall velocity (BFV), measured in seconds, is a measure of the time it takes for a steel ball weighing 0.13g +/- 0.02g to sink to the bottom of a sample of viscose solution having a depth of 205mm.

As an alternative technique for quantifying the quality of a viscose solution, the fibre count method can be used, in which the quantity of residual fibres in the solution is measured.

In addition to viscose processing methods, alternative techniques for producing cellulose shaped articles are known. More recently, the use of ionic liquids to form cellulose dopes has been disclosed in, for example, EP1458805, EP1893651, EP1805131, US2009/0084509, GB1011446.

There remains a need in the art to treat non-dissolving pulps to render them suitable for use in methods for producing shaped articles from cellulose.

Thus, according to a first aspect of the present invention, there is provided a method of producing cellulose shaped articles comprising the steps of:

a) exposing non-dissolving cellulose-containing pulp to electron beam radiation originating from a plurality of locations,
b) forming a solution or dope comprising the cellulose-containing pulp, and
c) casting a cellulose shaped article from the solution.

As mentioned above, the skilled artisan will understand what is meant by a non-dissolving pulp. S/he will identify that such pulps exhibit one or more of the following properties: relatively high hemi-cellulose content (typically around 10% or greater), relatively low alpha-cellulose content (typically about 90% or lower, more typically in the range of about 83% to about 89%), less refined, relatively high degrees of polymerisation (DP) (typically about 700 to about 1200) and / or have relatively low quality control, as compared to dissolving pulps.

For the avoidance of doubt, the presence of additional processing steps may be, and most likely will be, performed prior to step a) and / or between steps a) to c). Such steps will be discussed below in greater detail. It will be recognised that such steps, especially those performed between steps a) and b) may alter the appearance or properties of the pulp. Thus, where reference is made in step b) to the formation of a solution or dope comprising cellulose-containing pulp, it will be appreciated that the pulp will not necessarily be in the form of a pulp per se, but may be in the form of a processed version of the pulp, for example a slurry, solution or crumb prepared from the treated, non-dissolving pulp.

The shaped articles which are produced according to the processes of the present invention are most preferably fibres. Other products which may also be formed include ropes, yarns, cloths or cigarette filters. These other products may be formed directly from the cellulose solution, or may be formed from fibres spun from the cellulose solution.

For the avoidance of any doubt, the term ‘shaped articles’ shall not encompass cellulose sheets, films, laminates or the like.

The use of electron beam radiation to treat cellulose-containing pulps is known and has been employed in commercial processes for many years. The treatment of pulps with electron beam radiation has typically been carried out by passing a layer or sheet of pulp by a fixed electron beam source, for example, using a conveyor. Such techniques, however, have never been capable of rendering non-dissolving pulps suitable for use in cellulose shaped article production processes, especially the viscose process.

In fact, it has been observed by the inventors that when non-dissolving pulps are subjected to conventional electron beam treatment steps, their solubility in solvents and dopes used conventionally in cellulose shaped article production methods is actually reduced. Without wishing to be bound by theory, it is believed that when conventional electron beam treatment methods, which typically involve pulps being treated with high-voltage electron radiation (typically in the order of 10 meV) from a single, fixed radiation source are applied to non-dissolving pulps, this has the effect of curing or closing up the treated surface of the pulp, reducing its already diminished dissolution properties.

However, it has unexpectedly been identified that exposing non-dissolving pulps to electron beam radiation emitted from a plurality of locations renders those pulps suitable for use as feedstocks in the viscose process.

Electron beam radiation may be emitted from any number of locations, for example, from two, three, four, five or six locations. However, in preferred aspects of the present invention, electron beam radiation is emitted from two locations, most preferably, from above and below the pulp. The electron beam radiation may be emitted from a single, movable electron beam source, or from a plurality of electron beam sources which may independently be fixed or movable. The emission of electron beam radiation from the plurality of locations may be simultaneous or sequential.

Preferably, the voltage of the electron beam radiation to which the non-dissolving pulp is exposed will be lower than that used in conventional electron beam treatment processes. For example, the electron beam radiation emitted from one, some or all of the locations will be about 1.5 meV or lower, about 1.0 meV or lower, about 800 keV or lower, about 600 keV or lower, about 500 keV or lower, about 400 keV or lower, about 300 keV or lower, about 250 keV or lower, or even about 200 keV or lower.

Any electron beam emitting apparatus known to those skilled in the art which is capable of emitting the required voltage and dose of radiation may be employed in the process of the present invention.

For example, medium voltage equipment capable of delivering doses of electron beam radiation at a voltage of 750 keV to 1.5 meV can be used. Treatment services employing such equipment are offered by a range of companies, for example AquaMed. Such apparatus is advantageous as the pulp processing speeds (i.e. the treatment speeds) are high. However, in view of the emission of higher voltage electron beam radiation, more shielding around the electron beam source is required, which makes manipulation of the apparatus and / or the pulp to achieve irradiation from at least two locations is, in some instances, challenging.

These difficulties can be ameliorated through the use of low voltage equipment, for example that used in coating curing systems. Examples of such apparatus are provided, at least in the UK, by PCT Engineering Systems. The apparatus is capable of delivering curtain beam doses of electron beam radiation at a voltage of up to 300 keV. The width of the beam is adjustable depending on the area of pulp to be treated and treatment is achieved with an acceptable level of consistency. As a result of the emission of relatively low voltage electron beam radiation, minimal shielding is required, making the apparatus more manipulable for treating pulp from a plurality of locations and / or using a plurality of said devices in different locations simultaneously and / or sequentially without any risk to the user's health.

In certain embodiments, treatment of the non-dissolving pulp with equal amounts of electron beam radiation from the different locations is preferred. However, in alternative arrangements, the amount of radiation emitted from the different locations varies by about 100 keV or lower, about 80 keV or lower, about 60 keV or lower, about 50 keV or lower, about 40 keV or lower, about 30keV or lower, about 20 keV or lower, about 10 keV or lower, or about 5 keV or lower.

The overall dose of electron beam radiation to which the pulp is exposed may vary. In preferred aspects of the present invention, the pulp is exposed to a dose of electron beam radiation in the order of about 0.5 to about 5.0 mRad (about 5 to about 50 kgy), about 1.0 to about 4.0 mRad (about 10 to about 40 kgy), about 1.5

mRad to about 3.5 mRad (about 15 to about 35 kgy), about 2.0 mRad to about 3.0 mRad (about 20 to about 30 kgy), or about 1.0 to about 2.0 mRad (about 10 to about 20kgy). In embodiments where the pulp is fed past the electron beam/s to expose the pulp to radiation, the feed speed can be controlled to ensure that the target dose is administered.

The dose and voltage of radiation to which the non-dissolving pulp is exposed may be varied depending on the source, density, area, thickness and / or weight of the pulp being treated. Pulp which is treated in accordance with the present invention may have a thickness ranging from about 0.1mm, about 0.5 mm, about 1.0mm, about 5.0mm, or about 10.0mm to about 100mm, about 50mm, about 20mm, about 15mm, or about 10mm. The weight of the pulp which is treated in the process of the present invention may range from about 200 g/m^2, about 400 g/m^2, about 600 g/m^2, or about 700 g/m^2 to about 2000 g/m^2, about 1500 g/m^2, about 1200 g/m^2, about 1000 g/m^2, or about 800 g/m^2.

The non-dissolving pulp may be exposed to the electron beam radiation on a continuous basis (e.g. through use of conveyor means) or on a batch basis.

The treated pulp will preferably exhibit a degree of polymerisation of about 600 or lower, about 500 or lower, about 400 or lower, or most preferably about 300 or lower. This constitutes a significant improvement over the degree of polymerisation of untreated non-dissolving pulps, which typically is around 800 to 1400. Surprisingly, these advantageous results can be obtained using significantly lower voltage and / or doses of radiation than have been employed conventionally.

Prior to, simultaneously with, or following exposure of the pulp to electron beam radiation, the pulp may be subjected to one or more preliminary processing steps. For example, in the case of fluff pulps, these may be supplied in sheet form and it may be desirable to fluff or shred them, for example using a high shear mixer. Additionally or alternatively, the pulp may be subjected to a drying step, for example, by placing it in an oven and heating it to a temperature of, e.g., about 40°C to 100°C prior to, simultaneously with, or following electron beam treatment. As a further potential preliminary processing step, pulp may be delaminated.

In a preferred embodiment of the present invention, the pulp is subjected to reduced temperature treatment.

Without wishing to be bound by theory, it is believed that by exposing pulp to cold temperatures, the fibrous nature of the wood pulp is disrupted, potentially breaking hydrogen bonding and making the cellulose fibres more accessible.

Reduced temperature treatment is achieved by exposing the pulp to low temperatures, for example 0°C or lower, -50°C or lower, -100°C or lower, -150°C or lower or -180°C or lower.

Reduced temperature treatment can be effected by storing or holding the pulp in a low temperature environment, for example, an industrial freezer. Additionally or alternatively the pulp may be exposed to a low temperature agent, for example a cryogenic liquid such as liquid nitrogen, liquid helium, liquid hydrogen, liquid oxygen, liquid neon or mixtures thereof. If a liquid low temperature agent is employed, the pulp is preferably saturated and / or submerged therein.

In preferred arrangements, the reduced temperature treatment has a duration of about 60 minutes or less, more preferably about 30 minutes or less, about 20 minutes or less, or about 15 minutes or less.

Following treatment with electron beam radiation in accordance with the process of the present invention, the treated pulp may then be subjected to one or more steps employed in conventional processes for producing cellulose shaped articles. For the avoidance of any doubt, it is not essential that the steps of the present invention are performed on an in-line basis; they can be performed off-line, using separate apparatus, separated processing lines, in separate facilities, *et cetera*.

The treated pulp may be subjected to one or more of the following steps typically employed in the viscose process: i) dissolution / slurrying; ii) steeping; and/or iii) xanthation. Additionally, the cellulose containing solution formed in step (b) is preferably obtained by dissolution of cellulose to form viscose (hereinafter referred to as vissolution or vissolving).

Regarding step i), this is typically performed by forming a solution or slurry of cellulose-containing pulp in a basic liquid, for example a caustic solution, typically comprising an alkali metal hydroxide such as sodium hydroxide. Conventionally, the concentration of the caustic solution used with dissolving pulps is 18% to 20% by weight. The concentration of the cellulose in the solution or slurry is typically in the range of about 2% to 15% by weight.

In step ii), a solution or slurry of cellulose is steeped in a basic solution for a period of time. This results in the basic solution penetrating the cellulose, resulting in the partial formation of the alkali salt of cellulose, for example the sodium salt. As with step i), the basic liquid is generally a caustic solution, typically comprising an alkali metal hydroxide such as sodium hydroxide. Conventionally, the concentration of the caustic solution used with dissolving pulps is 18% to 20% by weight. The concentration of the cellulose in the solution or slurry is typically in the range of about 2% to 15% by weight. Steeping is generally conducted for about 10 to 120 minutes and at a temperature equal to or greater than about 50°C.

The same process conditions may be employed if step ii) is performed in the process of the present invention. However, surprisingly, it has been found that advantageous results can be obtained when the treated non-dissolving pulp is exposed to milder conditions.

Thus, in preferred embodiments of the present invention, step ii) is performed by steeping the non-dissolving treated pulp in a caustic solution of 16% to 18% alkali metal hydroxide. In particularly preferred embodiments, the treated pulp is steeped in a caustic solution having a concentration of about 16.5% to about 17.5%, about 17.5% to about 18%, about 17% to about 18%, about 16.6% to about 17.0%, or about 17.2% to about 17.8% alkali metal hydroxide by weight. Caustic solutions of the same concentrations may be used to form a slurry or solution in step i) as outlined above.

It has also unexpectedly been found that steeping pulp treated according to the process of the present invention at lower temperatures than those used conventionally results in an alkali cellulose that can be used to form viscose solutions exhibiting improved properties. Thus, in preferred embodiments of the present invention, steeping is performed, at least partially, at a temperature in the range of about 30°C to about 50°C, about 35°C to about 48°C, about 35°C to about 45°C, about 38°C to about 42°C, or about 40°C to about 48°C.

It has been found that the preferred steeping conditions of the present invention, which can be used to produce viscose solutions exhibiting good filterability, may result in the removal of less hemicellulose from the cellulose pulp than if conventional steeping conditions are used with dissolving pulps. It was previously considered that the greatest possible amount of hemicellulose should be removed from the pulp to maximise filterability of the resulting viscose solution. However, it has unexpectedly been found that while a significant proportion of native hemicellulose should be removed from the pulp, retention of a small amount appears to actually contribute to the quality of the resulting viscose solution.

Thus, in preferred embodiments of the present invention, the cellulose containing solution formed in step (b) preferably contains from 0.1% to about 1.0%, about 0.8%, about 0.6% or about 0.5% of hemicellulose, by weight of the total amount of cellulose present.

In the viscose process as conventionally practiced, manganese may be added to the steeping liquor to reduce the DP of the cellulose pulp. It is typically added in an amount of 40 to 500ppm (by weight of the mixture).

While manganese may be employed in the same way in the process of the present invention, as a result of the advantageous properties arising from the electron beam treatment of non-dissolving pulp, the use of manganese is not essential to obtain viable viscose solutions. Thus, in a preferred embodiment of the present invention, manganese is not added to or is present in the solution or slurry steeped in step ii).

One or more steeping additives may be present in or added to cellulose containing slurries or solutions employed in the process of the present invention. These function by holding open the cellulose structure and the skilled artisan will be familiar with such materials. Examples of steeping additives which may be used include glycerol and / or alkoxylated alcohols, especially ethoxylated alcohols. These may be added to the solution or slurry in any of the steps of the present invention, most preferably in steps i) and / or ii). An example of an especially preferred steeping additive is Berol 388. Where used, a steeping additive such as Berol 388 is preferably added in an amount of about 0.1% to about 5.0%, about 0.5% to about 5%, about 1% to about 4%, or about 0.5% to about 2% by weight of cellulose.

Additionally or alternatively, one or more swelling agents may be present or added to the slurry or solution comprising treated cellulose which is processed in the present invention. Preferably, the one or more swelling agents are added to the slurry or solution in steps i) and / or ii). Specific examples of swelling agents that may be employed in the process of the present invention include propylene glycols, polyethylene glycols, polyvinyl alcohols or polyacrylates.

An additional step conventionally performed in the viscose process is xanthation (step iii)). Pulp treated according to the process of the present invention, or slurries or solutions comprising such pulp, may be subjected to such a step.

In preferred embodiments of the present invention, prior to the commencement of step iii), a slurry or solution comprising the treated cellulose pulp may be subjected to drainage steps (to remove excess basic liquid, for example by pressing), shredding and / or aging steps. If performed, the drainage step and / or the shredding step will preferably result in a cellulose crumb product.

The alkali cellulose product obtained from any drainage step which is performed preferably includes about 32% or less of cellulose and / or about 16% or less alkali material (most preferably alkali metal hydroxide, such as sodium hydroxide).

Conventionally, xanthation is achieved by contacting alkali cellulose formed from dissolving pulps at a temperature of 30°C or higher with 26% to 29% of carbon disulphide, by weight of the cellulose present. For example, alkali cellulose may be added to a churn into which gaseous, liquid or aqueous carbon disulphide is introduced (churn xanthation).

The use of higher quantities of carbon disulphide has been previously found to be problematic as the rate of formation of a sodium trithiocarbonate, an unwanted by-product of a reaction between carbon disulphide and caustic solutions, has been found to increase, especially when xanthation is conducted at elevated temperatures.

While treated non-dissolving cellulose pulp (or crumb, slurries or solutions formed from such pulp) may be subjected to conventional processing conditions in a xanthation step, if performed in the process of the present invention, it has unexpectedly been found that optimal results are obtained when the conventional processing conditions are adjusted.

More specifically, if electron beam irradiated non-dissolving cellulose pulp obtained in accordance with the process of the present invention, or crumb, slurries or solutions formed from such pulp, are subjected to a xanthation step, this is preferably carried out at a temperature of about 30°C or lower, more preferably at about 20°C to about 30°C, about 22°C to about 28°C, about 24°C to about 26°C, or about 25°C to about 30°C.

Additionally or alternatively, said treated pulp, crumb, slurry or solution is preferably contacted with about 30% or more carbon disulphide, by weight of the cellulose present, more preferably about 30% to about 40%, about 30% to about 35% carbon disulphide, about 32% to about 38% carbon disulphide or about 34% to about 38% carbon disulphide. It has unexpectedly been found that increasing the quantity of carbon disulphide used during xanthation reduces the viscosity of viscose solutions formed from the xanthated cellulose.

In preferred arrangements of the present invention, a viscose solution is prepared from the non-dissolving cellulose-containing pulp treated according to the process of the present invention, or from crumb, slurries or solutions prepared therefrom.

This is achieved by dissolving the treated cellulose-containing pulp (or crumb, slurry or solution prepared therefrom) in a basic liquid, for example a caustic solution, typically comprising an alkali metal hydroxide such as sodium hydroxide. The liquid is preferably aqueous.

A quantity and concentration of basic liquid is preferably used which results in a viscose solution having a cellulose content (CIV) of about 5% to 15%, about 5% to 13%, about 5% to about 10%, or about 7% to about 10% and / or a caustic content (SIV) of about 2% to about 10%, about 4% to about 8%, about 5.5% to about 7.5%, or about 6% to about 7%.

Vissolution is preferably carried out at a temperature of about 10°C to about 25°C, about 15°C to about 20°C, about 18°C to about 22°C or about 16°C to about 18°C.

In the process of the present invention, a mercerisation step may be performed. This will preferably be performed following steeping and / or prior to xanthation. The purpose of the mercerisation step is to improve the properties of the cellulose contained in the pulp, for example, by reducing the degree of polymerisation in the cellulose.

As conventionally practiced, the mercerisation step involves removing a portion of an alkali liquid (and optionally adding fresh alkali liquid) from a slurry or solution of dissolving cellulose pulp in alkali liquid to attain a target cellulose content and / or a target alkali or soda content typically at least about 33% cellulose and / or at least about 16% alkali. Such processing conditions may be employed in the process of the present invention.

Alternatively, in the process of the present invention, different target cellulose and / or alkali contents may be preferable. More specifically, in preferred arrangements of the present invention, a treated alkali cellulose product optimally includes about 32% or less of cellulose and / or about 16% or less alkali material (most preferably alkali metal hydroxide, such as sodium hydroxide).

However, given that the pulp will preferably have attained and exhibit a target DP following electron beam treatment in accordance with the process of the present invention, the mercerisation step can be excluded from the process. In one preferred embodiment of the present invention, a slurry or solution containing cellulose prepared in accordance with the present invention subjected to a steeping step (step ii) is preferably cooled to prevent mercerisation occurring. For example, the solution or mixture may be cooled to a temperature of about 50°C or less, about 40°C or less, about 30°C or less, or most preferably, to a temperature of about 25°C or less.

As an alternative to employing pulps treated according to the present invention in a viscose-type process, including one or more of the steps mentioned above, the pulp may be used in an ionic liquid cellulose regeneration process. In such processes, pulps are mixed with and / or dissolved in a molten ionic liquid. Preferred ionic liquids include those which are liquid at room temperature, for example 1-ethyl-3-methyl-imidazolium acetate or 1-butyl-3-methylimidazolium acetate (hereinafter referred to as EMIM acetate and BMIM acetate, respectively) as well as other ionic liquids disclosed in EP1458805, EP1893651, EP1805131, US2009/0084509, GB1011446.

To facilitate dissolution, one or more dissolution promoters may be present in or added to the ionic liquid solution or dope. Those skilled in the art will be familiar with such materials. In preferred embodiments of the present invention, specific examples of dissolution promoters which may be used include polar aprotic materials, especially dimethyl sulphoxide, dimethylacetamide, tetrahydrofuran, dimethylformamide, formamide, N-methylmorpholine-N-oxide, pyridine, acetone, dioxane, N-methylpyrrolidone, piperyline sulfone and hexamethylphosphoramide or mixtures thereof and / or nitrogen-containing bases, such as pyridine, ammonia, morpholine, diethanolamine, triethanolamine, piperidine, triethylamine, urea or mixtures thereof.

A cellulose-containing solution formed from a pulp treated according to the process of the present invention preferably exhibits a K value of at least 400, more preferably of at least 500, at least 600, or at least 700.

Additionally or alternatively, a cellulose-containing solution formed from a pulp treated according to the process of the present invention preferably exhibits one or more of the following characteristics: an Rv of about 200 or higher, more preferably about 500 or higher, a TVW of about 100 or higher and a fibre count of about 100 fibres / gram or lower, or more preferably 20 fibres / gram or lower.

Generally, as a result of the treatment to which the pulp is subjected to as part of the present invention, cellulose-containing solutions formed entirely from treated, non-dissolving pulps may be prepared. However, those skilled in the art may nevertheless wish to produce solutions from a mixture of dissolving and non-dissolving pulps. Accordingly, in preferred processes of the present invention, at least about 15% of the pulp used in the process of the present invention will be a treated non-dissolving pulp. In other words, at least about 15% of the cellulose steeped in step (ii) and / or present in the solution formed in step (b) and / or present in the solution from which the cellulose shaped article is cast in step (c) will be obtained from a treated non-dissolving pulp.

In more preferred embodiments, at least about 25%, about 50%, about 70% about 90% about 95% or even about 98% of the cellulose steeped in step (ii) and / or present in the solution formed in step (b) and / or present in the solution from which the cellulose shaped article is cast in step (c) will be obtained from a treated non-dissolving pulp.

The process of the present invention further comprises the step of casting a cellulose shaped article from the cellulose solution, i.e. from the viscose solution or from an ionic liquid-cellulose dope or solution. The techniques for doing so will be well known to those skilled in the art. For example, in preferred embodiments, where the shaped articles are cellulose fibres, those fibres are preferably formed by extruding the cellulose solution through a spinnerette, to produce a fibrous material. However, any fibre-forming techniques and apparatus may be employed.

Likewise, in embodiments of the present invention, where cellulose shaped articles other than fibres are prepared from the cellulose solution, the cellulose solution may be moulded, formed or shaped into the desired arrangement using conventional techniques known to those skilled in the art.

Additionally, in embodiments where cellulosic articles are formed from fibres prepared from the cellulose solution, the cellulose fibres may be converted into those articles using any techniques known to those skilled in the art.

The shaped cellulose solution is preferably then transferred into a casting bath including a casting solution.

According to a second aspect of the present invention, there is provided a cellulose shaped article obtained according to the method of the first aspect of the present invention.

According to a third aspect of the present invention, there is provided a system for processing cellulose comprising at least one electron beam source and a means for exposing untreated cellulose-containing pulp to an electron beam emitted from the at least one electron beam source, the at least one electron beam source capable of emitting electron beams from a plurality of locations.

In a first embodiment, the system comprises a single electron beam source which is capable of moving or being moved to a plurality of different locations for emission of electron beam radiation toward the cellulose-containing pulp. In an alternative embodiment, the system comprises a plurality of electron beam sources which independently may or may not be capable of moving or being moved.

The means for exposing untreated cellulose pulp preferably comprise conveyor means, such as a conveyor belt. In such embodiments, the cellulose-containing pulp is preferably provided as a sheet or layer on the conveyor means and is moved by the conveyor means into the electron beams emitted from the plurality of locations. Additionally or alternatively, one or more electron beam sources may move or be moved to irradiate the pulp from a plurality of locations. In such embodiments, at least one of the locations is preferably above the conveyor and at least one of the locations is preferably below the conveyor.

For the avoidance of any doubt, references to features of the first aspect of the present invention discussed above are optionally applicable to the product of the second aspect and the system of the third aspect of the present invention, where appropriate.

The invention will now be illustrated in the following examples.

Example 1 – Comparison of E-Beam Treatment Methods – DP of Treated Pulps

A range of non-dissolving pulp samples provided by Weyerhauser were subjected to electron beam irradiation treatment in accordance with techniques used conventionally (one-sided at a voltage of 1.5meV) and in accordance with the process of the present invention (two-sided, with electron beam sources positioned above and below the pulp feed, delivering electron beam radiation at a voltage of 250 to 280 keV from each source). The degree of polymerisation (DP) was assessed before and after treatment and the results are provided below and also in Figures 1a to 1e.

Table 1 – Results of Electron Beam Treatment Using Conventional Techniques

	Conventional Processing Techniques					
Pulp	**Basis Weight (g/M^2)**	**Initial DP**	**Dose (kgy)**	**Final DP**	**DP Reduction**	**% DP Reduction**
Pearl 429	775	705	0	705	0	0
	775	705	3	589	116	16
	775	705	6	535	170	24
	775	705	12	460	245	35
	775	705	24	381	324	46
	775	705	36	334	371	53
	775	705	48	313	392	56
Fluff 416	760-775	1123	0	1123	0	0
	760-775	1123	3	796	327	29
	760-775	1123	6	682	441	39
	760-775	1123	12	544	579	52
	760-775	1123	24	437	686	61
	760-775	1123	36	393	730	65
	760-775	1123	48	320	803	72
Peach	766	587	0	587	0	0
	766	587	3	457	130	22
	766	587	6	408	179	30
	766	587	12	351	236	40
	766	587	24	295	292	50
	766	587	36	287	300	51
	766	587	48	260	327	56

SBSK	1040	1153	0	1153	0	0
	1040	1153	3	851	302	26
	1040	1153	6	749	404	35
	1040	1153	12	598	555	48
	1040	1153	24	475	678	59
	1040	1153	36	432	721	63
	1040	1153	48	371	782	68
NBSK	859	1205	0	1205	0	0
	859	1205	3	812	393	33
	859	1205	6	696	509	42
	859	1205	12	557	648	54
	859	1205	24	451	754	63
	859	1205	36	408	797	66
	859	1205	48	338	867	72

Table 2 – Results of Electron Beam Treatment Using Inventive Techniques

	Inventive Processing Techniques						
Pulp	**Applied Voltage**	**Basis Weight (g/M^2)**	**Initial DP**	**Dose (kgy)**	**Final DP**	**DP Reduction**	**% DP Reduction**
Pearl	250keV	775	705	0	705	0	0
	250keV	775	705	3.1	551	154	22
	250keV	775	705	6.3	462	243	34
	250keV	775	705	15.9	393	312	44
	250keV	775	705	30.7	310	395	56
Peach	250keV	766	587	0	587	0	0
	250keV	766	587	1.5	506	81	14
	250keV	766	587	3.1	478	109	19
	250keV	766	587	6.3	414	173	29
	250keV	766	586	16.4	358	228	39
Fluff 416	250keV	760-775	1123	0	1123	0	0
	250keV	760-775	1123	4.4	713	410	37
	250keV	760-775	1123	8.7	622	501	45
	250keV	760-775	1123	16.8	478	645	57
	250keV	760-775	1123	38.6	368	755	67
NBSK	260keV	859	1205	0	1205	0	0
	260keV	859	1205	4	808	397	33
	260keV	859	1205	7.9	658	547	45
	260keV	859	1205	16.7	508	697	58

	260keV	859	1205	39.5	384	821	68
SBSK	280keV	1040	1153	0	1153	0	0
	280keV	1040	1153	4.4	749	404	35
	280keV	1040	1153	8.7	633	520	45
	280keV	1040	1153	17.2	520	633	55
	280keV	1040	1153	36.7	396	757	66

As can be seen, by employing two-sided electron beam treatment, reductions in DP comparable to those observed using conventional techniques are observed. Importantly however, these results are achieved using significantly lower voltage electron beam radiation *and* substantially lower doses of electron beam radiation.

This provides numerous advantageous options to those skilled in the art, including the capability to obtain pulp having an acceptable DP from a non-dissolving pulp and the possibility of doing so using less energy as well as the possibility to replace conventionally employed medium or high dose electron beam apparatus with less hazardous low dose apparatus.

Further, as is apparent from Figures 1a to 1e, which show the observed reductions in DP of the different pulps that were tested, it can be seen that all pulps responded to treatment using the inventive technique to some extent (meaning that the inventive technique is not limited to use with specific non-dissolving pulp types), and in the case of a number of pulps, to a greater extent.

Example 2 – Comparison of E-Beam Treatment Methods – Viscose Properties

A series of viscose solutions were prepared using either cellulose-containing pulp treated according to the process of the present invention, or pulp treated using conventional, single location electron beam treatment. Viscose solutions were prepared employing the processing conditions set out in the table below.

Table 3 – Viscose Processing Conditions

Exp No.	Pulp	DP	Steeping				Xanthation	
			NaOH (%)	Temp (°C)	Time (mins)	Berol 388 (% of Cello)	CS_2 (%)	Temp (°C)
1	Inventive	396	16.8	40	15	0	36	25
	Conventional	381	16.8	40	15	0	36	25
2	Inventive	396	17.75	40	15	0	36	25
	Conventional	381	17.75	40	15	0	36	25
3	Inventive	462	17.75	50	15	4	36	25
	Conventional	460	17.75	50	15	4	36	25
4	Inventive	396	17.75	50	15	1	31	30
	Conventional	381	17.75	50	15	1	31	30
5	Inventive	396	17.75	50	15	1	36	25
	Conventional	381	17.75	50	15	1	36	25

The fibre count and Rv of the resulting viscose solutions were tested and the results are provided in the table below:

Table 4 – Obtained Viscose Solution Properties

Exp No.	Pulp	Viscose Quality	
		Fibre Count	Rv
1	Inventive	17	45
	Conventional	38	35
2	Inventive	0	130
	Conventional	12	74
3	Inventive	4	311
	Conventional	5	216
4	Inventive	7	549
	Conventional	22	329
5	Inventive	0	850
	Conventional	9	586

As can be seen, the properties of the viscose solutions prepared from pulps treated according to the process of the present invention were superior to pulps prepared from conventionally treated pulps which were processed using the same conditions. This is especially surprising given that the initial DP of the inventive-treated pulps was slightly higher than the conventionally treated pulps.

Example 3 – Comparison of E-Beam Treatment Methods – Viscose Properties

Viscose solutions were prepared using either cellulose-containing pulp treated according to the process of the present invention or untreated pulp. The processing conditions employed to prepare the viscose solutions are set out in the table below.

Table 5 – Viscose Processing Conditions

Exp No.	Pulp	Steeping				Xanthation	
		NaOH (%)	Temp (°C)	Time (mins)	Berol 388 (% of Cello)	CS_2 (%)	Temp (°C)
1	Untreated	17.75	50	15	1	36	25
2	Inventive	17.75	50	15	1	36	25

The Rv of the resulting viscose solutions were tested and the results are provided in the table below:

Table 6 – Obtained Viscose Solution Properties

Exp No.	Pulp	Viscose Quality (Rv)
1	Untreated	285
2	Inventive	850

As is apparent, there is a dramatic increase in viscose quality in solutions prepared from pulps treated according to the process of the present invention, as compared to untreated pulps.

Example 4 – E-Beam Treatment Efficiency

The consistency and distribution of e-beam treatment was investigated. A reel of Pearl 429 pulp was subjected to e-beam treatment according to the present invention. Following this, the radius of the pulp reel was divided up into 4 equal parts (Sample 1 – pulp on the outside of the reel, Sample 4 – pulp on the core of the reel).

At each sample point, sections were cut to test the DP for both edges (North and South) and the centre of the reel. The pulp samples were delaminated and the DP of the top surface, bottom surface and an average DP of the pulp sample was taken. Prior to testing for DP, each sample was cut-up, fluffed in a high shear mixer to increase the surface area, and stored in an oven at 60°C.

Samples from each of the four parts of the e-beam treated reel were then used to prepare viscose solutions. The processing conditions employed to prepare the viscose solutions are set out in the table below.

Table 7 – Viscose Processing Conditions

Exp No.	Pulp	Steeping					Xanthation	
		NaOH (%)	Temp (°C)	Time (mins)	Berol 44 (ml)	Berol 388 (ml)	CS_2 (%)	Temp (°C)
1	Pearl 429	17.5	42	15	4.0	2.5	29	27
2	Pearl 429	17.5	42	15	4.0	2.5	29	27
3	Pearl 429	17.5	42	15	4.0	2.5	29	27
4	Pearl 429	17.5	42	15	4.0	2.5	29	27

The Rv, Ball Fall Velocity (BFV), Fibre Count, Cellulose in Viscose content (CiV) and Soda in Viscose content (SiV) of the resulting viscose solutions were tested and the results are provided in the table below.

Table 8 – DP and Viscose Solution Properties

Sample No.	Edge of Reel	Side of Pulp	DP	Av. DP	Overall Av. DP	Range	S.D	BF	FC	Rv	TVW (g/30min)	CIV	SIV
1	North	Top	355	365	371	32	11	40	7	141	184.4	9.08	6.05
		Bottom	365										
		Average	374										
	Centre	Top	378	380									
		Bottom	374										
		Average	387										
	South	Top	365	370									
		Bottom	361										
		Average	384										
2	North	Top	365	370	372	32	12	41	17	141	180.5	9.25	6.09
		Bottom	361										
		Average	384										
	Centre	Top	384	381									
		Bottom	368										
		Average	390										
	South	Top	358	367									
		Bottom	361										
		Average	381										
3	North	Top	345	346	349	24	7	36	7	129.4	213.5	8.82	5.84
		Bottom	341										
		Average	351										
	Centre	Top	348	353									
		Bottom	345										
		Average	365										
	South	Top	348	348									
		Bottom	348										
		Average	348										
4	North	Top	378	384	388	29	9	39	15	193.9	180.5	8.76	5.82
		Bottom	381										
		Average	393										
	Centre	Top	384	395									
		Bottom	393										
		Average	407										
	South	Top	384	384									
		Bottom	384										
		Average	384										

Figure 2 shows the relationship between the viscose quality (Rv) and the standard deviation of each of the samples.

The Rv value for laboratory viscose is usually considerably higher than that of the equivalent industrial viscose (manufactured at a plant). Laboratory viscose with an Rv value of greater than 100 is generally considered acceptable for industrial processing.

The optimum DP for Pearl 429 has previously been found to be in the range of about 380 to 400, as this ensures good processability and good quality of the final product.

From the DP and standard deviation results, it can be seen that there is fairly uniform e-beam treatment across the reel. Furthermore, Samples 1, 2 and 4 have DPs falling within the desired range.

Sample 3 has a slightly lower DP, which suggests over-treatment of the pulp in this part of the reel. However, the pulp has an acceptable Rv value of 129.4 which shows that the over-treatment has not been substantially detrimental.

Without wishing to be bound by theory, it is believed that so long as the pulp is uniformly treated with e-beam treatment, even if there is slight over-treatment, the quality of the viscose produced will be acceptable.

CLAIMS

1. A method of producing cellulose shaped articles comprising the steps of:
    a) exposing non-dissolving cellulose-containing pulp to electron beam radiation originating from a plurality of locations,
    b) forming a solution or dope comprising the cellulose-containing pulp, and
    c) casting a cellulose shaped article from the solution.

2. The method of Claim 1, wherein electron beam radiation is emitted from two locations.

3. The method of Claim 1 or 2, wherein electron beam radiation is emitted from locations above and below the pulp.

4. The method of any one of Claims 1 to 3, wherein the voltage of the electron beam radiation emitted at one or more of the plurality of the locations is about 1.5 meV or lower.

5. The method of any one of Claims 1 to 4, wherein the voltage of the electron beam radiation emitted at one or more of the plurality of the locations is about 500 keV or lower.

6. The method of any one of Claims 1 to 5, wherein the voltage of the electron beam radiation emitted varies by about 50 keV or lower.

7. The method of any one of Claims 1 to 6, wherein the dose of electron beam radiation to which the pulp is exposed is about 0.5 mRad to about 5.0 mRad.

8. The method of any one of Claims 1 to 7, wherein the dose of electron beam radiation to which the pulp is exposed is about 1.5 mRad to about 3.5 mRad.

9. The method of any one of Claims 1 to 8, wherein the pulp has a thickness of about 0.1mm to about 100mm.

10. The method of any one of Claims 1 to 9, wherein the pulp has a weight of about 200 g/m^2 to about 1200 g/m^2.

11. The method of any one of Claims 1 to 10, wherein, following exposure to electron beam radiation in step a), the pulp exhibits an average degree of polymerisation of about 500 or lower.

12. The method of any one of Claims 1 to 11, wherein, following exposure to electron beam radiation in step a), the pulp exhibits an average degree of polymerisation of about 400 or lower.

13. The method of any one of Claims 1 to 12, wherein prior to step b), the pulp is subjected to one or more additional treatment steps selected from fluffing, shredding, drying, delamination and / or reduced temperature treatment.

14. The method of Claim 13, wherein reduced temperature treatment involves the pulp being cooled to about -150°C or lower.

15. The method of Claim 13 or Claim 14, wherein the reduced temperature treatment involves the pulp being saturated and / or submerged in a cryogenic liquid.

16. The method of Claim 15, wherein the cryogenic liquid is selected from liquid nitrogen, liquid helium, liquid hydrogen, liquid oxygen, liquid neon or mixtures thereof.

17. The method of any one of Claims 1 to 16, wherein the cellulose-containing solution is prepared by performing one or more of the steps of:

    i. Slurrying / dissolving the cellulose-containing pulp treated in step a)
    ii. Steeping a solution or slurry of cellulose-containing pulp, and / or
    iii. Xanthation,

    wherein the solution formed in step b) is obtained by vissolution of cellulose to form a viscose solution.

18. The method of Claim 17, wherein the cellulose-containing pulp is steeped in a slurry or solution comprising a caustic solution having a concentration of about 16% to about 18% by weight.

19. The method of Claim 17 or 18, wherein the cellulose-containing pulp is steeped in a slurry or solution comprising a caustic solution having a concentration of about 16.5% to about 17.5% by weight.

20. The method of any one of Claims 17 to 19, wherein the cellulose-containing pulp is steeped in a slurry or solution having a temperature of about 30°C to about 50°C for at least part of the steeping stage.

21. The method of any one of Claims 17 to 20, wherein the cellulose-containing pulp is steeped in a slurry or solution having a temperature of about 40°C to about 48°C for at least part of the steeping stage.

22. The method of any one of Claims 17 to 20, wherein the cellulose-containing pulp is steeped in a slurry or solution having a temperature of about 35°C to about 45°C for at least part of the steeping stage.

23. The method of any one of Claims 17 to 22, wherein the cellulose-containing pulp is steeped in a slurry or solution which is substantially free of manganese.

24. The method of any one of Claims 17 to 23, wherein the cellulose-containing pulp is steeped in a slurry or solution which comprises a steeping additive.

25. The method of Claim 24, wherein the steeping additive is ethoxylated alcohol.

26. The method of Claim 24 or 25, wherein the steeping additive is Berol 388.

27. The method of any one of Claims 17 to 26, wherein prior to xanthation, the cellulose-containing pulp, or a slurry or solution prepared therefrom is subjected to one or more of a drainage step, a shredding step and or an aging step.

28. The method of any one of Claims 17 to 27, wherein xanthation is at least partially carried out at a temperature of about 20°C to about 30°C.

29. The method of any one of Claims 17 to 28, wherein xanthation is carried out by contacting cellulose-containing pulp, or solutions, slurries or crumb prepared therefrom, with carbon disulphide.

30. The method of Claim 29, wherein about 30% to about 40% of carbon disulphide is used, by weight of the total cellulose present.

31. The method of Claim 29 or Claim 30, wherein about 32 to about 38% of carbon disulphide is used, by weight of the total cellulose present.

32. The method of any one of Claims 17 to 31, wherein vissolution is performed, at least partially, at a temperature of about 10°C to about 25°C.

33. The method of any one of Claims 17 to 32, wherein the viscose solution prepared in step b) has a caustic content of about 4% to about 8% by weight of the solution.

34. The method of any one of Claims 17 to 33, wherein the viscose solution prepared in step b) has a cellulose content of about 5% to about 10% by weight of the solution.

35. The method of any one of Claims 17 to 34, wherein upon completion of step ii., the temperature of the slurry or solution is reduced to prevent mercerisation occurring.

36. The method of any one of Claims 1 to 16, wherein the cellulose-containing solution is prepared by contacting the cellulose-containing pulp treated in step a) with an ionic liquid and agitating the mixture.

37. The method of Claim 36, wherein the ionic liquid comprises EMIM acetate or BMIM acetate.

38. The method of any one of Claims 1 to 37, wherein the cellulose-containing solution formed in step b) exhibits one or more of: an Rv of about 200 or higher, a TVW of about 100 or higher and / or a fibre count of about 100 fibres / gram or lower.

39. The method of any one of Claims 1 to 38, wherein the cellulose-containing solution formed in step b) exhibits one or more of: an Rv of about 500 or higher and / or a fibre count of 20 fibres / gram or lower.

40. The method of any one of Claims 1 to 39, wherein the cellulose-containing solution formed in step b) exhibits a K value of at least about 400.

41. The method of any one of Claims 1 to 40, wherein the cellulose-containing solution formed in step b) exhibits a K value of at least about 600.

42. The method of any one of Claims 1 to 41, wherein at least about 15% of the cellulose steeped in step (ii) and / or present in the solution formed in step (b) and / or present in the solution from which the cellulose shaped article is cast in step (c) will be obtained from a treated non-dissolving pulp.

43. The method of any one of Claims 1 to 42, wherein at least about 50% of the cellulose steeped in step (ii) and / or present in the solution formed in step (b) and / or present in the solution from which the cellulose shaped article is cast in step (c) will be obtained from a treated non-dissolving pulp.

44. The method of any one of Claims 1 to 43, wherein at least about 90% of the cellulose steeped in step (ii) and / or present in the solution formed in step (b) and / or present in the solution from which the cellulose shaped article is cast in step (c) will be obtained from a treated non-dissolving pulp.

45. The process of any one of Claims 1 to 44, wherein the shaped articles are fibres.

46. The process of any one of Claims 1 to 44, wherein the shaped articles are ropes, yarns, cloths or cigarette filters.

47. The process of Claim 45, further comprising the step of forming the cellulose fibres cast in step c) into an article.

48. The process of Claim 47, wherein the article is a rope, yarn, cloth or cigarette filter.

49. A cellulose shaped article obtained from the process of any one of Claims 1 to 48.

50. A system for processing cellulose comprising at least one electron beam source and a means for exposing untreated cellulose-containing pulp to electron beams emitted from the at least one electron beam source, the at

least one electron beam source capable of emitting electron beams from a plurality of locations.

51. The system of Claim 50, wherein the system comprises a single electron beam source which is capable of moving or being moved to a plurality of different locations for emission of electron beam radiation toward the cellulose-containing pulp.

52. The system of Claim 51, wherein the system comprises a plurality of electron beam sources which independently may or may not be capable of moving or being moved.

53. The system of Claim 52, wherein the system comprises electron beam sources located above and below the means for exposing untreated cellulose-containing pulp to an electron beam.

54. The system of any one of Claims 50 to 53, wherein the means for exposing untreated cellulose pulp to an electron beam comprise conveyor means

55. The system of Claim 54, wherein the conveyor mean comprises a conveyor belt.

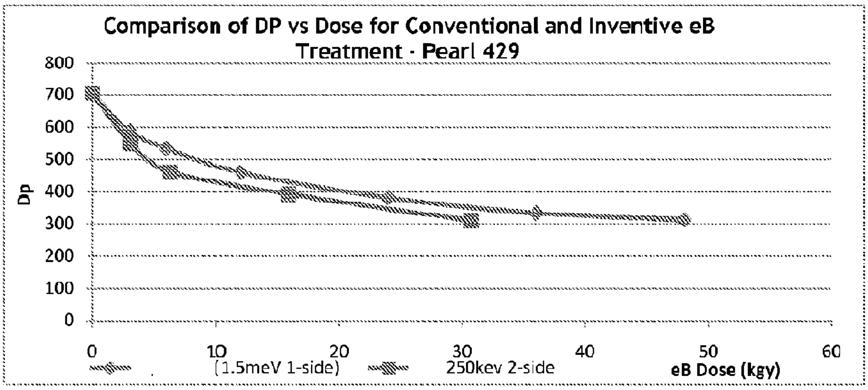

Figure 1A

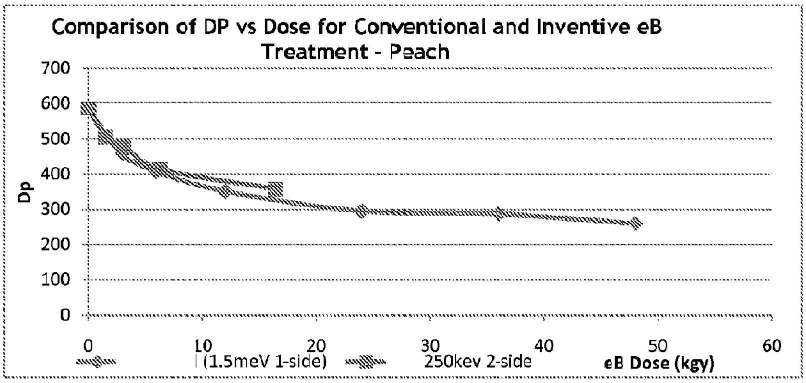

Figure 1B

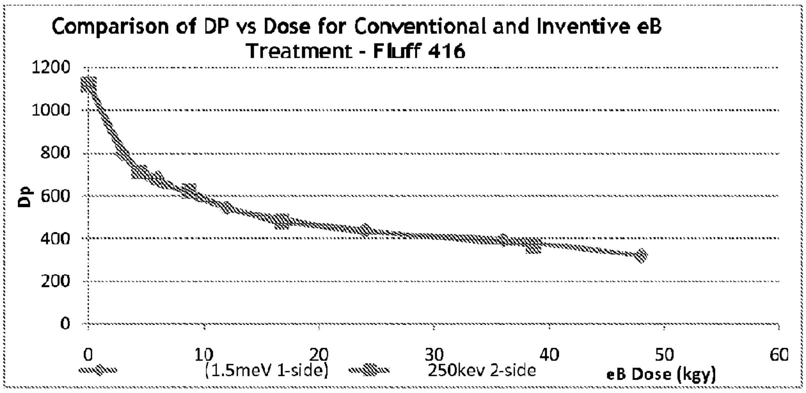

Figure 1C

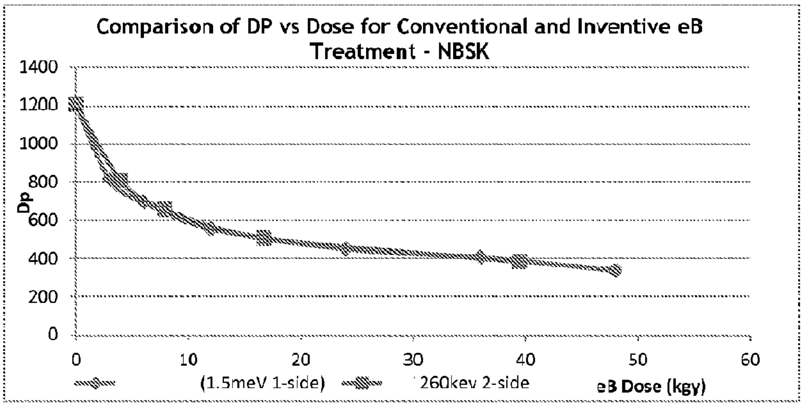

Figure 1D

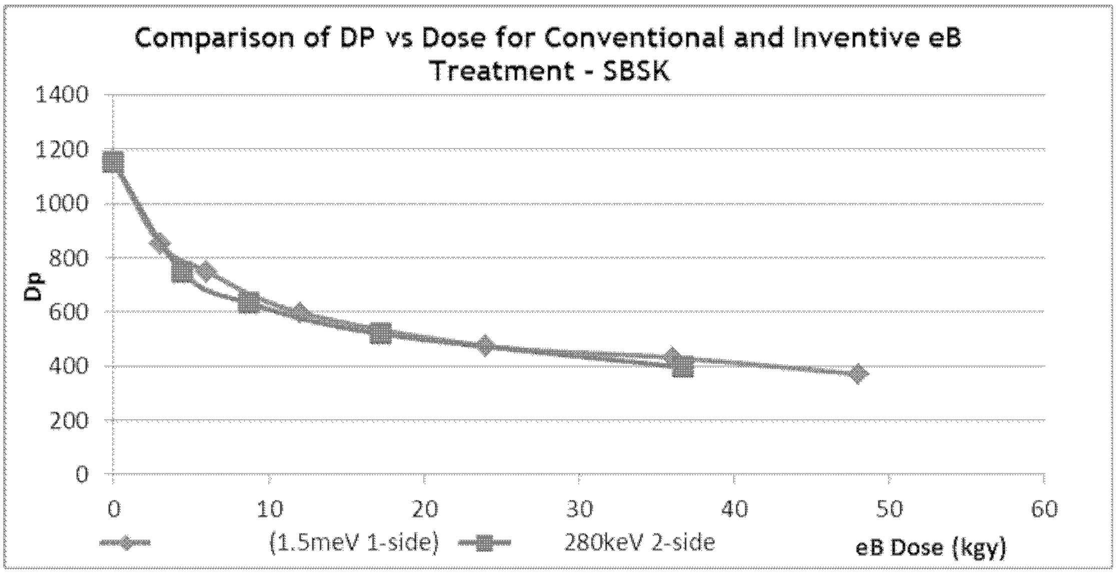

Figure 1E

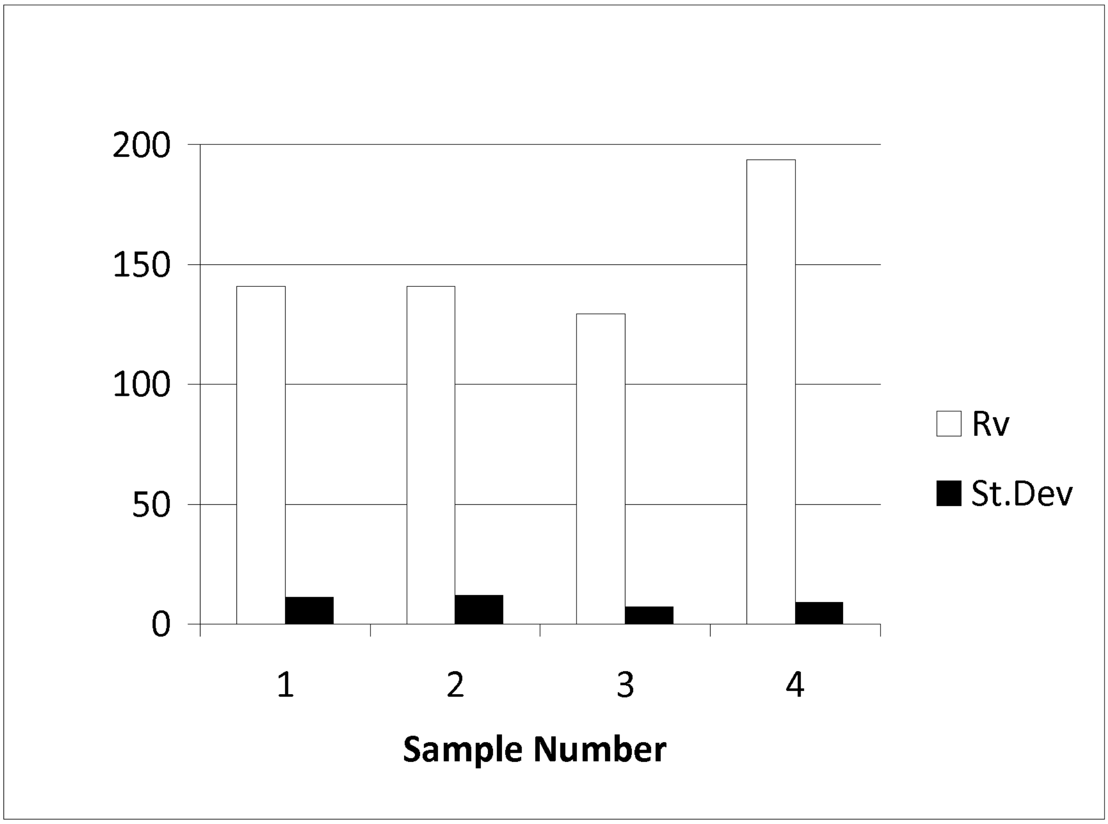

Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/051140

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J3/28 C08J3/09 C08J5/18 A24D3/10 D01F2/00
ADD.

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)
C08J A24D D01F

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 538 130 B1 (FISCHER KLAUS [DE] ET AL) 25 March 2003 (2003-03-25) column 3, line 42 - column 4, line 32 column 5, lines 7-30; examples -----	49
A	US 2009/321025 A1 (WEIGHTMAN DEREK ANDREW [ZA] ET AL) 31 December 2009 (2009-12-31) page 2, paragraphs 28,36,37,40,41,44; examples ----- -/--	1-48

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 27 July 2012	Date of mailing of the international search report 07/08/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Masson, Patrick

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	LOPATA V J ET AL: "New electron beam facility for R&D and production at acsion industries", NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH, SECTION - B:BEAM INTERACTIONS WITH MATERIALS AND ATOMS, ELSEVIER, AMSTERDAM, NL, vol. 208, 1 August 2003 (2003-08-01), pages 102-105, XP004438703, ISSN: 0168-583X, DOI: 10.1016/S0168-583X(03)00652-9 figures; table 1	50-55
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X	WO 97/33918 A1 (HOECHST AG [DE]; COURTAULDS PLC [GB]; HIDASI GEZA [DE]; POGGI TATJANA) 18 September 1997 (1997-09-18) page 3 page 6, line 27 - page 7, line 3; claims; examples	49
A	US 5 788 939 A (MUELLEDER EDUARD [AT] ET AL) 4 August 1998 (1998-08-04) column 2, line 35 - column 3, line 7 column 4, lines 34-44; example 2	1-48
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	DE 29 41 624 A1 (WOLFEN FILMFAB VEB) 8 May 1980 (1980-05-08) page 4, paragraph 2; claims; examples -----	1-48
X	US 2008/003429 A1 (LUO MENGKUI [US] ET AL) 3 January 2008 (2008-01-03) page 1, paragraph 2-7; claims -----	49

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