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(54) **High bulking resilient fibers through cross linking of wood pulp fibers with polycarboxylic acids.**

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- (73) Proprietor: **JAMES RIVER CORPORATION**
Tredegar Street
P.O. Box 2218
Richmond VA 23217 (US)
- (72) Inventor: **Kokko, Bruce Jerome**
James River Corporation,
1915 Marathon Avenue
Neenah, WI 54956 (US)
- (74) Representative: **Cropp, John Anthony David et**
al
MATHYS & SOUIRE
100 Grays Inn Road
London, WC1X 8AL (GB)

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Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates generally to fibers exhibiting improved resilient bulking and absorbent properties and paper products comprising said fibers. More particularly, this invention relates to an improved method of preparing resilient bulking fibers by crosslinking wood pulp fibers with polycarboxylic acids.

Description of the Related Art

15 It is known in the art that resilient bulking fibers are useful for the preparation of bulkier and more absorbent paper structures. Such paper structures are useful for the manufacture of products such as handsheets, towels, tissues, filters, paperboard, diapers, sanitary napkins, hospital dressings and the like. One method for obtaining resilient bulking fibers is by crosslinking cellulose fibers by treatment with a chemical compound. US-A-3,819,470 discloses modified cellulosic fibers characterized by reduced swellability and a reduced capability of natural fiber-to-fiber bonding when compared to unmodified cellulosic fibers and having a substantive polymeric compound reacted with and attached to the fibers. US-A-20 4,431,481 (equivalent to EP-A-0090588) discloses modified cellulosic fibers produced by treating the fibers with copolymers of maleamic acid. Other known techniques include treatment of fibers with cationic urea formaldehyde resins, (US-A-3,756,913), methylol ureas and melamines (US-A-3,440,135), formaldehyde (US-A-3,224,926), with the condensation product of acrolein and formaldehyde, (US-A-3,183,054), bisacrylamides (EP-A-0,213,415), and treatment with glyoxal or glutaric dialdehyde (WO-A-88104704, US-A-25 4,822,453 and US-A-4,853,086). US-A-4822453 proposes the use of an organic acid such as citric acid in combination with zinc nitrate as a catalyst for the crosslinking action.

The crosslinking methods of the prior art, however, tend to suffer from the disadvantages of toxicity, high cost, or poor effectiveness. Of these, toxicity is especially disadvantageous in view of the mounting concerns over the environment and safety of the workers. Because of these concerns, most currently available bulking fibers and the methods for making them are not commercially acceptable or will be challenged.

Thus, crosslinkers such as epichlorohydrin, divinylsulfone, bisacrylamides, formaldehyde, and formaldehyde-based reagents such as 4,5-dihydroxy-1,2-dimethylol-ethylene urea (common textile finish) present serious hazards to workers and consumers. Formaldehyde-free reagents such as 4,5-dihydroxy-1, 2-dimethyl-ethylene urea, while safer, are very expensive. Other formaldehyde-free reagents such as glyoxal, glutaric dialdehyde, and various resins, while generally considered non-hazardous and reasonably priced, are less effective at producing bulking resilient fibers. For example, treatment of cellulosic fibers with maleamic copolymers or other resins, as taught in US-A-4,431,481, results in fibers having equivalent bulk to fibers without chemical treatment that were heated to the same elevated temperatures as utilized with the resin treatment.

The formation of nits and knots is a common problem in the preparation of bulking resilient fibers through chemical crosslinking. Nit formation is particularly prevalent when faster reacting agents, such as aldehydic compounds, or when polymeric agents are used. Practitioners of the art usually employ debonding agents, mechanical defibration such as hammermilling, and screening to reduce the nit and knot contents of treated fibers. Such measures tend to be costly and can be deleterious to fiber and paper quality.

The prior art does not disclose the use of polycarboxylic acids as crosslinkers or coreactants with other crosslinking systems for the production of bulking absorbent fibers, although the textile industry has demonstrated the use of polycarboxylic acids as crosslinkers or coreactants with other crosslinkers for the enhancement of wrinkle-resistance and durable-press properties in cotton fabrics (US-A-3,526,048 and US-A-4,820,307, and Text. Res. J. (1967), 37, 933 and (1972), 42, 274). Also cellulosic fibers and powders have been crosslinked with citric acid to produce ion exchange materials (US-A-2,759,787).

The present invention overcomes the problems and disadvantages of the prior art directed to papermaking by providing high bulking resilient fibers with little or no nits or knots obtained through crosslinking of wood pulp fibers with polycarboxylic acids such as citric acid.

It is an object of the present invention to provide such resilient bulking fibers in a manner which will minimize the cost and increase the effectiveness of the fibers produced.

It is an additional object of the present invention to minimize the hazards to workers and the environment during preparation of these fibers.

Another object of the present invention is to increase the anionicity of the fibers such that the fibers are more receptive to specific additives and are themselves more conducive to making acceptable paper substrates.

Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

SUMMARY OF THE INVENTION

To achieve the foregoing objects, and in accordance with the purposes of the invention as embodied and broadly described herein, there is provided a resilient bulking fiber comprising individualized crosslinked wood pulp cellulosic fibers having intra-fiber chemical bonds characterised in that the intra-fiber crosslink bonds derive from a polycarboxylic acid, and the degree of crosslinking is at least that sufficient to induce in said individualized fibers at least one of the following, namely twisting, curling and resilient bulking tendency.

There is also provided a method for preparing resilient bulking fibers by:

- (a) contacting wood pulp cellulosic fibers with a crosslinking agent;
- (b) individualizing the cellulosic fibers; and
- (c) curing the individualized cellulosic fibers to form intra-fiber cross-link bonds derived from said crosslinking agent between cellulose molecules within individual fibers of the cellulosic fibers, characterised in that a polycarboxylic acid is employed as the crosslinking agent.

Individualizing the treated fibers prior to heating them to effect crosslinking ensures that the crosslinking is intra-fiber; that is the crosslink bonds are primarily between cellulose molecules of a single fiber. This is in contrast to inter-fiber cross-linking where the bonds are formed between cellulose molecules of different fibers. The resulting dry bulking fibers can be incorporated into products through conventional papermaking techniques. These fibers resist relaxation during papermaking, retaining their bulking behaviour throughout the papermaking process.

The invention further provides the use of polycarboxylic acid as the cross-linking agent to induce twisting and curling in individualized wood pulp cellulosic fibers by the formation of intra-fiber crosslink bonds.

Also provided is an absorbent paper product comprising cross-linked wood pulp cellulose fibers in accordance with the invention to provide improved bulking and absorbent properties. The crosslinked fibers may contain both intra-fiber and interfiber bonds. The paper product may also contain non-crosslinked fibers which may be wood fibers and which may comprise the majority of the product on a weight basis. Examples of wood fibers are pre-dried and never dried Scandinavian bleached spruce kraft, Southern pine bleached kraft, secondary fibers, Southern and Northern softwood krafts and never dried Northern softwood bleached kraft. The paper products may be, for example, handsheets, towels, tissues, filters, paperboard, diapers, sanitary napkins and hospital dressings.

Fig. 1 graphically depicts the Attenuated Total Reflectance (ATR) of CAFC fibers (cf Example 4).

Fig. 2 graphically depicts the ATR spectrum of TC fibers (cf Example 2).

Fig. 3 graphically depicts the ATR spectrum of CA fibers (cf Example 6).

Fig. 4 is a microphotograph of fibers that were oven dried and cured without citric acid.

Fig. 5 is a microphotograph of fibers that were oven dried and cured with citric acid.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will now be made in detail to the present preferred embodiment of the invention. In accordance with the present invention there is provided resilient bulking fibers and a method for their preparation by crosslinking individualized wood pulp cellulose fibers with polycarboxylic acids. The terminology "individualized crosslinked fibers" as used herein, refers to cellulosic fibers that have primarily intrafiber chemical crosslink bonds. That is, the crosslink bonds are primarily between cellulose molecules of a single fiber, rather than between cellulose molecules of separate fibers.

The cellulose fibers are treated with an aqueous solution comprising a polycarboxylic acid and, if desired, an additional agent such as sodium hydroxide or other caustic agent or a coreactant/accelerator. It is preferable to select the coreactant/accelerator from the class of inorganic phosphorus compounds. It is

more preferable to select the coreactant/accelerator from the group consisting of phosphates, phosphites, hypophosphites, pyrophosphates and metaphosphates. It is most preferable to use an inorganic phosphorus compound such as monosodium phosphate.

Dry lap or never dried wood pulp fibers can be used, although it is preferable to use never dried fibers.

5 It is our experience that starting with the never-dried fiber results in maximum bulking levels after crosslinking regardless of the type of cellulose crosslinker used. Not wishing to be bound by any theory, it is believed that never-dried fibers allow for homogeneous distribution of crosslinking chemical in the cell wall, remain in a more individualized state during the crosslinking process, and more readily adopt twisted and curled configurations than do predried fibers.

10 Any wood pulp fibers may be used, although it is preferable to use chemical thermal mechanical pulps, Southern and Northern softwood bleached kraft pulps, and secondary fibers.

According to the present invention, individualized wood pulp cellulosic fibers are crosslinked by a polycarboxylic acid. The degree of crosslinking is at least that sufficient to induce twisting and curling and/or resilient bulking tendency in said individualized fibers. The upper limit would be reached when the degree of crosslinking renders the fibers unfit for the intended use.

15 Individualized crosslinked fibers according to this invention thus include those crosslinked by from less than 1 mole % to more than 25 mole %, calculated on a cellulosic anhydroglucose molar basis, of a polycarboxylic acid crosslinking agent, although from 1 to 25 mole % is preferred.

Any polycarboxylic acid known to crosslink cellulose may be used to crosslink the fibers according to the present invention. Preferred polycarboxylic acids include citric acid, propane tricarboxylic acid, maleic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid and benzene tetracarboxylic acid. It is also contemplated to use polycarboxylic acid precursors and derivatives that will produce the polycarboxylic acid under the reaction conditions utilized to crosslink the fibers. The most preferred polycarboxylic acid is citric acid because it is an inexpensive, nontoxic, environmentally safe, readily available, naturally occurring polycarboxylic acid.

25 The polycarboxylic acid may be present in any concentration in the aqueous solution to allow for a sufficient number of crosslinks. It is advantageous to use in the range of a 3-10% aqueous solution of polycarboxylic acid, with about a 5% aqueous solution being most preferred.

A caustic agent may be used, if desired, including sodium hydroxide.

30 After the fibers are treated with the aqueous solution, the fibers may be dewatered by conventional papermaking techniques, for example, through the use of a screw press. The dewatering is done to any consistency, although higher consistencies are desirable for economical drying. Preferably, the fibers are dewatered to a consistency of at least 30%. In order to maximize the bulking and resilient characteristics of the crosslinked fibers, it is important to minimize compression forces experienced by the fibers prior to crosslinking and particularly during dewatering.

35 The dewatered fibers may be dried by any method that allows individualization of fibers (i.e., minimizes nits, knots, fisheyes, etc.). For example the fibers may be azeotropically dried in a solvent, preferably toluene. Alternatively, the filtered (i.e. dewatered) fibers may be fluff dried using a hot gas such as air or superheated steam.

40 After the fibers have been dried to an individualized state, they are then cured by conventionally known means to bring about the crosslinking reaction. For example, the fibers may be cured by heating them at a temperature in the range of from 150 °C to 180 °C for in the range of about one-half of a minute to about ten minutes.

45 Drying and curing can be accomplished either separately or concurrently in either batch or continuous operations.

In order to maximize the bulking and resilient characteristics of the fibers prepared according to the present invention it is desirable to conduct drying at a lower temperature than that used for curing.

50 Drying and curing of the treated fibers can be achieved by any means that allows heating of the fibers to elevated temperatures, for example, ovens, or heating in hot gas streams such as air, steam, superheated steam, or inert gases such as argon or nitrogen. It is preferred to use reducing atmospheres during drying and curing, such as is achievable with systems like superheated steam or inert gases like nitrogen and argon, to minimize charring, darkening, and degradation of the fibers.

The cured fibers thus prepared can then be dispersed for use. Preferably, the dispersion step involves contacting the cured fibers with water at an elevated temperature.

55 These bulking fibers may then be used -- alone or in blends -- to prepare products that exhibit improved bulking and absorbent properties. The improvement in absorbency relates both to faster rate of absorbency and to increased fluid-holding capacity. The amounts of crosslinked fibers used to prepare the products are readily determinable by those skilled in the art. For instance, filtration and absorbent product

applications will often be made 100% from the fibers of the present invention. On the other hand, towel and tissue paper products may be made by blending fibers according to the present invention with a majority of conventional wood pulp fibers. In such applications, it may be preferable to use crosslinked fibers in an amount of 25% or less by weight of the paper product.

5 Additional advantages and modifications will readily occur to those skilled in the art. The invention in its broader aspects is, therefore, not limited to the specific details and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

10 The following examples further illustrate preferred embodiments of the present invention. The examples should in no way be considered limiting, but are merely illustrative of the various features of the present invention.

Example 1:

15 Never dried Northern bleached softwood kraft fibers (NSWK) were dispersed in a 10% aqueous solution of citric acid, to which 0.03 equivalents of sodium hydroxide (based on equivalents citric acid) had been added. The resultant fibers were filtered to approximately 30% consistency, azeotropically dried in toluene, filtered, and heated in an oven at 160 °C for 10 min. The cured fibers were then disintegrated in 100 °C water for 30 min. (the water temperature drops to 45 °C during this time). The resultant fibers are hereafter referred to as "CATC".

Example 2:

25 Example 1 was repeated without citric acid to produce fibers hereafter referred to as "TC".

Example 3:

30 The fibers described in Examples 1 and 2 were made into pressed British handsheets according to standard methods using the furnish compositions described in Table 1. As can be seen from the data provided in Table 1, sheets made with the furnish containing the CATC fibers had the highest bulk after pressing. Thus, for every 1% incorporation of CATC fibers in a furnish containing NSWK fibers, a 2.5% increase in dry sheet bulk was seen after pressing.

Example 4:

35 Example 1 was repeated except that no sodium hydroxide was added to the citric acid solution, the fibers were fluff dried with hot air in lieu of azeotrope drying in toluene, and curing was done at 180 °C for 2.8 minutes. The resultant fibers are hereafter referred to as "CAFC".

40 Example 5:

Example 4 was repeated without citric acid to generate fibers hereafter referred to as "FC".

Example 6:

45 Example 4 was repeated without the oven curing step to generate fibers hereafter referred to as "CA".

Example 7:

50 Example 4 was repeated without citric acid and without the oven curing step to generate fibers hereafter referred to as "FD".

Example 8:

55 The fibers obtained in Examples 4-7 were used to prepare British handsheets as described in Example 3. The pressed bulk data for the resultant sheets are provided in Table 2.

The crosslinking presumably occurs by the formation of diester bonds between cellulose chains. The existence of ester linkages in the CATC and CAFC fibers is clearly evident from the band at 1728 cm⁻¹

obtained by IR spectroscopy (for example see Figure 1). Such ester linkages are absent in the untreated or uncured fibers (for examples see Figures 2 and 3). The percent covalently bound citric acid was measured in the CAFC fibers by titration according to the method described in Text. Res. J. (1967), 37:933 and found to be 7 wt% (based on weight of oven dried fiber). This means that 23% of the available citric acid had actually reacted with the fiber.

The citric acid crosslinking reaction appeared to impart additional kink and curl to the fibers that were otherwise not achieved by the heat treatments alone. This suggestion was supported by comparison of microphotographs of fibers that were oven dried and cured without citric acid (Figure 4) with microphotographs of fibers that were oven dried and cured with citric acid (Figure 5).

The citric acid crosslinking reaction rendered the NSWK fiber more anionic. This was readily apparent by treating the crosslinked fibers with methylene blue. A deep blue color was retained in the crosslinked fibers, whereas little dye was taken up by the untreated NSWK fibers. The total charge of citric acid crosslinked fibers, made according to Example 4, was 76 meq/100 g. The total charge of untreated fibers was 4 meq/100 g. This anionicity is a further advantage of the fibers of the present invention over those prepared according to the past art, as the polycarboxylic acid crosslinked fibers should be more receptive to cationic additives important to papermaking. For example, the strength of sheets made from the crosslinked fibers should be recoverable without compromising the bulk enhancement by incorporation of a cationic strength resin.

The polycarboxylic acid crosslinking reaction did not appear to damage the NSWK fibers. Thus, the average fiber length was not changed by the crosslinking reaction. Furthermore, the integrity of the fibers was unchanged by the crosslinking reaction as evidenced by microscopic examination (compare Figures 4 and 5). There was some brightness reduction due to the crosslinking reaction (see Table 1).

Example 9:

The successful achievement of bulking fibers is by no means limited to crosslinking with citric acid. Any polycarboxylic acid known to crosslink cellulose will work. To demonstrate this, NSWK fibers were crosslinked with butanetetracarboxylic acid according to the method described in Example 1. The resultant fibers, hereafter referred to as "BTATC", were then made into handsheets according to the method described in Example 3. The physical data on these sheets are provided in Table 3. The existence of ester bonds between cellulose and butanetetracarboxylic acid was verified by IR spectroscopy. As can be calculated from the data in Table 3, a 25% incorporation of the BTATC fibers in the NSWK furnish results in a 92% increase in pressed sheet bulk. Furthermore, there was no brightness loss seen in the preparation of the BTATC fibers.

Example 10:

Partial neutralization of the citric acid prior to fiber treatment is not necessary (See Example 4) for the successful preparation of high bulking resilient fibers as described above. Thus, Examples 1-3 were repeated without the use of sodium hydroxide in the preparation of the treatment solution, and the resultant fibers (i.e. CAT fibers) had equivalent performance to that of the CATC fibers (compare data in Table 4 with that in Table 1). Since the citric acid treated fibers were at 25% consistency prior to drying, 39% of available citric acid (i.e. that acid contained in the dry fiber prior to curing) had reacted with the NSWK fibers to produce the CAT fibers described in this example.

Example 11:

Example 10 was repeated except a treatment solution containing only 5 wt% citric acid was used. As can be seen in Table 4, comparable bulking performance is observed with the resultant CAT fibers relative to those prepared with solutions having twice the level of citric acid. Furthermore, there is a marked improvement in brightness accompanying the reduction of citric acid in the treatment bath. It should also be noted that 53% of the available citric acid had reacted with the NSWK fibers to produce the CAT fibers described in this example.

Example 12:

Example 10 was repeated except a 3 wt% aqueous solution of citric acid was used for the treatment. As can be seen in Table 4, there was a slight reduction in the bulking ability realized with the CAT fiber

prepared under these conditions. Nevertheless, a 2% bulk enhancement is predicted for every 1% incorporation of these fibers in a NSWK furnish. Furthermore, essentially no reduction in brightness was observed with these fibers relative to the control. As was the case with the CAT fibers prepared according to Example 10, about 39% of the available citric acid had reacted with the NSWK fibers to produce the CAT fibers described in this example.

The percent bound citric acid levels as determined by titration (7) are consistently lower than those determined by ion chromatography. The latter method is considered to be more reliable as it is not predicated on an assumption of the number of active equivalents of carboxyl functionality during base hydrolysis.

The results of the above examples suggest that the bulking resilient fibers can be obtained using dilute solutions of polycarboxylic acids without the involvement of other chemical additives. Such a simple treatment chemistry greatly enhances the attractiveness of the present invention. Nevertheless, it has been demonstrated by others that certain additives, such as sodium dihydrogen phosphate or sodium hypophosphite, can apparently accelerate the reaction of polycarboxylic acids with cotton fibers. Text. Chem. Color. (1989), 21, 2,13. Such acceleration is useful for the present invention, as shown in Example 13.

Example 13

NSWK fibers were dispersed in an aqueous solution that contains 5% citric acid and 5% monosodium phosphate, filtered to about 25% consistency, fluff dried, and cured at 180° for 90 seconds. As can be seen in Table 5, the resultant fibers (PCAT) are extremely bulking. The amount of bound citric acid reached in this catalyzed system was 69% of that available. The effectiveness of the monosodium phosphate to accelerate reaction of citric acid with fiber is further exemplified by the observation of 1% bound citric acid after fluff drying alone (PCATU). No bound citric acid has been observed during fluff drying of fibers treated with only citric acid. Some covalently bound phosphate was also detected by ion chromatographic analysis of hydrosylate of PCAT fibers. Thus, phosphate appears to be coreacting along with citric acid, with the cellulose.

Example 14

The citric acid crosslinking treatment is effective at producing bulk and resiliency enhancement in a wide variety of wood pulps. Different wood pulps were treated according to Example 13, unless otherwise stated, and made into pressed 65 g/m² handsheets. The bulk data is provided in Table 6.

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Table 1

Physical Data for Pressed
British Handpapers

Furnish	B.W. (g/m ²)	Dry Bulk (cm ³ /g)	Wet Bulk (cm ³ /g)		Break Length (km)	Bkght. %
			Under Load ^a	After Load ^a		
100% NSWK ^b	25.8 ± 0.3	3.2 ± 0.2	2.29 ± 0.02	2.82 ± 0.03	6.2 ± 0.5	72
75% NSWK, 25% TC ^c	25.0 ± 0.5	3.8 ± 0.4	2.71 ± 0.01	3.40 ± 0.08	3.4 ± 0.2	72
75% NSWK, 25% CATC ^d	25.3 ± 0.9	5.2 ± 0.3	3.8 ± 0.2	4.7 ± 0.3	2.1 ± 0.3	68

- a) 100 g/cm²
- b) Untreated never dried Northern bleached softwood kraft fibers.
- c) Toluene dried, oven cured NSWK.
- d) Toluene dried, oven cured, citric acid treated NSWK.

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Table 2
Data for Pressed British Handsheets

<u>Furnish Composition</u>	<u>Bulk (cm³/g)</u>	<u>D.M. (g/m²)</u>
100% NSWK ^a	2.5 ± 0.1	24.9 ± 0.7
75% NSWK, 25% FC ^b	3.6 ± 0.2	25.0 ± 1.0
75% NSWK, 25% CAC ^c	2.9 ± 0.1	25.8 ± 0.5
75% NSWK, 25% FD ^d	2.9 ± 0.1	25.9 ± 0.2
75% NSWK, 25% CAFCE ^e	4.0 ± 0.2	26.0 ± 1.0

- a) Untreated never dried Northern bleached softwood kraft fibers.
- b) Fluff dried, oven cured (180°C/2.8 min) NSWK.
- c) Fluff dried, citric acid treated NSWK.
- d) Fluff dried NSWK.
- e) Fluff dried, oven cured (180°C/2.8 min), citric acid treated NSWK.

Table 3
Physical Data for Pressed British Handpapers

Furnish Composition	B.W. (g/m ²)	Dry Bulk (cm ³ /g)	Break Length (µm)	Bright (%)	Under Load ^a	After Load ^a	Abs. (g/g)
100% NSWK ^b	243 ± 0.1	25 ± 0.1	55 ± 0.6	80	23	27	2.9
75% NSWK, 25% TIC ^c	256 ± 0.1	26 ± 0.3	42 ± 0.2	81	23 ± 0.2	30 ± 0.2	31 ± 0.2
75% NSWK, 25% BIATC ^d	267 ± 0.1	46 ± 0.1	23 ± 0.2	80	39 ± 0.1	49 ± 0.1	46 ± 0.1

- a) 100 g/cm²
- b) Untreated never dried Northern bleached softwood kraft fibers.
- c) Toluene dried, oven cured NSWK.
- d) Toluene dried, oven cured butanetetracarboxylic acid treated NSWK.

TABLE 4

Data for Pressed British Handsheets (25 g/m²)

	CA in Bath ^a	Wt% Bound CA ^b (c)	Pressed Dry Bulk (cm ³ /g)	B.L. KM	Bright.
100% NSWK ^d	--	--	2.5 ± 0.1	5.5 ± 0.6	80
75% NSWK ^d	--	--	2.8 ± 0.1	4.4	81
25% TC ^e					
75% NSWK ^d					
25% CAT ^f	10	12.3 (11.6)	4.2 ± 0.2	2.5 ± 0.2	72
	5	9.0 (7.9)	4.0 ± 0.1	2.9 ± 0.3	77
	3	5.5 (3.5)	3.8 ± 0.1	2.7 ± 0.2	79
75% NSWK ^d					
25% CT ^g	10	--	3.5 ± 0.1	--	--
75% NSWK ^d					
25% Th	--	--	2.8 ± 0.1	--	--

- a) Wt % citric acid in treatment solution (no sodium hydroxide added).
 b) Citric acid covalently bound to CAT fibers as determined by ion chromatography.
 c) Determined by titration (7).
 d) Never dried Northern bleached softwood kraft fibers.
 e) Toluene dried oven cured NSWK fibers.
 f) Citric acid treated (no sodium hydroxide added), toluene dried, oven cured NSWK fibers.
 g) Citric acid treated (no sodium hydroxide added), toluene dried, NSWK fibers.
 h) Toluene dried NSWK fibers.

TABLE 5
Data for Pressed British Handsheets (25 g/m²)

Furnish	% CA ^a In Bath	% MSP ^b In Bath	Pressed Dry Bulk (cm ³ /g)
100% NSWK ^c	-	-	2.5 ± 0.1
75% NSWK ^c 25% PCAT ^d	5	5	5.5 ± 0.2 ^e
75% NSWK ^c 25% PCATU ^f	5	5	2.8 ± 0.1
75% NSWK ^c 25% FDC ^g	-	-	3.1 ± 0.2

- a) Wt% of citric acid in aqueous bath solution.
- b) Wt% of monosodium phosphate in aqueous bath solution (a).
- c) Bleached Northern softwood kraft fibers.
- d) CA/MSP treated NSWK fibers, fluff dried and cured at 180°C for 90 sec.
- e) A few nits were present.
- f) CA/MSP treated NSWK fibers, fluff dried not cured.
- g) Fluff dried NSWK fibers cured at 180°C for 90 sec.

Table 6

Citric acid crosslinking of different wood pulps	
Furnish ^a	Bulk (cm ³ /g)
100% Husum ^b (predried)	1.8
100% Husum ^b (never dried)	1.6
100% SSWK ^c (never dried)	1.8
100% Secondary fibers ^d	1.8
25% Treated Husum (predried) ^e	2.3 ^k
25% Treated Husum (never dried) ^f	2.6 ^k
25% Treated SSWK ^{g,i}	2.4
25% Treated secondary fibers ^h	2.3 ^k
25% Treated CTMP ^{l,m}	2.8 ^k
25% CTMP (never dried)	2.2
100% NSWK (never dried) ^j	1.6

a) Made into pressed 65 g/m² British handsheets

b) Scandinavian bleached spruce kraft pulp (untreated)

c) Southern pine bleached kraft pulp (untreated)

d) Long fiber fraction of Ponderosa secondary fibers (untreated)

e) 75% untreated predried Husum

f) 75% untreated never dried Husum

g) 75% untreated SSWK

h) 75% untreated secondary fibers

i) 75% NSWK

j) Never dried Northern softwood bleached kraft pulp (untreated)

k) Some nits present

l) Dried and cured with superheated steam at 180 ° C for 30 seconds

m) Starting CTMP was never dried

Claims

1. Individualized crosslinked wood pulp cellulosic fibers having intra-fiber chemical bonds characterised in that the intra-fiber crosslink bonds derive from a polycarboxylic acid, and the degree of crosslinking is at least that sufficient to induce in said individualized fibers at least one of the following, namely twisting, curling and resilient bulking tendency.
2. Individualized wood pulp cellulosic fibers as claimed in claim 1 crosslinked by from 1 mole % to 25 mole %, calculated on a cellulosic anhydroglucose molar basis, of a polycarboxylic acid crosslinking agent.
3. Individualized crosslinked wood pulp cellulosic fibers as claimed in claim 1 or claim 2 in which the polycarboxylic acid crosslinking agent is selected from citric acid and butanetetracarboxylic acid.
4. A resilient fibrous bulking pulp comprising individualized crosslinked wood pulp cellulosic fibers as claimed in any one of claims 1 to 3.
5. A method for preparing resilient bulking fibers by:
 - (a) contacting wood pulp cellulosic fibers with a crosslinking agent;
 - (b) individualizing the cellulosic fibers; and
 - (c) curing the individualized cellulosic fibers to form intra-fiber cross-link bonds derived from said crosslinking agent between cellulose molecules within individual fibers of the cellulosic fibers, characterised in that a polycarboxylic acid is employed as the crosslinking agent.
6. A method as claimed in claim 5 wherein step (a) comprises mixing wood pulp cellulosic fibers with an aqueous solution of polycarboxylic acid.

7. A method as claimed in claim 6 wherein step (b) comprises dewatering and drying the fibers.
8. A method as claimed in claim 7 wherein the dewatering comprises pressing the cellulosic fibers through a screw press.
- 5 9. A method as claimed in claim 7 or claim 8 wherein the fibers are dewatered to a consistency of at least 30%.
- 10 10. A method as claimed in any one of claims 7 to 9 wherein the drying comprises fluff drying.
11. A method as claimed in claims 10 wherein the fluff drying is effected with hot gases.
12. A method as claimed in any one of claims 7 to 11 wherein the drying is effected with superheated steam.
- 15 13. A method as claimed in any one of claims 7 to 12 wherein the drying is effected in a reducing atmosphere.
14. A method as claimed in any one of claims 7 to 9 wherein the drying step comprises azeotropically drying the fibers in a solvent.
- 20 15. A method as claimed in any one of claims 7 to 14 wherein the drying step is performed at a temperature lower than that used for curing in step (c).
- 25 16. The method of any one of claims 5 to 15 wherein the curing is effected in a reducing atmosphere.
17. The method of any one of claims 6 to 16 wherein said aqueous solution is 3-10% aqueous solution of a polycarboxylic acid.
- 30 18. The method of any one of claims 6 to 17 wherein the aqueous solution includes a caustic agent.
19. The method of any one of claims 6 to 17 wherein said aqueous solution comprises citric acid and a coreactant/accelerator.
- 35 20. The method of claim 19 wherein said coreactant/accelerator is selected from phosphates, phosphites, hypophosphites, pyrophosphates and metaphosphates.
21. The method of claim 20 wherein the coreactant/accelerator is monosodium phosphate.
- 40 22. The method of any one of claims 5 to 21 wherein said polycarboxylic acid is selected from citric acid and butanetetracarboxylic acid.
23. The method of any one of claims 5 to 22 wherein the curing step comprises heating the fibers at a temperature in the range of from 150 to 180 °C for a time period in the range of from 0.5 to 10 minutes.
- 45 24. The method of any one of claims 5 to 23 wherein said wood pulp fibers are selected from chemical thermal mechanical pulps, Southern and Northern softwood bleached Waft pulps, and secondary fibers.
25. The method of any one of claims 5 to 24 wherein said wood pulp fibers are never-dried fibers.
- 50 26. An improved resilient bulking and absorbent paper product comprising crosslinked wood pulp cellulose fibers to provide improved bulking and absorbent properties, characterised in that the crosslinked fibers are as claimed in any one of claims 1 to 3 or are obtained by a method as claimed in any one of claims 5 to 25.
- 55 27. A paper product as claimed in claim 26 wherein said crosslinked wood pulp cellulose fibers contain both intra-fiber and interfiber bonds.

28. The paper product of claim 26 or 27 further comprising non-crosslinked fibers.
29. The paper product of claim 28 wherein said non-crosslinked fibers comprise the majority of said product, on a weight basis.
- 5 30. The paper product of claim 28 or claim 29 wherein said non-crosslinked fibers are wood fibers.
31. The paper product of claim 30 wherein said wood fibers are selected from predried or never dried Scandinavian bleached spruce kraft, Southern pine bleached kraft, secondary fibers, Southern softwood kraft, Northern softwood kraft, and never dried Northern softwood bleached kraft.
- 10 32. The paper product of any one of claims 26 to 31 wherein said paper product is selected from handsheets, towels, tissues, filters, paperboard, diapers, sanitary napkins, and hospital dressings.
- 15 33. The use of polycarboxylic acid as the cross-linking agent to induce twisting and curling in individualized wood pulp cellulosic fibers by the formation of intra-fiber crosslink bonds.

Patentansprüche

- 20 1. Individualisierte vernetzte Holzstoffcellulosefasern mit in der Faser befindlichen chemischen Bindungen, dadurch gekennzeichnet, daß die Vernetzungsbindungen innerhalb der Faser von einer Polycarbonsäure abgeleitet sind und der Vernetzungsgrad mindestens ausreicht, um in diesen individualisierten Fasern ein Verdrillen, Kräuseln oder elastisches Ausdehnen auszulösen.
- 25 2. Individualisierte vernetzte Holzstoffcellulosefasern nach Anspruch 1, die mit 1 bis 25 Mol-%, berechnet auf der Molbasis von Celluloseanhydroglucose, eines Polycarbonsäurevernetzungsmittels vernetzt sind.
3. Individualisierte vernetzte Holzstoffcellulosefasern nach Anspruch 1 oder 2, in denen das Polycarbonsäurevernetzungsmittel aus Citronensäure und Butantetracarbonsäure ausgewählt ist.
- 30 4. Elastische faserartige Dickpulpe, die individualisierte vernetzte Holzstoffcellulosefasern nach einem der Ansprüche 1 bis 3 umfaßt.
5. Verfahren zur Herstellung elastischer Dickfasern durch:
- 35 a) Inkontaktbringen von Holzpulpecellulosefasern mit einem Vernetzungsmittel,
b) Individualisierung der Cellulosefasern und
c) Härten der individualisierten Cellulosefasern, um innerhalb der Faser befindliche, von diesem Vernetzungsmittel abgeleitete Vernetzungsbindungen zwischen Cellulosemolekülen innerhalb individueller Fasern der Cellulosefasern zu bilden,
- 40 dadurch gekennzeichnet, daß eine Polycarbonsäure als Vernetzungsmittel verwendet wird.
6. Verfahren nach Anspruch 5, bei dem in Schritt (a) die Holzpulpecellulosefasern mit einer wäßrigen Lösung von Polycarbonsäure vermischt werden.
- 45 7. Verfahren nach Anspruch 6, bei dem in Schritt (b) die Fasern entwässert und getrocknet werden.
8. Verfahren nach Anspruch 7, bei dem die Fasern beim Entwässern durch eine Schneckenpresse gepreßt werden.
- 50 9. Verfahren nach Anspruch 7 oder 8, bei dem die Fasern bis zu einer Konsistenz von mindestens 30 % entwässert werden.
10. Verfahren nach einem der Ansprüche 7 bis 9, bei dem das Trocknen Auflockerungstrocknen umfaßt.
- 55 11. Verfahren nach Anspruch 10, bei dem das Auflockerungstrocknen mit heißen Gasen durchgeführt wird.
12. Verfahren nach einem der Ansprüche 7 bis 11, bei dem das Trocknen mit supererhitztem Dampf durchgeführt wird.

13. Verfahren nach einem der Ansprüche 7 bis 12, bei dem das Trocknen in einer Reduktionsatmosphäre erfolgt.
- 5 14. Verfahren nach einem der Ansprüche 7 bis 9, bei dem im Trockenschritt die Fasern azeotrop in einem Lösungsmittel getrocknet werden.
15. Verfahren nach einem der Ansprüche 7 bis 14, bei dem der Trockenschritt bei einer niedrigeren Temperatur als das Härten in Schritt (c) durchgeführt wird.
- 10 16. Verfahren nach einem der Ansprüche 5 bis 15, bei dem das Härten in einer Reduktionsatmosphäre erfolgt.
17. Verfahren nach einem der Ansprüche 6 bis 16, bei dem die wäßrige Lösung eine 3 - 10%ige wäßrige Lösung einer Polycarbonsäure ist.
- 15 18. Verfahren nach einem der Ansprüche 6 bis 17, bei dem die wäßrige Lösung ein Ätzmittel umfaßt.
19. Verfahren nach einem der Ansprüche 6 bis 17, bei dem die wäßrige Lösung Citronensäure und/oder einen Coreaktanten/Beschleuniger umfaßt.
- 20 20. Verfahren nach Anspruch 19, bei dem der Coreaktant/Beschleuniger aus Phosphaten, Phosphiten, Hypophosphiten, Pyrophosphaten und Methaphosphaten ausgewählt ist.
21. Verfahren nach Anspruch 20, bei dem der Coreaktant/Beschleuniger Mononatriumphosphat ist.
- 25 22. Verfahren nach einem der Ansprüche 5 bis 21, bei dem die Polycarbonsäure aus Citronensäure und Butantetracarbonsäure ausgewählt ist.
23. Verfahren nach einem der Ansprüche 5 bis 22, bei dem beim Härtungsschritt die Fasern über einen Zeitraum von 0,5 bis 10 Minuten bei einer Temperatur im Bereich von 150 bis 180 °C erhitzt werden.
- 30 24. Verfahren nach einem der Ansprüche 5 bis 23, bei dem die Holzpulpefasern aus chemisch-thermischen mechanischen Pulpen, gebleichten Kraftpulpen aus Southern und Northern Softwood (südlichem und nördlichem Weichholz) und Sekundärfasern ausgewählt sind.
- 35 25. Verfahren nach einem der Ansprüche 5 bis 24, bei dem die Holzpulpefasern niemals getrocknete Fasern darstellen.
26. Verbessertes elastisches absorbierendes Dickdruckpapier, das vernetzte Holzpulpecellulosefasern umfaßt, die ihm verbesserte Ausdehnungs- und Absorptionseigenschaften verleihen, dadurch gekennzeichnet, daß die vernetzten Fasern einem der Ansprüche 1 bis 3 entsprechen oder nach einem Verfahren der Ansprüche 5 bis 25 hergestellt wurden.
- 40 27. Papierprodukt nach Anspruch 26, bei dem die vernetzten Holzpulpecellulosefasern Bindungen aufweisen, die sich sowohl innerhalb der Faser als auch zwischen den Fasern befinden.
- 45 28. Papierprodukt nach Anspruch 26 oder 27, das außerdem nichtvernetzte Fasern umfaßt.
29. Papierprodukt nach Anspruch 28, bei dem die nichtvernetzten Fasern den größten Teil des Produkts auf Gewichtsbasis ausmachen.
- 50 30. Papierprodukt nach Anspruch 28 oder 29, bei dem die nichtvernetzten Fasern Holzfasern sind.
- 55 31. Papierprodukt nach Anspruch 30, bei dem die Holzfasern aus vorgetrocknetem oder niemals getrocknetem Scandinavian Spruce Kraft (gebleicht), Southern Pine Kraft (gebleicht), Sekundärfasern, Southern Softwood Kraft, Northern Softwood Kraft sowie niemals getrocknetem gebleichtem Northern Softwood Kraft ausgewählt sind.

32. Papierprodukt nach einem der Ansprüche 26 bis 31, bei dem das Papierprodukt aus Handtüchern, Trockentüchern, mehrlagigem Papier, Filtern, Pappe, Windeln, Monatsbinden und im Krankenhaus verwendeten Verbänden ausgewählt ist.
- 5 33. Verwendung von Polycarbonsäure als Vernetzungsmittel, um in individualisierten Holzpulpecellulosefasern durch die Bildung von Vernetzungsbindungen innerhalb der Fasern ein Verdrillen oder Kräuseln auszulösen.

Revendications

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1. Fibres cellulosiques de pâte de bois réticulées individualisées ayant des liaisons chimiques à l'intérieur des fibres, caractérisées en ce que les liaisons de réticulation à l'intérieur des fibres proviennent d'un acide polycarboxylique et que le degré de réticulation est au moins suffisant pour induire dans ces fibres individualisées au moins l'une des tendances suivantes, à savoir, torsion, ondulation, bouffant élastique.

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2. Fibres cellulosiques de pâte de bois individualisées suivant la revendication 1, réticulées par une quantité de 1 à 25% en moles calculée sur une base molaire d'anhydroglucose cellulosique, d'un agent de réticulation de type acide polycarboxylique.

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3. Fibres cellulosiques de pâte de bois individualisées suivant les revendications 1 ou 2, dans lesquelles l'agent de réticulation de type acide polycarboxylique est choisi parmi l'acide citrique et l'acide butanetetra-carboxylique.

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4. Pâte bouffante fibreuse élastique comprenant des fibres cellulosiques de pâte de bois réticulées individualisées suivant l'une quelconque des revendications 1 à 3.

5. Procédé pour la préparation de fibres bouffantes élastiques par:

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(a) mise en contact des fibres cellulosiques de pâte de bois avec un agent de réticulation;

(b) individualisation des fibres cellulosiques; et

(c) durcissement des fibres cellulosiques individualisées pour former des liaisons de réticulation à l'intérieur des fibres dérivées de cet agent de réticulation entre des molécules de cellulose à l'intérieur des fibres individuelles des fibres cellulosiques, caractérisé en ce qu'un acide polycarboxylique est employé en tant qu'agent de réticulation.

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6. Procédé suivant la revendication 5, dans lequel l'étape (a) comprend le mélange des fibres cellulosiques de pâte de bois avec une solution aqueuse d'acide polycarboxylique.

7. Procédé suivant la revendication 6, dans lequel l'étape (b) comprend l'élimination de l'eau et le séchage des fibres.

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8. Procédé suivant la revendication 7, dans lequel l'élimination de l'eau comprend le pressage des fibres cellulosiques à travers une presse à vis.

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9. Procédé suivant les revendications 7 ou 8, dans lequel les fibres sont débarrassées d'eau jusqu'à une consistance d'au moins 30%.

10. Procédé suivant l'une quelconque des revendications 7 à 9, dans lequel le séchage comprend un séchage donnant du bouffant.

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11. Procédé suivant la revendication 10, dans lequel le séchage donnant du bouffant est effectué avec des gaz chauds.

12. Procédé suivant l'une quelconque des revendications 7 à 11, dans lequel le séchage est effectué avec de la vapeur surchauffée.

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13. Procédé suivant l'une quelconque des revendications 7 à 12, dans lequel le séchage est effectué dans une atmosphère réductrice.

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14. Procédé suivant l'une quelconque des revendications 7 à 9, dans lequel l'étape de séchage comprend le séchage azéotropique des fibres dans un solvant.
- 5 15. Procédé suivant l'une quelconque des revendications 7 à 14, dans lequel l'étape de séchage est réalisée à une température inférieure à celle qui est utilisée pour le durcissement dans l'étape (c).
16. Procédé suivant l'une quelconque des revendications 5 à 15, dans lequel le durcissement est effectué dans une atmosphère réductrice.
- 10 17. Procédé suivant l'une quelconque des revendications 6 à 16, dans lequel cette solution aqueuse est une solution aqueuse de 3 à 10% d'un acide polycarboxylique.
18. Procédé suivant l'une quelconque des revendications 6 à 17, dans lequel la solution aqueuse comprend un agent caustique.
- 15 19. Procédé suivant l'une quelconque des revendications 6 à 17, dans lequel la solution aqueuse comprend de l'acide citrique et un coréactif/accélérateur.
- 20 20. Procédé suivant la revendication 19, dans lequel ce coréactif/accélérateur est choisi parmi des phosphates, des phosphites, des hypophosphites, des pyrophosphates et des métaphosphates.
21. Procédé suivant la revendication 20, dans lequel le coréactif/accélérateur est du phosphate monosodique.
- 25 22. Procédé suivant l'une quelconque des revendications 5 à 21, dans lequel cet acide polycarboxylique est choisi parmi l'acide citrique et l'acide butanetétracarboxylique.
- 30 23. Procédé suivant l'une quelconque des revendications 5 à 22, dans lequel l'étape de durcissement comprend le chauffage des fibres à une température comprise dans la gamme de 150 à 180 °C pendant une période de temps comprise dans la gamme de 0,5 à 10 minutes.
- 35 24. Procédé suivant l'une quelconque des revendications 5 à 23, dans lequel ces fibres de pâte de bois sont choisies parmi des pâtes mécaniques thermiques chimiques, des pâtes pour papier d'emballage fort blanchies de bois tendres du Nord et du Sud, et des fibres secondaires.
- 40 25. Procédé suivant l'une quelconque des revendications 5 à 24, dans lequel ces fibres de pâte de bois sont des fibres jamais séchées.
- 45 26. Produit amélioré de papier absorbant et bouffant élastique comprenant des fibres cellulosiques de pâte de bois réticulées pour fournir des propriétés améliorées de bouffant et d'absorption, caractérisé en ce que les fibres réticulées sont suivant l'une quelconque des revendications 1 à 3 ou sont obtenues par un procédé suivant l'une quelconque des revendications 5 à 25.
27. Produit de papier suivant la revendication 26, dans lequel ces fibres cellulosiques de pâte de bois réticulées contiennent à la fois des liaisons à l'intérieur des fibres et entre les fibres.
- 50 28. Produit de papier suivant les revendications 26 ou 27 comprenant de plus des fibres non réticulées.
29. Produit de papier suivant la revendication 28, dans lequel ces fibres non réticulées constituent la majorité de ce produit, sur une base pondérale.
30. Produit de papier suivant les revendication 28 ou 29, dans lequel ces fibres non réticulées sont des fibres de bois.
- 55 31. Produit de papier suivant la revendication 30, dans lequel ces fibres de bois sont choisies parmi des fibres blanchies pour papier d'emballage fort de sapin de Scandinavie pré-séchées ou jamais séchées, des fibres blanchies pour papier d'emballage fort de pin du Sud, des fibres secondaires, des fibres pour papier d'emballage fort de bois tendre du Sud, des fibres pour papier d'emballage fort de bois

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tendre du Nord et des fibres pour papier d'emballage fort de bois tendre du Nord, jamais séchées.

5 **32.** Produit de papier suivant l'une quelconque des revendications 26 à 31, dans lequel ce produit de papier est choisi parmi des serviettes, des torchons, des mouchoirs, des filtres, du carton, des couches, des serviettes hygiéniques et des pansements pour hôpitaux.

10 **33.** Utilisation d'un acide polycarboxylique en tant qu'agent de réticulation pour induire une torsion ou une ondulation dans des fibres cellulosiques de pâte de bois individualisées par la formation de liaisons de réticulation à l'intérieur des fibres.

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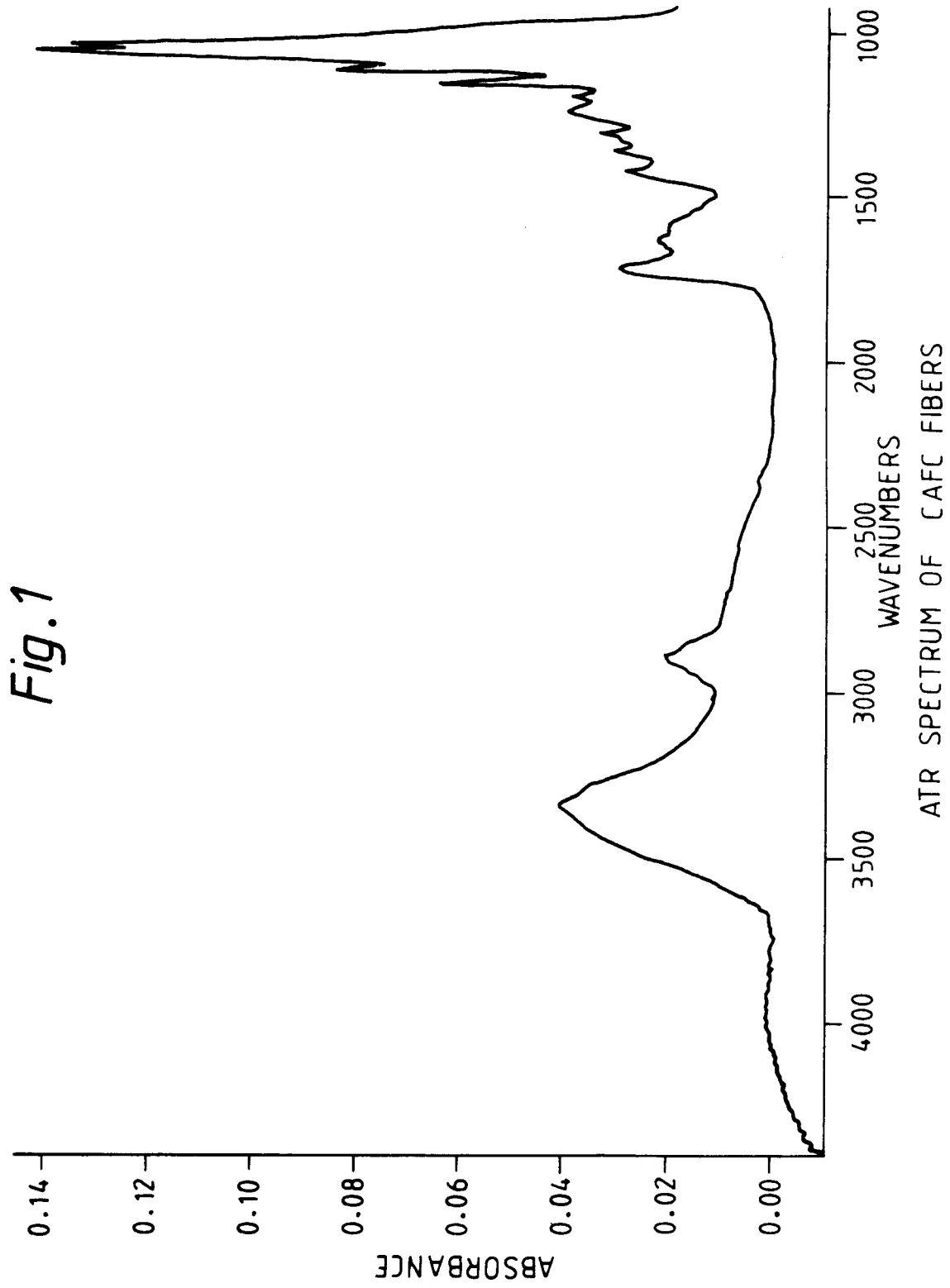
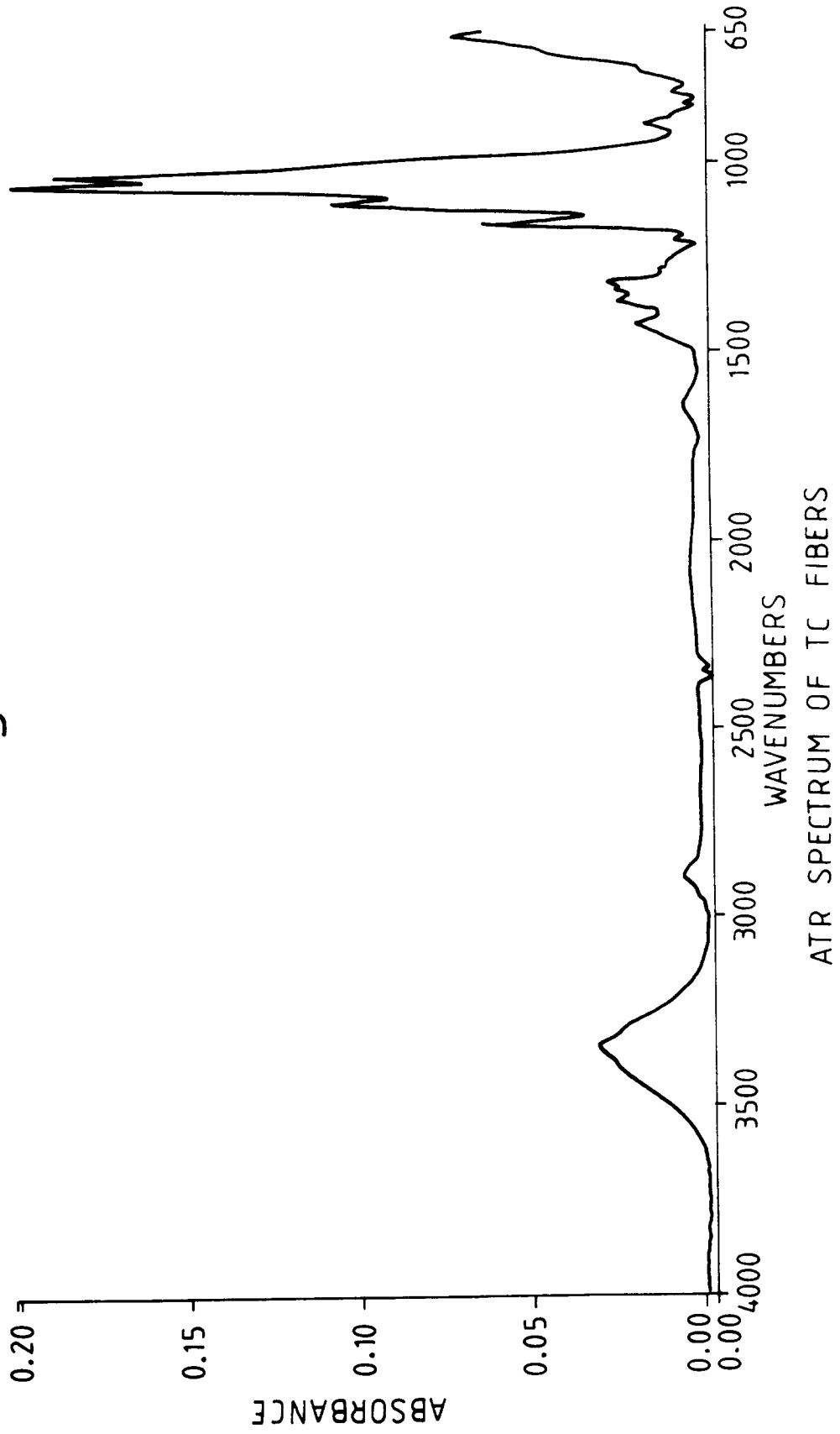


Fig. 2



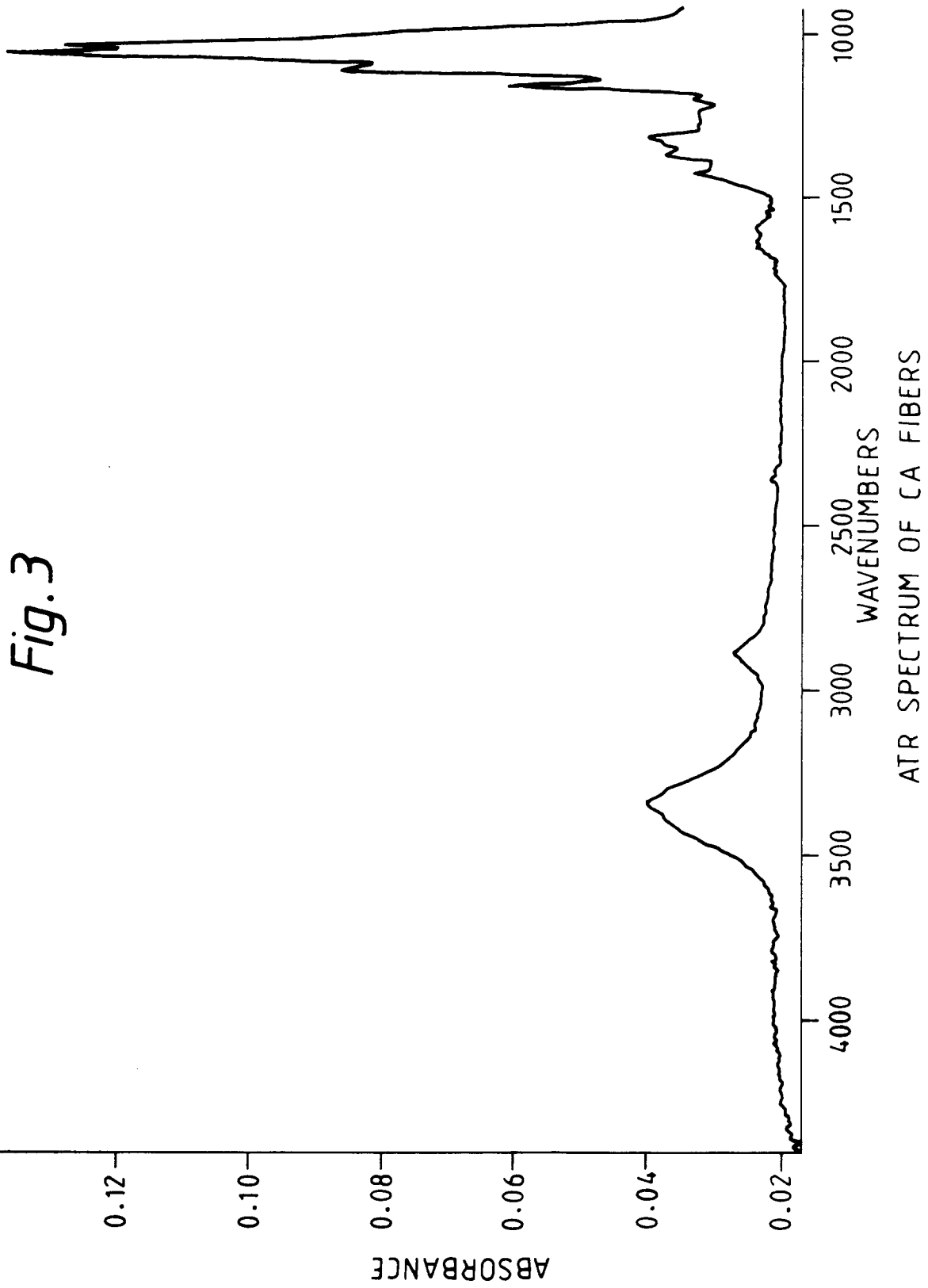


Fig.4



CONTROL

Fig.5



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