

Sept. 4, 1973

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3,756,913

MODIFIED CELLULOSIC FIBERS AND PRODUCTS CONTAINING SAID FIBERS

Filed June 18, 1971

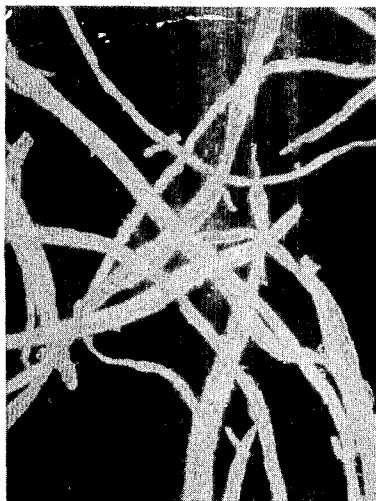


FIG. 1

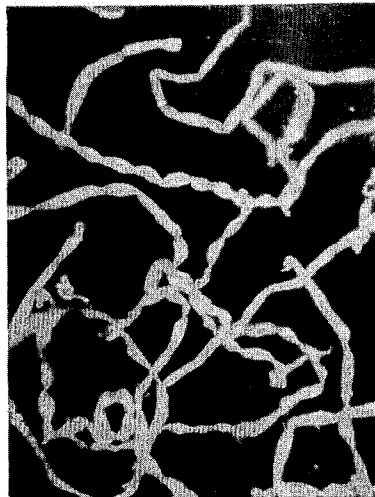


FIG. 2

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3,756,913

MODIFIED CELLULOSIC FIBERS AND PRODUCTS CONTAINING SAID FIBERS

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Filed June 18, 1971, Ser. No. 154,393

Int. Cl. B22c 17/08

U.S. Cl. 162-183

21 Claims

ABSTRACT OF THE DISCLOSURE

Twisted, flexible, modified, cellulosic fibers which exhibit improved properties, such as reduced swellability, comprise wood pulp fibers coated with a substantive polymeric compound. The above-mentioned fibers are produced by a three-step process which comprises treating an aqueous slurry of the cellulosic fibers with a substantive polymeric compound, drying the treated fibers to cause the polymeric compound to react with itself and with the fibers under conditions wherein the fibers are relatively free from contact with one another, and re-fiberizing the treated and dried fibers under dry conditions to separate individual modified fibers. The modified fibers are useful in the preparation of coherent, dry-formed webs having improved properties, such as enhanced wet and dry resiliency, increased breaking length, and improved shape retention when either wet or dry.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates, generally, to modified, cellulosic fibers, to a process for preparing said fibers, to improved cellulosic webs containing said fibers and to a process for preparing said webs. More particularly this invention relates to twisted, flexible, modified cellulosic fibers characterized by improved properties, such as reduced swellability. The fibers are cellulosic fibers which have been coated with a substantive polymeric compound. These modified fibers are produced by a three-step process which comprises treating an aqueous slurry of the fibers with a substantive polymeric compound, drying the treated fibers, under conditions wherein the fibers are relatively free from contact with one another, to cause the polymeric compound to react with itself and with the fibers, and re-fiberizing the treated and dried fibers under dry conditions to separate the individual, treated fibers. Coherent, dry-formed, cellulosic webs having improved properties, such as increased breaking length, enhanced wet and dry resiliency and the ability to retain their shape when either wet or dry are prepared utilizing these modified fibers.

Description of the prior art

In the preparation of a conventional dry-formed web a disorganized mass of fibrous material is subjected to a drawing action such as would occur with a licker-in roll which separates the individual fibers. The individual fibers are then removed from the roll and conveyed in a high-velocity air suction stream which carries the fibers to a wire mesh or reticulated cylindrical condenser where they are deposited in the form of a web. The web is compressed as, for example, by a pressure roll and subsequently removed from the forming apparatus, usually by a conveyor.

The fibrous materials commonly employed in the preparation of dry-formed webs include both wood pulp and other cellulosic materials such as rayon. Webs, or batts as they are commonly referred to, prepared from wood pulp fibers have low cohesive and tensile strength, do not retain their shape and volume when compressed or mois-

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tened, and have relatively low capillary action and fluid retention. When a batt of such fibers is saturated with fluid, it mats, becomes distorted and falls apart readily.

One disclosed method of producing a web which is said to have increased cohesive strength, good shape and volume stability, and increased fluid retention and capillary action is disclosed in U.S. Pat. 3,017,304 issued to Burgeni. This method involves applying controlled amounts of moisture to the surface of a wood pulp batt, or web, and thereafter applying pressure within controlled limits to form a densified, highly compacted cellulosic fibrous layer which is integral with the remainder of the loosely compacted, fibrous body of the web. The densified layer is formed as a result of inter-fiber bonds between the moistened and compressed fibers similar to the bonds between fibers in a wet-formed paper sheet.

The use of stiff, cross-linked, cellulosic fibers is also well-known, primarily in the wet-laid, paper-making field. See, for example, U.S. Pat. 3,069,311 (Harpham et al.), U.S. Pat. 2,010,635 (Kantorowicz), U.S. Pat. 3,224,926 (Bernardin) U.S. Pat. 3,434,918 (Bernardin), U.S. Pat. 3,440,135 (Chung) and U.S. Pat. 3,455,778 (Bernardin). All of the above-mentioned patents obtain the cross-linked fibers by impregnating the cellulosic fibers with a monomeric cross-linking agent followed by heating to cause a cross-linking reaction to take place. Several inherent disadvantages have prevented the wide scale commercial use of any of these previously available cross-linked fibers. These disadvantages include the following:

(1) many of the monomers used to obtain these fibers are unstable and difficult to work with; (2) impregnation of the fibers often requires storage of the wet pulp for periods of time up to four days; (3) because the reaction between the cross-linking agent and the cellulose is limited, a significant period of time at elevated temperatures is required to effect complete cross-linking. (Since the cellulosic fibers are heat-sensitive and will char or burn if the fiber temperature becomes too high, extended periods of time at lower temperatures are often required to achieve complete cross-linking); and (4) the resultant cross-linked fibers are stiffened to such an extent that subsequent refining in a conventional paper-making process would cause destruction of the fibers by reducing them to a powder.

One method of producing modified cellulosic fibers is described in a patent application filed concurrently herewith by David L. Shaw and Edward A. Wodka and entitled "Modified Cellulosic Fibers and Method for Preparation Thereof." The modified fibers prepared by the process described therein are most useful in the preparation of improved sheet materials prepared from an aqueous, fiber slurry and are not, due to the process by which they are made, particularly useful in the preparation of dry-formed webs. There has not heretofore been available a modified, cellulosic fiber designed for use in the preparation of dry-formed webs having the improved properties hereinbefore enumerated.

SUMMARY OF THE INVENTION

In accordance with the present invention modified cellulosic fibers, characterized by improved properties, such as reduced swellability, are produced by a three-step process which comprises treating an aqueous slurry of the fibers with a substantive polymeric compound, drying the treated fibers under conditions wherein the fibers are relatively free from contact with one another to cause the polymeric compound to react with itself and with the fibers, and re-fiberizing under dry conditions to separate individual treated fibers. This process results in the production of novel twisted, flexible cellulosic fibers formed by the interaction of the fibers and the substantive polymeric compound. The modified fibers are especially useful in the preparation of coherent, dry-formed, cellulosic

webs having improved properties such as increased breaking length, enhanced wet and dry resiliency and the ability to retain their shape when either wet or dry.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photomicrograph of the unmodified cellulosic fibers conventionally employed in the preparation of dry-formed webs.

FIG. 2 is a photomicrograph of twisted, flexible cellulosic fibers prepared in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention modified cellulosic fibers are prepared by a three-step process. In the first step, an aqueous slurry of cellulosic fibers is treated with a substantive polymeric compound. In the second step, the treated fibers are dried in a non-restrained environment to cause the polymeric compound to react with itself and with the fibers. Finally, the treated and dried fibers are refiberized under dry conditions to separate the individual modified fibers. Each step in the process is discussed in detail below:

(1) Chemical treatment.—It has been found that any cellulosic fiber normally employed in paper-making and other sheet or web-forming operations can be modified by treatment in accordance with the present invention. These include dried or never dried, groundwood, chemical or semi-chemical pulps and secondary fibers. The fibers are preferably treated as an aqueous slurry.

After the fiber slurry is formed there is added a substantive polymeric compound such as any of the water-soluble, thermosetting, cationic resins well-known in the art for increasing the wet strength of cellulosic sheet materials, including, for example, urea-formaldehyde resins, melamine-formaldehyde resins, glyoxal-acrylamide resins, and polyamide-epichlorohydrin resins. The amount of polymeric compound added can be varied over a wide range depending upon the type of pulp employed, the properties desired in the modified fiber, the other chemicals added, the drying and refiberizing conditions employed, etc. It has been found that satisfactory results are achieved when the polymeric compound is added in an amount equal to from about 0.5% to about 6.0% of the bone dry weight of the fibers, and it is preferred to add this amount of the polymeric compound. It has been found that when the above amounts of the polymeric compound are added to the pulp slurry from about 0.5% to about 3.5% of the polymer based on the bone dry weight of the fibers is retained by the fibers. The amount of resin retained by the fibers can be determined utilizing the Kjeldahl method for nitrogen analysis.

It is also preferred, when working with certain polymers such as urea-formaldehyde and melamine-formaldehyde, to add a mineral acid, such as sulfuric acid, with the polymeric compound. It is especially preferred to add the acid in an amount sufficient to adjust the pH of the aqueous fiber slurry to from about 3.0 to about 5.5. Without wishing to be bound by any particular theory, but to aid in explaining the present invention, it is believed that the acid acts as a catalyst to accelerate the reaction of the polymeric compound during the drying step.

To assist in the production of individual modified fibers, with a minimum expenditure of energy during the refiberizing step, it is preferred to add a surface-active agent as part of the chemical treatment. These compounds, which are known in the paper-making art to interfere with natural fiber-to-fiber bonding, may be added to the pulp slurry before, after or simultaneously with the addition of the polymeric compound. Cationic surface-active agents have been found to be especially useful. These include compounds such as Quaker 2000 and Velvetol CHR, which are high molecular weight quaternized imidazolines available from Quaker Chemical Corporation, Con-

shohocken, Pa.; dialkylamide diethyl ammonium sulfate, available from Ryco, Inc., Conshohocken, Pa., as Rycofax 618; dihydrogenated tallow dimethyl ammonium chloride, available from Ashland Oil and Refining Co., New York, N.Y., as Adogen 432; dimethyl dialkyl tallow ammonium chloride, also available from Ashland Oil and Refining Company as Adogen 442; Arquad 2HT75, which is a dialkyl dimethyl ammonium chloride available from Armour Industrial Chemical Company, Chicago, Ill.; Cellulube QN, which is a quaternary ammonium paper softener available from The Tanatex Chemical Corp., Lyndhurst, N.J.; and Avitex ML, which is a quaternary alkyl-olamine available from E. I. de Pont de Nemours & Co., Inc., Wilmington, Del. Although the amount of surface active agent added has not been found to be narrowly critical to the operability of the present invention, it is especially preferred to add these compounds in an amount equal to from about 0.1% to about 2.0% of the bone dry weight of the fibers.

After the chemicals have been added the slurry is agitated, dewatered, and concentrated by pressing or centrifugal extraction. It is especially preferred to remove water until the fibers are at a consistency of approximately 40% solids.

(2) Drying.—The chemically treated fibers are dried to remove water, and thereby cause the polymeric compound to react with itself and with the fibers. When drying fibers for use in dry-formed products it has been found to be essential that the fibers be dried in an environment in which they are relatively free from contact with one another. Methods which are well-known in the pulping art, such as fluff drying and flash drying, can be employed. It is especially preferred to employ the flash drying technique to achieve a lower amount of fibers per cubic volume of air in the dryer and the resultant maximum freedom between the fibers.

The exact drying conditions employed can be varied depending upon a variety of factors such as the pulp employed, the amount and type of chemicals added, the properties desired in the final modified pulp, etc. When flash drying is employed it is especially preferred to suspend the pulp for from about 1 to about 5 minutes in a stream of air preheated to a temperature of from about 400° to about 450° F.

(3) Refiberizing.—The individual treated and dried fibers are separated by subjecting them to a mechanical treatment which results in separation of the individual fibers. It has been found to be necessary to keep the fibers in as dry a condition as possible during the refiberizing operation although small amounts of water may be sprayed onto the fibers, if required, to aid in the refiberizing operation.

Illustrative of the types of equipment useful in carrying out the refiberizing operation are devices such as hammer-mills, disc refiners, carding devices and screens.

Fibers produced by the above process are shown in FIG. 2. The unexpectedly twisted shape of these fibers can be compared with the shape of the unmodified fibers, conventionally employed in the preparation of dry-formed web, shown in FIG. 1. The twisted fibers produced in accordance with the present invention are also flexible and can be utilized in conventional, web-forming equipment without breaking or powdering. These fibers are coated with a substantive polymeric compound and are characterized by improved properties, such as reduced swellability. The fibers can be used, either alone, or in combination with untreated cellulosic fibers, in the preparation of coherent, dry-formed webs having improved properties, such as enhanced wet and dry resiliency, increased breaking length and improved shape retention when either wet or dry.

Dry-formed webs comprising an entangled mass of twisted, flexible, cellulosic fibers are easily prepared from these fibers. The resulting webs have the high bulk, low density and fast absorbency properties which are typical

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of dry-formed web products. They also can be subjected to any of the known post-treatments, such as the application of binders, pressing, and embossing, which are normally applied to dry-formed webs. In addition to retaining the expected properties of dry-formed webs, products prepared with the modified fibers of this invention also have several unexpected properties which make them particularly useful in commercial products. These include:

Coherency, meaning that the unpressed webs have a measurable integrity as compared to the almost complete lack of integrity with webs prepared from the unmodified fibers normally employed;

Enhanced wet and dry resiliency, meaning that the webs are able to recover or maintain a substantial part of their original size, or height, as compared to webs prepared from unmodified fibers;

Shape retention when either wet or dry, meaning that the webs have the ability to maintain a substantial part of their original shape as compared to webs prepared from unmodified fibers which become distorted and fall apart easily;

Ability to retain, even when the web is under pressure, an amount of absorbed liquid which is greater than that retained by webs prepared from unmodified fibers.

In addition to these new and unexpected properties, webs prepared with these modified fibers also exhibit improved typical properties, such as increased bulk and lower density, due primarily to the fact that the inherent coherency of the webs eliminates much of the previous need to press the formed web to remove it from the forming apparatus.

In order to describe the present invention so that it may be more clearly understood, the following examples are set forth. These examples are set forth primarily for the purpose of illustration, and any enumeration of detail contained therein should not be interpreted as a limitation on the concept of this invention.

The test results reported in the examples were determined by the following standard procedures:

Swellability was determined by the method described in TAPPI vol. 58, No. 9, pages 494-496 (1965) in an article by P. N. Yiannos entitled "Swellability of Pulp Determined by Isopropanol Retention." When dried pulps were employed the pulp was dispersed, at a consistency of 0.4%, for one minute in a Waring Blender instead of being soaked in water overnight.

Breaking length which is an indication of the coherency, or integrity, of the dry formed product was measured on the unpressed webs in accordance with TAPPI Standard No. T220m. Breaking length is determined from the basis weight and tensile strength of the webs. The basis weights were measured in accordance with TAPPI Standard No. T410-05-61. Tensile strength was measured in accordance with TAPPI Standard No. T404-T5-66. When measuring the tensile strength of webs prepared from unmodified fibers it was necessary to support the web during insertion into the testing apparatus due to the lack of integrity of the web.

Percentage of initial height retained when wet, which is an indication of the resiliency of the web, was determined by measuring (a) the initial no-load thickness of the web and (b) the no-load thickness of the web after thorough wetting and light pressing. The percentage was determined as the ratio of the wet thickness to the initial thickness.

Dry springback, which is an indication of the shape retained by the web when wet, was determined by measuring (a) the no-load thickness of the web after thorough wetting and light pressing and (b) the no-load thickness of the web after it had been allowed to re-dry. The springback was determined as the ratio of the re-dried thickness to the wet thickness.

EXAMPLE I

Bleached, southern pine, Kraft, slush pulp at 1% consistency was treated with 6%, based on the bone dry

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weight of the pulp, of a cationic, urea-formaldehyde resin and 1.25%, also based on the bone dry weight of the pulp, of Quaker 2000, a high molecular weight quaternized imidazoline available from Quaker Chemical Corp., Conshohocken, Pa. The urea-formaldehyde resin was added as an aqueous solution containing approximately 28% by weight of the resin. The Quaker 2000 was also added as an aqueous solution containing 95% by weight of the Quaker 2000. The pH of the pulp slurry was maintained at from about 4.0 to about 4.5 during the chemical addition by the use of concentrated sulfuric acid.

The treated pulp was thickened to a consistency of from about 35% to about 40%, mechanically fluffed and dried to a final dryness of about 85% by passage through a two-stage high velocity flash drying system. In the flash drying operation the pulp was suspended in air pre-heated to a temperature of from about 400° F. to about 450° F. The temperature of the air, containing evaporated water, removed from the fibers was maintained at from about 200° F. to about 250° F. as measured at the cyclone separator after each of the two drying stages.

After storage for two weeks analysis of the fibers by the Kjeldahl method for nitrogen determination indicated that about 3.0% urea-formaldehyde resin, based on the bone dry weight of the pulp, was retained by the fibers.

The treated and dried pulp was refiberized by passage through a basket-shaped 20 mesh screen equipped with a means for agitating the pulp. This resulted in the production of individual twisted flexible fibers coated with a cationic urea-formaldehyde resin. The fibers had a swellability of 37.4 cc./100 g. as compared to a sample of unmodified, flash dried, bleached, southern pine, Kraft pulp which had a swellability of 127.2 cc./100 g.

The individual fibers were formed into a web by drawing them through a chamber in an air stream and depositing them on an 80 mesh flat screen. The dry-formed web containing 100% of the modified cellulosic fibers produced in accordance with the present invention had sufficient integrity to be lifted from the screen by hand. By comparison a web prepared from unmodified fibers had to be supported when removed from the wire to prevent disintegration of the web.

Tests on the web gave the following results:

Breaking length, meters	2.0
Percentage of initial height retained by wet sheet	21
Dry springback	2.5

By comparison a web prepared from a sample of unmodified, flash dried, bleached, southern pine, Kraft pulp had the following physical properties:

Breaking length, meters	1.1
Percentage of initial height retained by wet sheet	7
Dry springback	1.6

A final comparison was made with a conventional web prepared from the normally-used bleached, western spruce, sulfite, dry lap pulp. This web had the following properties:

Breaking length, meters	0.2
Percentage of initial height retained by wet sheet	5
Dry springback	1.0

EXAMPLE II

Several samples of bleached, southern pine, Kraft, slush pulp were treated with varying amounts of an aqueous solution containing 27.3% by weight, cationic, urea-formaldehyde resin and an aqueous solution containing 95% by weight of solid Quaker 2000. The treatments and the subsequent drying and refiberizing steps were carried out as in Example I. The results of tests on the fibers and on dry-laid webs, also prepared as in Example I, are given in the following table. The percentage of chemical was the amount of solid chemical added to the pulp slurry based on the bone dry weight of the pulp fibers.

Percent resin	Percent Quaker 2,000	Swell-ability (cc./100 g.)	Breaking length (meters)	Percentage of initial height retained by wet sheet	Dry spring-back
0.....	0	127.2	1.1	7	1.6
1.5.....	1.0	68.7	1.9	10	2.8
3.0.....	1.0	44.0	1.4	11	2.7
6.0.....	1.25	37.4	2.0	21	2.5

EXAMPLE III

Several different bleached wood pulp samples were treated with a resin and a debonder, dried and refiberized to produce modified pulps by the following laboratory procedure:

20 grams of the pulp were suspended in 2 liters of water in a British disintegrator. The pH of the suspension was adjusted to 4.0 with concentrated sulfuric acid and aqueous solutions of the resin and debonder were added. The slurry was filtered through a Buckner funnel to approximately 50% dryness, mechanically fluffed by brief agitation in a Waring Blender, and dried by heating in an air convection oven for 40 minutes at 250° F. During drying the fluffed fibers were spread out on a tray to allow the maximum amount of freedom and minimum contact of the fibers with one another. The treated and dried pulps were refiberized and formed into webs as in Example I.

The pulps and chemical treatments employed were:

Sample A.—Southern pine, Kraft, pulp was treated with an aqueous solution containing 6%, based on the bone dry weight of the pulp, of urea-formaldehyde resin and a second aqueous solution containing 1.5%, also based on the bone dry weight of the pulp of, Quaker 2000.

Sample B.—Western spruce, sulfite, pulp was treated with an aqueous solution containing 3%, based on the bone dry weight of the pulp of solid cationic, glyoxal acrylamide resin available from American Cyanamid Company, Stamford, Conn. as 631NC, and a second aqueous solution containing 1.5%, also based on the bone dry weight of the pulp, of Rycofax 618, a dialkylamide diethyl ammonium sulfate available from Ryco, Inc., Conshohocken, Pa.

Sample C.—Southern hardwood, Kraft, pulp was treated with an aqueous solution containing 3%, based on the bone dry weight of the pulp of polyureide-formaldehyde resin prepared as described in U.S. patent application Ser. No. 866,387 entitled "Wet-Strength Resins and Processes for Making and Using Same" filed by R. Avis and a second aqueous solution containing 1.5%, also based on the bone dry weight of the pulp, of Rycofax 618.

Sample D.—Northern spruce, Kraft, pulp was treated with an aqueous solution containing 3%, based on the bone dry weight of the pulp, of solid melamine formaldehyde resin.

Dry-laid webs prepared from these modified pulps had the following properties:

Pulp sample	Breaking length (meters)	Percentage of initial height retained by wet sheet	Dry springback
A.....	2.4	17.0	1.9
B.....	0.9	7.0	1.3
C.....	0.5	9.0	1.7
D.....	1.6	8.0	1.1

EXAMPLE IV

Southern pine, Kraft, slush pulp was treated with 6% of a cationic, urea-formaldehyde resin and 1.25% of Quaker 2000, dried and refiberized as in Example I. Dry-

laid webs were prepared, as in Example I, from the modified pulp alone and in combination with untreated, bleached, southern pine, Kraft, dry lap pulp. The results of tests run on the webs are given in the following table.

Percent modified	Percent unmodified	Breaking length	Percentage of initial height retained by wet sheet	Dry springback
100.....	—	2.0	21	2.5
75.....	25	0.9	9	1.9
50.....	50	0.6	8	1.6
25.....	75	0.5	7	1.9
0.....	100	0.2	5	1.0

What is claimed is:

1. A method of preparing modified cellulosic fibers which comprises:
 - a. treating an aqueous slurry of cellulosic fibers with a substantive polymeric compound,
 - b. dewatering and drying the treated fibers to cause the polymeric compound to react with itself and with the fibers under conditions wherein the fibers are relatively free from contact with one another, and refiberizing the treated and dried fibers under dry conditions to separate individual fibers.
2. A method, as claimed in claim 1, in which the cellulosic fibers are wood pulp fibers.
3. A method, as claimed in claim 1, in which the polymeric compound is a water-soluble, thermosetting, cationic resin.
4. A method, as claimed in claim 3, in which the resin is a urea-formaldehyde resin.
5. A method, as claimed in claim 1, in which the polymeric compound is added to the fiber slurry in an amount equal to from about 0.5% to about 6.0% of the bone dry weight of the fibers.
6. A method, as claimed in claim 1, in which the amount of the polymeric compound retained by the fibers is equal to from about 0.5% to about 3.5% of the bone dry weight of the fibers.
7. A method, as claimed in claim 1, in which the pH of the fiber slurry is maintained at from about 3.0 to about 5.5 during the addition of the polymeric compound.
8. A method, as claimed in claim 7, in which the pH is maintained by the addition of a mineral acid.
9. A method, as claimed in claim 1, in which a surface active agent is added to the aqueous fiber slurry.
10. A method, as claimed in claim 9, in which the surface active agent is cationic.
11. A method, as claimed in claim 10, in which the surface active agent is a quaternary ammonium compound.
12. A method, as claimed in claim 11, in which the quaternary ammonium compound is an imidazoline.
13. A method, as claimed in claim 11, in which the quaternary ammonium compound is an alkyl ammonium salt.
14. A method, as claimed in claim 9, in which the surface active agent is added to the fiber slurry in an amount equal to from about 0.1% to about 2.0% of the bone dry weight of the fibers.
15. A method, as claimed in claim 1, in which the fibers are dried as a fluff.
16. A method, as claimed in claim 1, in which the fibers are flash dried.
17. A method, as claimed in claim 1, in which the fibers are dried at an elevated temperature,

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18. A method, as claimed in claim 16, in which the fibers are dried by suspending the fibers in a stream of air preheated to from about 400° F. to about 450° F.

19. A method, as claimed in claim 18, in which the fibers are dried for a period of time of from about 1 to about 5 minutes.

20. A method, as claimed in claim 1, in which the treated and dried fibers are refiberized by a hammer mill.

21. A method, as claimed in claim 1, in which the treated and dried fibers are refiberized by a dry-screening device.

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U.S. Cl. X.R.

8—116.3; 162—9, 100, 158, 166