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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
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Trámite : 002 PATENTES 0 1 REGISTRO/ 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

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Señores
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES
E. S. D.

REF.: Expediente No. 00 089.076 solicitud de Patente a nombre de
KIMBERLY – CLARK WORLDWIDE, INC.

RAMIRO CASTRO DUQUE, vecino de Bogotá, portador de la tarjeta profesional No. 1003 del Consejo Superior de la Judicatura, obrando como apoderado de la Sociedad **KIMBERLY – CLARK WORLDWIDE, INC.**, según lo acredita el documento de poder protocolizado en la Secretaría General bajo el No. 17397, de acuerdo con el Artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina, me permito solicitar que se examine si la invención contenida en la solicitud en referencia es patentable.

De acuerdo con lo anterior, me permito anexar el recibo oficial de caja No. 03-11,654 por valor de \$335.000.

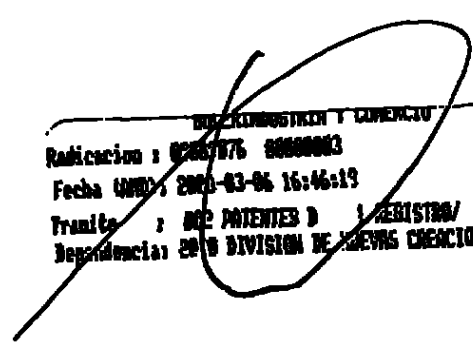
Señor Superintendente,


RAMIRO CASTRO DUQUE
C.C. No. 170.322 de Bogotá
Código 340
T.P. No.1003 del C.S.J.
Cra. 7 No. 16-56 Piso 9

Marzo 06, 2003
CPB/hsr.

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Industria y Comercio
SUPERINTENDENCIA



Radicación : 0200176 80000003 Folios: 2
Fecha UNOD: 2000-03-06 16:46:19
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NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 03 - 11,634
FECHA : FEBRERO 14 DE 2003

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	050-00110-6	2198049	14/02/2003	20,230,000.00

***** C O N C E P T O *****

CANT. RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	335,000.00
	TOTAL :	\$ 335,000.00

SOM: TRESCIENTOS TREINTA Y CINCO MIL PESOS

RESPONSABLE :



RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 16 de Septiembre de 2005

Doctor

RAMIRO CASTRO DUQUE

Representante **KIMBERLY – CLARK WORLDWIDE, INC.**

ASUNTO	Radicación No.	00-89076
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	068
	Folios	8592

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica

1) Documentos estudiados:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 5 a 15 de la solicitud en estudio.
- b) Para el presente estudio se tendrán en cuenta los dibujos comprendidos en los folios 28 a 29 de la solicitud en estudio.
- c) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 10 reivindicaciones en los folios 16 a 17 de la solicitud en estudio.
- d) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 22 de noviembre de 2000, y en el momento de la radicación **Si se reclamo prioridad de la primera solicitud presentada en Estados Unidos US 60/167435**

2) Objeto de la Invención

- a) Las reivindicaciones 1 a 10 de la solicitud en estudio se refieren a
 - i) 1.- Un producto tisú que comprende: una lámina de fibras, lámina que tiene incorporados en ella: un agente de resistencia temporal en húmedo que es capaz de establecer enlaces hemiacetales con las fibras de dicha lámina para impedir la degradación inmediata de dicha lámina cuando dicho producto tisú se ponga en contacto con agua; y un agente alcalino para interactuar con dicha lámina para aumentar la degradación de dicha lámina cuando dicho producto tisú se ponga en contacto con agua.

- ii) 7.- Un producto tisú que comprende: una lámina de fibras **celulosicas**, lámina que tiene incorporados en ella: un agente de resistencia temporal en húmedo que es capaz de establecer enlaces hemi-acetales con las **fibras celulosicas** de dicha lámina para impedir la degradación inmediata de dicha lámina cuando dicho producto tisú se ponga en contacto con agua; y un agente alcalino para interactuar con dicha lámina para aumentar la degradación de dicha lámina cuando dicho producto tisú se ponga en contacto con agua, **agente alcalino que se encuentra presente en dicha lámina en una cantidad desde alrededor del 0,1% a alrededor del 5%.**
- iii) 9.- Un proceso para conformar un producto tisú...
- b) Los anteriores productos y su procedimiento de fabricación buscan obtener un producto tisú que se pueda eliminar por el inodoro sin causar problemas en los conductos sépticos
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a D 21 H 21/20

3) Claridad de la Solicitud

- a) El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

"Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior.- Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará reivindicación dependiente múltiple."

El capítulo reivindicatorio no es claro toda vez que:

- i) No se encuentra correctamente redactado. Por su estructura todas las reivindicaciones deben constar de dos partes. Una primera parte, el preámbulo, sirve para situar el objeto de la invención dentro de un contexto técnico, es lo que se conoce y sobre lo que no se reclama ningún privilegio. La segunda parte, o parte característica, define lo que se considera novedoso y se desea proteger. Estas dos partes están separadas por expresiones como 'caracterizado por' o similares.

En la redacción del presente capítulo, en especial en las reivindicaciones independientes, no se observa claramente lo que el solicitante considera como nuevo y que considera como conocido. En un momento podría pensarse que lo que el mismo solicitante denomina agentes de resistencia temporal el solicitante lo considera como nuevo según la redacción de la reivindicación. Sin embargo, en el folio 5 lo da

por conocido. Al estudiar la descripción, al parecer, lo único que propondría como nuevo el solicitante es el componente alcalino. Por lo mismo, el solicitante deberá corregir el capítulo y tratar de establecer una correcta redacción de las reivindicaciones.

- ii) Técnicamente no es claro ni es de común que exista la expresión "agentes de resistencia temporal". De la misma forma, tampoco es claro que los mencionados "agentes" formen "enlaces hemi-acetales con las fibras de dicha láminas". Parece como si se entrara en el campo de la especulación, pues esa afirmación no es fácil de demostrar. De acuerdo a lo observado en la solicitud, existen ciertos compuestos que tienen ciertas formas de comportamiento. Dicho compuestos están específicamente definidos de acuerdo a lo encontrado en la solicitud. Sería más conveniente que el solicitante defina las reivindicaciones por los compuestos o de lo contrario, sería conveniente que el solicitante explique más detenidamente y de una forma más amplia el porque de dichos comportamientos.
- iii) Las reivindicaciones 3 y 4 son prácticamente iguales y no se observa una diferencia que permita considerar que merezcan estar simultáneamente. Se sugiere eliminar una de las dos.
- iv) No se pueden aceptar expresiones tales como 'alrededor de...'. Deben eliminarse
- v) No se precisa la materia sobre la cual se solicita protección. Cómo se explicará en el punto 4), la presente solicitud no posee unidad de invención, por lo que no está definida la materia sobre la cual se solicita protección.
- vi) No se pueden aceptar caracterizaciones hechas por el solicitante con pruebas que el mismo solicitante aplica y no son universalmente aceptadas. Esto no permite establecer una relación con el arte conocido, no pudiéndose entonces validar dichos parámetros. No se pueden aceptar dichas reivindicaciones
- vii) Si bien los procesos para elaborar tisúes son conocidos, se recomienda en la redacción de la reivindicación 9 plasmar dichos pasos generales siguiendo los parámetros del anterior punto i) y colocar en la parte característica el paso o los pasos que son nuevos. Esto es debido a que si bien los procesos son conocidos, ya existen otros procesos en la técnica que no siguen los lineamientos tradicionales y un lector desprevenido no encontrará clara esta reivindicación. Por lo tanto, se sugiere redefinir esta reivindicación con una secuencia lógica de pasos o etapas (plural, no singular).

De acuerdo a lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad de acuerdo a lo establecido en el Art. 30 de la Decisión 486.

4) Evaluación de la Unidad de Invención

El artículo 25 de la Decisión 486 de la Comisión de la Comunidad Andina establece

"La solicitud de patente sólo podrá comprender una invención o un grupo de invenciones relacionadas entre sí, de manera que conformen un único concepto inventivo" /

La presente solicitud carece de unidad de invención toda vez que configura DOS diferentes objetos. Aunque se dirigen a TISÚES la definición de la materia que caracteriza a cada una de las reivindicaciones independientes 1 y 7 es muy diferente entre sí. Esto permite afirmar que no se trata del mismo producto. Todo el problema radica en configurar varias reivindicaciones independientes con materia diferente. El solicitante debe establecer una sola reivindicación independiente dirigida al producto en la forma más simple de la solicitud de invención. Partiendo de allí establecer reivindicaciones dependientes que amplíen esa forma más simple hasta su forma más compleja.

De acuerdo a lo anterior, la presente solicitud no cumple con el requisito de unidad de invención de acuerdo al Art. 25 de la Decisión 486.

5) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece:

"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones D 21 H 21/20 y las más cercanas a ellas, se encontró que antes del 23 de noviembre de 1999 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con tisúes.

De acuerdo con lo establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

N°	Documento	Título	Fecha de Publicación
D1	EP 0408128	Absorbent paper comprising polymer modified fibrous pulps and wet laying process for the production thereof	1991.01.16
D2	WO 9824974	Method for making wet paper strength paper	1998.06.11
D3	EP 0 802 282	Process for preparing hydrolizable sheet	1997.10.22
D4	US 5830317	Soft tissue paper with biased surface properties containing fine particulate fillers	1998.11.03

6) Evaluación de los requisitos de patentabilidad

a) Evaluación de la novedad y el del Nivel Inventivo

El art. 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Una invención se considerará nueva cuando no está comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fechas de prioridad cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

D1 (EP 0408128) revela un producto tisú con fibras con compuestos que impiden la degradación de la lámina hasta que se le agrega un compuesto alcalino que le permite su degradación. En esencia es lo mismo que el solicitante desea proteger. Lo mismo se puede decir de los documentos D2 (WO 9824974) o D4 (US 5830317) que hablan de compuestos de poliacrilamida o compuestos poliméricos glioxilados,

D3 (EP 0 802 282) sugiere la liberación del agente alcalino al entrar en contacto con el agua.

Cómo se observa no se cumplirían los requisitos necesarios para que se le conceda el privilegio solicitado..

b) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisit que afecta
D1	EP 0408128	1 - 10	Novedad
			Nivel inventivo
D2	WO 9824974	1 - 10	Novedad
			Nivel inventivo
D3	EP 0 802 282	1 - 10	Nivel inventivo
D4	US 5830317	1 - 10	Novedad
			Nivel inventivo

7) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en la lista, de fecha

22 SET. 2005

Concepto Técnico N°	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
1431	202003	

107 105



Publication number: **0 408 128 A2**

EUROPEAN PATENT APPLICATION

Application number: 90201814.2

Int. Cl. 8: **D21H 11/20**

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Priority: 11.07.89 US 378154
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Designated Contracting States:
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Absorbent paper comprising polymer-modified fibrous pulps and wet-laying process for the production thereof.

Processes are described for making highly absorbent tissues and towels by wet-laying pulps comprising particular polycarboxylate polymer-modified fibrous pulps such as mildly hydrolyzed methyl acrylate-grafted softwood kraft pulps; these pulps have distinct protonated and alkali-metal-cation-exchanged states. The wet-laying processes are adapted to exploit the very different behavior of the polymer-modified fibrous pulps in function of the two states. The preferred wet-laying processes described herein are continuous processes embodying one or more on-line chemical treatment steps which chemically switch state of the polymer-modified fibrous pulp component in a wet web on the papermaking machine to improve the processing thereof by averting or minimizing tendencies to mechanically or thermally degrade.

EP 0 408 128 A2

more difficult to pump and may tend to precipitate. In more detail, when using potassium carbonate, which as noted is a highly preferred alkali on solubility grounds, the concentration is typically about 4 Molar, or higher, more preferably from about 4 Molar to about 8 Molar. When using sodium hydroxide as the alkali, the concentration is preferably from about 4 Molar to about 8 Molar. Potassium hydroxide may be substituted for sodium hydroxide. Other alkalis which may be used herein, but are rather poorer in terms of solubility, are illustrated by potassium bicarbonate, sodium bicarbonate and sodium carbonate.

In the interest of optimizing sheet control and minimizing the drying load in the final drying stage, the preferred consistency of the partially dewatered web lies in the range from about 40% to about 75% as measured upon entry to the ultimate thermal drying step (e).

10 The acidification step (a) in the instant process ensures having fibrous pulp type A in the protonated state at stages in the process where mechanical shear forces would otherwise harm its integrity; invariably, the protonated state is maintained in the web-forming stage (b) as well as the partial web-dewatering stage, here illustrated by the sequence of steps (c) of the papermaking operation.

Without being bound by theory, individual pulp fiber integrity measurements indeed suggest that the fibrous pulp type A component better tolerates the shear forces encountered during the wet-laying process without undue loss of its structural integrity in the protonated state, as compared with the alkali-metal-cation-exchanged state. It is furthermore believed that having the fibrous pulp type A component in the protonated state results in an embryonic web which is more readily mechanically dewatered than an otherwise identically formed web in which the fibrous pulp type A component is in the alkali-metal-cation-exchanged state.

In the above, it is to be noted that the extent of acidification is not merely that which would be required to start the wet-laying process with fibrous pulp type A component temporarily in the protonated state; the protonated state needs to be maintained in the wet-end operations, at least until the embryonic web is partially dewatered as noted, since the natural alkalinity reserves of the process water and/or the fibrous pulp type B are otherwise capable of deleteriously reverting the type A pulp to the relatively fragile and difficultly dewatered alkali-metal-cation-exchanged state during wet-laying.

In practical terms, the type A pulps can usefully be manufactured at a facility remote from the papermaking plant, and can be acidified to convert them to the protonated state prior to shipping. This has the advantage of being able to ship at rather low water content, typically from about 10% to about 20% solids. In general, even when the type-A pulp is shipped in the protonated state, it will still suffer from the above-identified reversion problem unless the practitioner further acidifies, to the extent necessary for the instant process. Thus, at the papermaking plant, more acid will generally still need to be added. Clearly, whether acidifying the type A pulp is done at the pulp manufacturing facility or inside the papermaking plant, or partially at each, is immaterial, since in either of these variations, an acidification step at the wet-end of the papermaking machine will (very preferably) be needed. Quite irrespective of the initial state of fibrous pulp type A, the total amount of acid used in the instant process is generally in excess of the total alkalinity given by the sum of the alkalinities of the type A and B pulps plus the papermaking process water. A satisfactory extent of acidification is conveniently measurable, given the knowledge that water draining from the foraminous member or members (e.g., the wire or drying fabrics) throughout steps (b) and (c) of the process should have a pH in the range from about 3 to about 5. Even more preferably, the pH of water draining from the web in each of steps (b) and (c) is in the range from about 3.5 to about 4.5 and the pH of a water sample, e.g., one extractable by squeezing a sample of the web, at the end of step (c) is in the range from about 6 to about 8, more preferably from 7 to about 8.

Also to be noted in relation to the acidifying step, if the fibrous pulp type A is initially in the protonated state, acidification of the pulp as a whole, to the necessary extent, may be accomplished quickly; there is no particularly critical time, and a few seconds' acidification time is generally sufficient. However, if fibrous pulp type A is not initially in the protonated state, sufficient acid contacting time, generally at least about 10 minutes, more preferably about 30 minutes to about 60 minutes, should be allowed to ensure that conversion to the protonated state occurs before the stock containing the type A pulp passes through the fan pump, where it is finally diluted and then passes to the headbox and wire. Clearly, such significantly long acidification times make it necessary, when the type A pulp receipts at the plant are in the alkali-metal-cation-exchanged state, to resort to acidifying the fibrous pulp type A in a stock chest having enough capacity to ensure that the continuous papermaking process will not be interrupted. Using such an arrangement, appreciable stock chest residence times, quite satisfactory for the present purposes, are common. The appearance of fibrous pulp type A may, if desired, be checked by microscopic examination. In the protonated state, discrete fibers of fibrous pulp type A are substantially unswollen, and at least on cursory examination, resemble conventional papermaking fibers to a much greater extent than in the alkali-metal-cation-exchanged state. In the latter state, discrete fibers of fibrous pulp type A are typically swollen

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to the extent of about 2.5 - fold to about 4 -fold, or even more, relative to the protonated state thickness.

In relation to the the above-described preferred embodiment, the alkali-adding process step (d) deliberately places the fibrous pulp type A in the alkali-metal-cation-exchanged, highly absorbent state. This may appear surprising in view of the greater difficulty of drying fibrous pulp type A in that state. Without being bound by theory, fibrous pulps type A, especially particular chemical forms thereof discussed more fully hereinafter, tend to undergo chemical reactions adverse to the ultimate absorbency of the paper sheet if the heating of the web is not limited as indicated. Most importantly, discovery that such adverse elevated temperature chemical reactions are minimized in the alkali-metal-cation-exchanged state, as compared with the protonated state of the fibrous pulp type A, provides grounds for deliberately introducing the alkali-
treatment step before the high temperature Yankee dryer in the above-described embodiment. On the other hand, keeping the type A pulp in the protonated state through as many as possible of the early stages of the process assists dewatering and helps retain integrity of the fibrous pulp type A at the wet-end. It has already been explained supra that pre-drying prior to alkali treatment is quite acceptable, even if the predryer temperatures seem to suggest the web attains high temperatures similar to those used at the Yankee, in view of the reality of great evaporative cooling effects on the web in the predryer.

In another highly preferred embodiment, the above-outlined process can readily be adapted to lay down a layered web, for example by using a multi-channel headbox, and a web having two or three layers is laid down in a single or twin-wire former of conventional design. When three layers are laid down, pulp A is typically in the inner layer and pulp B is typically used to form two outer layers.

As noted, it is preferred to use a second foraminous member for later stages of mechanically dewatering the embryonic web. Very preferably, the second foraminous member takes the form of an open-weave fabric or, even more desirably, takes the form of a deflection member as described by Trokhan in the above-referenced U.S. Patent 4,637,858.

Fibrous Pulps

Since numerous particulate materials, including "crumb-like" and regularly shaped hydrocolloid particles, have sometimes been referred to as "pulp" in the art, the term "fibrous pulp" is used herein to indicate that the pulps with which the instant invention is concerned, whether novel or conventional, generally have particle lengths and particle length-width (i.e., aspect) ratios typical of and suitable for wet-laying papermaking, and are not generally spherical or otherwise peculiarly shaped in any manner significantly detrimental to wet-laying.

Type A Pulp Materials

Although many materials variously characterized as "hydrogels", "super-absorbents", "absorbent polymers", "chemically modified cellulose", "polymer-modified pulp", etc. are known in the art, the terms "polymer-modified fibrous pulp", "fibrous pulp type A", or, for brevity, simply "type A pulp", used herein to refer to an essential starting-material, are more narrowly defined. Thus, the essential fibrous pulp type A herein can, in general, be considered as consisting essentially of a polymer-modified fibrous pulp having two distinct states: a protonated state, and an alkali-metal-cation-exchanged state. By definition, these states are associated with significant differences in chemical and physical properties. The terms used are not necessarily intended to insist upon absolutely complete substitution of all ion exchange sites by protons or alkali metal cations, respectively; only the extent of substitution which is practical is intended.

As characterized in the protonated state (whether wet or dry), the fibrous pulp type A generally has fibrous morphology. In the protonated state, the type A pulp fibers are relatively non-swollen and resemble, at least superficially, the unmodified form of conventional fibrous pulp from which the type A pulps originally derive. In contrast, in the alkali-metal-cation-exchanged state, the fibrous pulp type A has the form of a substantially fibrous polyanionic hydrocolloid. For practical purposes the anionic charge is mostly polycarboxylate-derived. In preferred embodiments such as certain hydrolyzed grafted fibers, the mechanism of water absorption by the type A pulp fibers in the alkali-metal-cation-exchanged state is not necessarily strictly hydrocolloidal, the structure of individual fibers offering the additional possibility of capillary wicking. Invariably however, the type A pulp in the alkali-metal-cation-exchanged state is characterized by hydrocolloidal swelling upon wetting. Whether absorbing water entirely hydrocolloidally or with an additional contribution by some other mechanism, the total water or aqueous fluid absorbency of fibrous pulp type A is at least about 20 g/g, more preferably in the range from about 20 g/g to about 60 g/g, as

Type B Pulp and Other Materials Used in the Process

The preceding discussion has emphasized the relatively unusual fibrous pulp type A component used in the instant wet-laying papermaking process. Fibrous pulp type B is conventional wet-layable fibrous pulp compatible with the type A pulps. More specifically, fibrous pulp type B is illustrated by a variety of conventional pulps such as kraft pulps of hardwood or softwood, chemithermomechanical pulps and sulfite pulps. Typical type B pulp is further illustrated by northern softwood kraft pulp, southern softwood kraft pulp, a mixture consisting essentially of northern softwood kraft pulp and eucalyptus pulp, and a mixture consisting essentially of northern softwood kraft pulp and chemithermomechanical pulp. When the type B pulp is a mixture, the relative proportions of the constituent conventional pulps may vary widely. Depending on the intended use of the paper structure, recycled pulps may also be used as type B pulp in the instant process. Preferred mixtures of conventional fibrous pulps used as the type B pulp component are illustrated by a type B pulp blend consisting essentially of 80 % kraft pulp and 40 % eucalyptus pulp; and another, consisting essentially of 70 % kraft pulp and 30 % chemithermomechanical pulp, dry basis.

The type B pulp can be used in admixture with the type A pulp at various levels. Preferably, the relative proportions of type A and type B pulps, together constituting the total pulp used herein, are such that the total pulp, dry basis, consists essentially of from about 1 % to about 20 %, more preferably about 3 % to about 15 %, most preferably 5% to about 15% fibrous pulp type A and from about 80 % to about 99 %, more preferably about 85 % to about 97 %, most preferably 85% to about 95% fibrous pulp type B.

As noted, the acid most suitable for use in the instant wet-laying process is sulfuric acid. Sulfuric acid is inexpensive and papermaking equipment is more tolerant of this acid than other relatively inexpensive acids, such as hydrochloric acid. Alkalis suitable for use herein include sodium hydroxide, sodium bicarbonate, sodium carbonate, potassium hydroxide, potassium bicarbonate and potassium carbonate. Preferably, the alkali is in the form of an aqueous solution, typically having high concentration, e.g., the maximum concentration consistent with the solubility of the alkali in water. Potassium carbonate is particularly preferred.

Optionally, various compatible chemically homogeneous carboxymethylcelluloses, powdered absorbent copolymers, resinous polymers, starch acrylates, etc., such as those referred to in background hereinabove, can also be used in the instant wet-laying process, provided that they are nonionic or anionic in character. No such materials, it will be clear, are included in defining the essential polymer-modified pulp (the type A pulp). Preferably, these particular optional materials will be avoided altogether.

Additional Embodiments of the Process also Incorporating Optional Compatible Wet-strength Additives

Although the present process is generally practiced in the absence of cationic wet-strength resins such as KYMENE, which harm the absorbency of the type A pulp, certain compatible wet-strength additives can be used herein. Such compatible wet-strength additives are generally nonionic or anionic, rather than cationic in character. Examples of compatible wet-strength additives are provided by the anionic or nonionic (but not the cationic) water-soluble ionic-hydrophilic vinylamide polymers of U.S. Patent 3,556,932, Coscia and Williams, issued January 19, 1971, incorporated herein by reference. It is emphasized that the cationic polymers identified in '932 are unsuitable for use herein, i.e., they are considered interfering cationic materials for purposes of the present process. Preferred compatible wet-strength additives are the glyoxylated anionic polyacrylamides of '932. More specifically, these preferred compatible wet-strength additives are illustrated by Examples 6, 7 and 9 of '932; the wet-strength additive of '932 Example 6 is especially preferred.

Use of a compatible wet-strength additive in accordance with the present invention differs specifically from '932 in that co-use of alum with the compatible wet-strength additive is not permitted since, as taught hereinabove, the alum is incompatible with the type A pulp.

The compatible wet-strength additives do not act as interfering materials, i.e., they do not harm the absorbency of the type A pulp. Furthermore, their crosslinking to generate wet-strength in the web very preferably occurs at temperatures which are significantly below those temperatures identified hereinabove as being capable of harming the absorbency of the type A pulp.

Preferred embodiments of the wet-laying process of the invention giving stronger webs than those more generally obtainable, involve an additional, wet-strength-adding step, comprising spray-on to the web, by means of a conventional spray-head, of the above-identified compatible wet-strength additives, said additional, wet-strength-adding step intervening at any stage of said process between step (b) and step (e).

Even more preferably, said additional, wet-strength-adding step is positioned immediately after step (d) and immediately prior to step (e).

5 Product Webs

The most commonly prepared absorbent structures in accordance with the invention will contain fibrous pulp type A in the alkali-metal-cation exchanged state, since the artisan will most likely practice not only the essential acidification step, but also the optional by highly preferred alkali-treatment step of the instant process. The corresponding absorbent structures contain fibrous pulp type A in the highly absorbent, alkali-metal cation-exchanged state, and the absorbent structure can directly be used as an absorbent article (e.g., a single-ply paper towel or wipe). Naturally, it is also possible to make more complex absorbent articles, for example multi-ply towels at least one ply is in accordance with the invention.

Naturally, if the practitioner is prepared to forego the advantages associated with the alkali-treatment step in the instant process, the acidic mixture of fibrous pulps type A and B can be used in accordance with the invention to make an "acidic" ply, which can be sandwiched between alkaline plies made from conventional pulp so as to secure particular multi-ply absorbent articles. When spills are wiped using this type of absorbent structure, the alkali is liberated and converts the type A pulp to the highly absorbent alkali-metal-cation exchanged state, in-situ.

More generally, the paper webs formed by the instant process are absorbent structure, more specifically sheets, which can be used in numerous forms of absorbent article where quick absorption and good water-absorbing capacity and retention of water or other aqueous fluids, is required, all without encountering significant aesthetic disadvantages such as "gel-feel" when the absorbent article is wet, or stiffness or absorbent material "shedding" when it is dry. The paper sheets of the invention are directly useful as single-ply tissues or towels, or are indirectly useful as an element of multi-ply disposable paper tissues, towels and wipes; or are further indirectly useful through conventional papermaking converting operations yielding catamenial articles and dressings of various kinds.

In addition to the process described in detail hereinabove, the invention encompasses a preferred embodiment of an absorbent structure, in the form of a wet-laid paper sheet, having the following characteristics:

The absorbent structure comprises from about 5% to about 15% of fibrous pulp type A. The pulp type A consists essentially of a polymer-modified fibrous pulp having distinct protonated and alkali-metal-cation-exchanged states. As characterized in the protonated state, pulp type A has relatively non-swollen fibrous morphology. As characterized in the alkali-metal-cation-exchanged state, pulp type A has the form of a substantially fibrous polyanionic hydrocolloid further characterized by hydrocolloidal swelling upon wetting, to the extent that said fibrous pulp type A has a water or aqueous fluid absorbency of from about 20g/g to about 80 g/g, measured by the TBGV method, and a rate of water or aqueous fluid absorption such that said fibrous pulp type A reaches at least 90% of its maximum water-absorbing capacity within 10 seconds, measured by the VELM method. The polymer-modified fibrous pulp (pulp type A) is characteristically fragile and difficult to dewater in the wet, alkali-metal-cation-exchanged state as compared with conventional papermaking fibers and is furthermore susceptible to deactivation as an absorbent upon exposure to either of both of the classes of cationic materials (i) multivalent metal ions such as are commonly present in papermaking process water and (ii) cationic polymers or cationic polyelectrolytes conventionally known for use in papermaking for improving paper wet-strength. Polymer-modified fibrous pulp type A is also characterized by a significant relative decrease in fragility, increase in ease of dewatering and increase in resistance to multivalent metal ions in the protonated state as compared with said alkali-metal-cation-exchanged state.

The balance (to 100%) of the absorbent structure comprises conventional papermaking pulp (type B pulp) and, optionally, non-interfering additives, such as the glyoxylated anionic or nonionic (but not cationic) polyacrylamides described in U.S. Patent 3,558,932.

The properties of the absorbent structure, i.e., the paper sheet, are as follows: density in the range from about 0.05 g/cm³ to about 0.25 g/cm³; mean water or aqueous fluid absorbency of the sheet in the range from about 2 g/g to about 10 g/g as measured by the TBGV method; and total wet tensile, machine direction plus cross-machine directions, in the range from about 500 g/inch (197 g/cm) to about 1500 g/inch (591 g/cm). Furthermore, the paper is the product of a process comprising both wet-laying said pulps and at least partially dewatering the resulting wet paper sheet whilst maintaining fibrous pulp type A in the protonated state; said wet-laying and partial dewatering operations being conducted in the substantial absence of interfering cationic materials.

Examples

The following examples illustrate particularly preferred type A fibrous pulps, and further illustrate the papermaking process of the invention. When any measurement is represented by two values, the units corresponding with the first value given are those of the experimental measurement (these units are commonly used by papermakers in the United States of America). The units of the second value, when present, are Metric System units, and are based on applying metric conversion factors to the first value. Unless otherwise indicated, the paper properties are reported for a single ply of paper, i.e., as directly produced using the machine illustrated in Fig. 1 hereinabove.

Example 1

Preparation of Polymer-Modified Pulp Fibers, fibrous pulp type A, by grafting and hydrolysis process:

Starting-Materials:

Conventional kraft pulp fibers are used as the substrate pulp; more specifically, southern softwood kraft (SSK), HP-11 grade, Foley Plant, from Procter and Gamble Cellulose, Buckeye, is quite suitable. Methyl Acrylate, used to polymer-modify the SSK pulp, is obtained from Polyscience Inc. or Pfaltz & Bauer Inc. Ceric Ammonium Nitrate (anhydrous, crystals) is obtained from Fisher Scientific Co.

The equipment comprises a grafting reactor, which is a conventional stainless steel stirred reactor of about 125 gallon (about 473 liter) capacity equipped with steam-heating coils. Also used is a centrifuge (Buck, Model 755, 30 inch (76.2 cm) diameter bowl, 5 horsepower (3.73 kW), 1725 rpm.) The same reactor is used for both the grafting step and the hydrolysis step.

The grafting of the substrate pulp is carried out as follows: Weigh out 3.5 kg bone dry HP-11 (SSK, Southern Softwood Kraft). Soak the HP-11 pulp fibers in about 110 gallons (about 416 liters) water overnight. Tap water can be used, but the water is more preferably demineralized. After overnight soak, add about 280 ml of concentrated nitric acid, mixing effectively but not at high shear; pass nitrogen gas into the resulting mixture, thereby purging air dissolved in the mixture. Continue light mixing and passage of nitrogen for about 30 minutes; a pH reading taken at this stage should preferably yield a pH value in the range from about 2.0 to about 2.5. Add 10.5 liters of methyl acrylate to the mixture and stir for about 20 minutes. Add 241 g of ceric ammonium nitrate dissolved in 2 liters of water. Mix for about 5 minutes. (An increase in mixing speed will generally be required at this stage to ensure good dispersion of ceric ammonium nitrate.) Stop mixing and passage of nitrogen. Allow the mixture to stand for about 4 hours, during which time the methyl acrylate-grafting reaction occurs. Pump the mixture into a centrifuge and wash with about 220 gallons (833 liters) demineralized water, using a centrifuge speed of about 1725 rpm to separate the wash water from the methyl acrylate-grafted pulp. Typically, about 12 kg of methyl acrylate grafted pulp (dry basis) is obtained. (This pulp illustrates pulp of the general type referred to elsewhere herein as "intermediate fibrous graft copolymer").

Hydrolysis of the methyl acrylate grafted pulp is carried out under mild conditions, as follows: Transfer the methyl acrylate-grafted pulp into the clean hydrolysis reactor. Add an amount of water calculated to give a mixture containing 2.5% solids and 97.5% water upon completion of the hydroxide addition step infra. Mix slowly and thoroughly. Add sodium hydroxide (fresh 50% aqueous solution) in an amount of about 0.82 liter/kg of methyl acrylate grafted pulp. Typically, about 10 liters of sodium hydroxide solution are required when operating at the scale of the instant example. Heat the mixture to about 90 °C by passing steam through coils in the reactor. Stop mixing. Let hydrolysis reaction proceed for about 2 hours. Pump the hydrolyzed methyl acrylate-grafted pulp mixture to a centrifuge.

Acid treatment and washing is now carried out as follows: Centrifuge the mixture to remove as much of the sodium hydroxide as possible. With the centrifuge running, pump in an acid solution (made from about 5 liters sulfuric acid (98%) in about 130 gallons (492 liters) of demineralized water), treating the hydrolyzed, methyl acrylate-grafted pulp with this acid solution until the pH of the effluent from the centrifuge drops to about 2.0. Carry out a follow-up washing with a second, more-dilute, acid solution (318 ml concentrated sulfuric acid in about 300 gallons (about 1136 liters) of demineralized water). After follow-up washing, centrifuge (1725 rpm) for about 15 minutes and remove the polymer-modified type A pulp fibers. Use these

fibers without further treatment as type A pulp in the Examples hereinafter. The absorbency (TBGV method) of the product type A pulp in the alkali-metal-cation-exchanged state is about 40 g/g (pH 8); in the protonated state, the absorbency (TBGV method) is about 4 g/g (pH 2).

Example 2

A paper sheet is produced in accordance with the process illustrated and described in connection with Fig. 1.

Fibrous pulp type A is the product of Example 1. Fibrous pulp type B is a mixture of chemithermomechanical pulp (Quesnel Co.) and bleached northern softwood kraft pulp (Grand Prairie, P&G Cellulose). The type A pulp is made up into a stock having a consistency of about 0.8% in chest 1 using water having a hardness of less than 5 ppm (calcium plus magnesium). Process water supplies used at other stages of the papermaking operation have hardness of about 100 ppm (calcium plus magnesium). No cationic materials, whether in the form of cationic wet-strength resins or aqueous polyvalent metal cations, are added at any stage. Aqueous concentrated sulfuric acid is in storage vessel 3; (corrosion-resistant steels are generally used in the construction of all process equipment herein which may be exposed to corrosive acids). The aqueous dispersion of type A pulp in chest 1 has a pH of about 3.5. The pH of the aqueous dispersion of type B pulp in chest 2 is about 3.5 and the consistency is about 3%. The headbox 12 is a Flood Roof Former, equipped with (a) a multi-orifice distribution plate to redirect incoming furnish and distribute it equally over the width of the first foraminous member, (b) a chamber to promote turbulence in the distributed flow and to prevent flocking, (c) a flow channel to carry the furnish to the first foraminous member and (d) distribution leaves to further promote turbulence. The consistency of the acidic stock at the headbox is about 0.15-0.2%. First foraminous member 15 is 84-mesh, 5-shed, M-design, with filament diameter of .17 inch (4.3 millimeters) in the warp and shuttle, specifically, 84-M DURAFORM Pilot Machine Fabric, obtainable from Albany International Corp., Appleton Wire Division. This foraminous member moves continuously at 500 feet per minute (about 152.4 meters per minute). Flow and wire movement are regulated so that a uniform, moist web (embryonic web) is laid down. The pH of water draining from this embryonic web is about 3.7. The embryonic web travels as shown in Fig. 1 until it is transferred by means of a conventional vacuum pickup shoe (not shown in Fig. 1). The location of the vacuum pickup shoe is conventional, i.e., between 22 and 27 and it is positioned so as to assist transfer of web 20 from first foraminous member 15 to second foraminous member 21. The vacuum pickup shoe operates at a vacuum of 8-9 inches of mercury (27.04 - 30.42 kiloPascal). Second foraminous member 21 is a woven synthetic transfer fabric, 31M x 2S, 3S, obtainable from Appleton Wire Division of Albany International Corp.

The paper web 21 arrives at a spray-and-vacuum box at the alternate position 29a and is there treated with aqueous potassium carbonate having a concentration of about 4 M (mole per liter) by means of a VIB sprayer, VIB Systems Inc., nozzle size 1 mm, 4 nozzles spaced over 18 inches (40.64 cm), air atomization. The alkali passes into the web, and there in-situ, takes type A pulp from the acidic state to the alkali-metal-cation-exchanged state. Some water and unreacted alkali are removed from the web by the spray-and-vacuum box 29a by applying a vacuum typical for tissue-paper making, e.g., about 8 - 9 inches of mercury (27.04 - 30.42 kiloPascal). The web now has a consistency of about 20.7 % and enters a conventional forced air predryer 28. This predryer is (in common with all the other parts of the paper machine which handle the wet paper web) so designed as to avoid compacting the web; instead, drying is here achieved by passing hot air through the moist paper web and through the second foraminous member. The predryer air inlet temperature is about 175 °C. The paper web has a consistency of about 50% on the second foraminous member leaving the predryer. The web continues motion indicated by motion arrow 28, and arrives at a conventional Yankee dryer arrangement 33, wherein the paper web is finally dried. The Yankee dryer includes conventional adhesive applicator means and a doctor blade for creping. The Yankee operates at a temperature of about 188 °C. A conventional polyvinyl alcohol glue (0.025% solution) is conventionally applied to bond the web to the dryer drum, and 15 % creping is applied. If desired, some calendaring and further converting operations may be carried out, e.g., to make two-ply towels. The properties of the resulting paper sheet are as follows:

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(57) Abstract			
The invention is a method for improving the efficiency of aqueous cationic wet strength additives by pretreating cellulose surfaces with reactive anionic compounds, thus providing the cellulose surface with additional anionic sites suitable for retaining a high proportion of said cationic wet strength additives on the cellulose. The wet strength additives on the cellulose surface are cured or reacted with the cellulose surface. The resulting fibrous material has unusually high wet strength with unusually low doses of cationic wet strength additive. The preferred reactive anionic compounds comprise compounds having a reactive group suitable for covalent bonding to hydroxyl groups on cellulose, and further having sulfonic or other anionic end groups capable of attracting cationic wet strength compounds in aqueous solution.			

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METHOD FOR MAKING WET STRENGTH PAPER

Background of the Invention

In the art of papermaking, chemical materials exist for improving the strength of paper when wetted with water or aqueous solutions, including body fluids such as urine, blood, mucus, menses, lymph and other body exudates. These materials are known in the art as "wet strength agents" and are commercially available from a wide variety of sources. Any material that when added to a paper web or sheet results in providing the sheet with a wet geometric tensile strength:dry geometric tensile strength ratio in excess of 0.1 will, for purposes herein, be termed a wet strength agent. Typically these materials are termed either as permanent wet strength agents or as "temporary" wet strength agents. For the purposes of differentiating permanent from temporary wet strength, permanent will be defined as those resins which, when incorporated into paper or tissue products, will provide a product that retains 50% or more of its original wet strength after exposure to water for a period of at least five minutes. Temporary wet strength agents are those which show less than 50% of their original wet strength after exposure to water for five minutes. Both classes of material find application in the present invention.

The substantivity or effectiveness of many cationic wet strength agents is limited by low retention of the wet strength agent on the cellulose fiber. Much of the applied chemical may not be retained on the fiber, but remains in solution or is washed off after application, for there are relatively few anionic sites on the cellulose surface to attract the charged wet strength agent, and in some cases there may be a large number of anionic sites on colloidal particles or other particles in the fiber suspension which may adsorb a large portion of the wet strength agent, limiting its effectiveness in increasing wet strength. Cationic additives are sometimes used to help neutralize excess anionic sites on colloidal particles or "anionic trash" in the suspension, to allow more of a subsequently added cationic wet strength resin to attach to the fiber surface and not to be preferentially absorbed onto non-fiber components.

Further, the presence of anionic additives or agents in the pulp has a deleterious effect on the efficiency of cationic wet strength agents. This adverse effect can be reduced by adding "cationic promoters" to the stock, as is known in the art of papermaking. Cationic promoters typically include polyethylenimine with a cationic charge of about 0.75 to 3.5 milliequivalents/gram, quaternized polyamines, such as polydiallyldimethylammonium chloride, or cationic starch. Commonly used cationic resins include polyquaternary amines and are available from Cytec Industries under the trade

names CYPRO 514, 515, 516. Cationic promoters are added to the stock in advance of the wet strength resins to ensure adequate mixing and adequate contact with the fibers. When used, the cationic resins are generally used in an amount of about 1 to 10 pounds per ton or 0.05 to 0.5%. The cationic promoter can be used at 0 to 0.5 wt %, typically the resins are used in an amount of about 0.02 to 0.3 wt % and preferably 0.1 to 0.2 wt %. The manufacturer of the promoter will typically recommend a pH for its use. The Cypro resins are effective over a pH of about 4 to 9.

However, the use of cationic promoters does not increase the number of anionic sites on the fiber surface itself, and may decrease the number of such sites, such that the intrinsic potential of the cationic wet strength agent to increase wet strength is still limited by inadequate attachment sites on the cellulose surface. The extent of anionic sites on the cellulose can be measured in terms of the carboxyl group content of cellulose, which is typically measured to be about 2 to 5 milliequivalent per 100 grams of cellulose, or higher.

Therefore, an object of the present invention is to increase the number of anionic sites on the surface of papermaking fibers by pretreating the fibers, thus increasing the substantivity of subsequently added cationic wet strength agents that form covalent bonds with the cellulose. A further object of the present invention is substantially increasing the wet strength of paper that can be achieved with a given dose of wet strength agent. In particular, an object of the present invention is to increase the wet strength that can be achieved with a given quantity of wet strength resin by a factor greater than 20%, preferably greater than 40%, more preferably greater than 50%, and most preferably greater than 70%. Another object of the invention is to provide a method for enhancing wet strength in paper capable of achieving wet tensile strength values in substantially unrefined paper of over 1500 g/in, preferably over 2000 g/in, and most preferably over 2300 g/in, based on a 60 gsm Tappi handsheet. A further object of the invention is to provide wet:dry strength ratios greater than about 0.2, preferably greater than about 0.3, more preferably above about 0.4, still more preferably between 0.2 and 0.5, and most preferably greater than 0.5.

Summary of the Invention

The present invention resides in a method in which cellulosic fibers are pretreated with a fiber reactive anionic compound to increase the substantivity of cationic wet strength agents. In this method, an aqueous slurry of papermaking fibers is treated with a substantially colorless fiber reactive anionic compound, wherein the fiber reactive anionic

compound comprises a fiber reactive moiety suitable for forming a covalent bond (for example, an ether-type linkage) with hydroxyl or other groups on the cellulose surface. The pH of the slurry must be adjusted to ensure that it is sufficiently high to drive the reaction of the reactive anionic compound with the cellulose. The slurry can be at a high fiber consistency, preferably from about 5 to about 50%. High consistency is desirable because it reduces the amount of water affected by the chemical treatment process and allows more efficient use of the fiber reactive anionic compound. Subsequently, the slurry is diluted, if necessary, and mixed with a cationic wet strength agent. The treated fibers are formed into a paper web using processes well known in the art and dried under conditions suitable for curing the wet strength agent.

The present invention also resides in a chemical treatment process that increases the number of anionic attachment sites for cationic polymers on cellulose by means of reaction between a triazine or other reactive group on a colorless reactive anionic compound further comprising at least one sulfonic or carboxylic group suitable for establishing an ionic bond with a cationic wet strength agent, followed by addition of a cationic polymer and alkalization to drive reaction of the reactive anionic compound with cellulose.

The invention also resides in a method of preparing paper with relatively high wet strength and low dry strength by first increasing anionic sites on the cellulose fibers with said fiber reactive anionic compound, followed by addition of a chemical debonder agent and a cationic wet strength agent. The debonder agent may be applied to the fibers while the fibers are in solution, followed by addition of the cationic wet strength agent, whereafter the paper is formed, dewatered, and dried. Alternatively, the debonder agent may be applied to dried or partially dried paper web that has been prepared with a fiber reactive anionic compound and a cationic wet strength agent. In either case, the debonder agent interferes with hydrogen bond formation, reducing the dry strength of the paper, while having relatively little effect on covalent bond formation. The result is a paper with an increased wet/dry tensile strength ratio. Such paper can have reduced stiffness and improved softness due to the reduced extent of hydrogen bonding, while still having high wet strength.

Detailed Description of the Invention

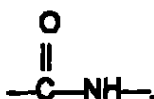
The first step in the method of this invention is providing an aqueous slurry of papermaking fibers. It is anticipated that wood pulp in all its varieties will normally comprise the papermaking fibers used in this invention. However, other cellulosic fibrous

pulps, such as cotton liners, bagasse, rayon, kenaf, milkweed fibers, and the like can be used. Wood pulps useful herein include both sulphite and sulfate pulps as well as mechanical and thermomechanical pulps all well known to those skilled in the art, including chemithermomechanical pulp and bleached chemithermomechanical pulp. High brightness pulps, including chemically bleached pulps, are especially preferred for tissue making, but unbleached or semi-bleached pulps may also be used. Pulps derived from both deciduous and coniferous trees can be used. Recycled fibers are included within the scope of the present invention.

The second step of the present invention is chemical pretreatment of the fibers by adding an effective amount of a fiber reactive anionic compound to the fiber slurry. The preferred amount of fiber reactive anionic compound added to the fiber slurry is from about 0.01 to about 4 wt % based on the dry fiber weight, preferably from about 0.05 to about 2 wt %, more preferably from about 0.08 to about 1.5%, and most preferably from about 0.1 to about 1 wt%. (All weight percentages referred to herein are on a dry basis unless otherwise stated.) The pretreatment of papermaking fibers to increase substantivity toward cationic compounds is achieved with colorless fiber reactive "dyes" modified to be without chromophore groups and further modified, if necessary, to ensure the presence of at least one anionic moiety such as a sulfonic or carboxylic group. The anionic moiety serves as the site for ionic bonds with cationic groups of a cationic wet strength agent, helping to form a bridge between the fiber and the wet strength agent to hold the wet strength agent on the fiber, thus increasing the effectiveness of a given dose of wet strength agent in a papermaking furnish.

Suitable reactive anionic compounds are organic molecules comprising at least one anionic moiety such as a sulfonyl or carboxyl group and at least one fiber reactive group capable of forming a covalent bond such as an ether-type linkage to a hydroxyl group on cellulose, selected from the group consisting of monohalotriazine, dihalotriazine, trihalopyrimidine, dihalopyridazinone, dihaloquinoxaline, dihalophthalazine, halobenzothiazole, acrylamide, vinylsulfone, β -sulfatoethylsulfonamide, β -haloethylsulfone, and methylol, with dihalotriazine believed to be particularly advantageous because of an ability to allow reaction with the fiber to occur at lower temperatures than monohalotriazine and related compounds; and with chlorine as the preferred halogen. The reactive anionic compound further comprises a bridging group between the fiber reactive moiety and the anionic group, said bridging group comprising an aliphatic, an aromatic, an inertly or essentially inertly substituted aromatic, a cyclic, a heterocyclic, or an inertly or essentially inertly substituted heterocyclic radical,

characterized by low absorption of visible light. In one embodiment, the bridging group is bonded to the fiber reactive moiety by means of an -NH-group or by a peptide bond involving the group

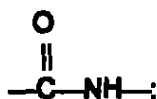


In another preferred embodiment, the reactive anionic compound is substantially water soluble and has a molecular weight less than 5,000, preferably less than 3000, more preferably less than 1500, and preferably between 300 and 1000.

More specific examples of suitable reactive anionic compounds are given by the formula:



wherein W is sulfonyl or carboxyl or salts thereof; R is either an aliphatic, an aromatic, an inertly or essentially inertly substituted aromatic, a cyclic, a heterocyclic, or an inertly or essentially inertly substituted heterocyclic radical, characterized by low absorption of visible light, and preferably being resistant to attack or cleavage at 70°C over a pH range of 6 to 8, preferably 6 to 9, more preferably 5 to 9, and most preferably 4 to 10; Y signifies NH or



X is a moiety suitable for forming a covalent bond such as an ether-type linkage to a hydroxyl group on cellulose, selected from the group consisting of monohalotriazine, dihalotriazine, trihalopyrimidine, dihalopyridazinone, dihaloquinoxaline, dihalophthalazine, halobenzothiazole, acrylamide, vinylsulfone, β -sulfatoethylsulfonamide, β -haloethylsulfone, and methylol, with dihalotriazine believed to be particularly advantageous because of an ability to allow reaction with the fiber to occur at lower temperatures than monohalotriazine and related compounds; and with chlorine as the preferred halogen; and

B is either hydrogen, a group of the formula Y-R, wherein Y and R are defined as above; or a group of the formula Y-R-W, wherein Y, R, and W are defined as above. A particular commercially available example of a suitable fiber reactive anionic compound, discovered to be useful for the present invention, is the nylon dye retardant Sandospace S produced by Clariant Corp., Charlotte, North Carolina. While the formula of Sandospace S is proprietary, chemical analysis and partial information from the supplier confirms that it has a chlorinated triazine group, aromatic structures, and sulfonic groups.

The above formula provides one class of suitable structures. Related structures within the scope of this invention can have multiple sulfonyl or carbonyl groups attached to various locations of the molecule, including on segments of the bridging group or even directly attached to part of the fiber reactive group. Multiple fiber reactive groups may also be attached to one or more bridging groups, allowing the reactive anionic compound to attach to multiple adjoining sites on a cellulose surface.

Whereas treatment with fiber reactive dyes are typically carried out in dilute slurries, such as about 2% consistency, it has been surprisingly discovered that the reaction of the present invention can be successfully carried out with low amounts of liquid, including high consistency fiber slurries with fiber consistencies over 5%, preferably between 5 and 50%, preferably greater than 10%, more preferably greater than 15%, and most preferably greater than about 20%, and desirably between 10 to 30% consistency. The reduced use of water improves process efficiency and reduces water treatment burdens. For high consistency treatment, it is desirable to employ high consistency mixers such as those recently known in the art of papermaking and bleaching. Hobart batch mixers, for example, may be useful in preparing the slurry at high consistency. Useful continuous high consistency mixers are produced by Sunda Defibrator, Norcross, Georgia, and other vendors. For best results, mixing should be done with adequate shear to thoroughly and uniformly mix the reagents with the fiber slurry.

The third step is adjusting the pH and temperature of the slurry to effectively drive the reaction between the fiber reactive anionic compound and the fiber. Once applied to an aqueous fiber slurry, the reactive anionic compound added in the second step may not react significantly with the cellulose until the pH and the temperature are both sufficiently high. Alkalization is typically necessary to raise the pH above 6, preferably above 7, more preferably above 8, still more preferably between 8 and 11, and most preferably between 8 and 10, in order to drive the reaction toward completion. Alkaline agents such as sodium hydroxide, trisodium phosphate, sodium bicarbonate, and sodium carbonate, either singly or in combination, are preferred for their low cost, their chemical effectiveness, their general compatibility with tissue making operations, and their ease of handling and processing, but other alkaline compounds may be selected as well, including but not limited to calcium oxide, potassium hydroxide, potassium carbonate, and related compounds.

Alkalization of the fibrous slurry can be done either before, during, or after addition of the reactive anionic compound to the fibers in the second step. Based on

experimental results, alkalization after addition of the reactive anionic compound is preferred because it results in higher yield and efficiency (higher substantivity of the wet strength agent, manifest by higher wet strength of paper at a given dosage of wet strength agent). Without limitation, it is believed that alkalization too early in the process can cause some hydrolysis of the reactive group of the reactive anionic compound, resulting in lower yield.

In an especially preferred embodiment of the invention, slightly more of an alkaline compound is added to the slurry than would be needed to neutralize the acidic byproduct of reaction between the reactive anionic compound and a hydroxyl group of the cellulose. For example, when the reactive group is monochloro triazine, the acidic byproduct is hydrogen chloride. Adding sufficient sodium hydroxide in the post-alkalization treatment to more than neutralize the hydrogen chloride, assuming complete reaction, has proven to be effective in achieving the desired reaction and the desired wet strength properties. Thorough mixing of the slurry during alkalization is desirable.

Simultaneously or subsequent to the alkalization, a temperature of 20°C to 150°C is typically needed for practically rapid reaction rates, with a preferred temperature range of 20 to 120°C, more preferably 20°C to 100°C, more preferably still 40 to 85°C, and most preferably 50 to 80°C. Of course, the optimum temperature will depend on which fiber reactive anionic compound is used. If the slurry is below a suitable temperature range, temperature elevation may be achieved by contact heating through the use of a heat exchanger, heated vessel walls, steam injection, or any of the many means known in the art. For uniformity of reaction, good mixing of the slurry during heating is desirable. The adjustment of temperature need not be simultaneous with the addition of alkaline compounds or with the addition of fiber reactive anionic compound, but preferably will follow addition of the alkaline compound. The proper temperature should be maintained for a sufficient period of time to drive the reaction to a useful degree of completion.

The fourth step is adding an effective amount of cationic wet strength agents and water to said aqueous slurry, creating a papermaking furnish. Mixtures of compatible wet strength resins, including those described previously, can be used in the practice of this invention. Additional compounds and fillers or solid components may be added. This step may be done simultaneously with the second step, or could even precede the second step, if desired, although better efficiency is obtained by performing the addition of cationic wet strength agents after chemical pretreatment of the fibers. Any amount of wet strength agent may be added, but for efficient use and reasonable cost it is desirable that less than about 30 pounds per ton or 1.5 wt % on a dry fiber basis be added, preferably

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between about 0.02 to 1.5 wt %, more preferably between 0.02 to 1.0 wt %, and most preferably between about 0.05 to 0.8 wt %. Any cationic wet strength agent suitable for papermaking may be used. For high wet resiliency tissue, preferable agents should be capable of forming covalent bonds with cellulose. In the usual case, the wet strength resins are water-soluble, cationic materials. That is to say, the resins are water-soluble at the time they are added to the papermaking furnish. It is quite possible, and even to be expected, that subsequent events such as cross-linking will render the resins insoluble in water. Further, some resins are soluble only under specific conditions, such as over a limited pH range. Wet strength resins are generally believed to undergo a cross-linking or other curing reactions after they have been deposited on, within, or among the papermaking fibers. Cross-linking or curing does not normally occur so long as substantial amounts of water are present.

Particular permanent wet strength agents that are of utility in the present invention are typically water soluble, cationic oligomeric or polymeric resins that are capable of either crosslinking with themselves (homocrosslinking) or with the cellulose or other constituent of the wood fiber. Such compounds have long been known in the art of papermaking. See, for example, U.S. Pat. Nos. 2,345,543 (1944), 2,926,116 (1965) and 2,926,154 (1960), all herein incorporated by reference. One class of such agents include polyamine-epichlorohydrin, polyamide epichlorohydrin or polyamide-amine epichlorohydrin resins, collectively termed "PAE resins." These materials have been described in patents issued to Kelm (U.S. Pat. Nos. 3,700,623 and 3,772,076 herein incorporated by reference) and are sold by Hercules, Inc., Wilmington, Delaware, as Kymene, e.g., Kymene 557H. Related wet strength agents are sold by Georgia Pacific under the name Amres, e.g., Amres 8855. Other suitable materials are marketed by Henkel Chemical Co., Charlotte, North Carolina. Materials developed by Monsanto and marketed under the Santo Res label are base-activated polyamide-epichlorohydrin resins that can be used in the present invention. These materials are described in patents issued to Petrovich (U.S. 3,885,158; U.S. 3,899,388; U.S. 4,129,528 and U.S. 4,147,586) and van Eenam (U.S. 4,222,921) all herein incorporated by reference.

Although they are not as commonly used in consumer products, polyethylenimine resins are also suitable for immobilizing fiber-fiber bonds. Another class of permanent-type wet strength agents includes aminoplast resins (e.g., urea-formaldehyde and melamine-formaldehyde).

The permanent wet strength agent is typically added to the paper fiber in an amount up to about 20 pounds per ton or 1.0 wt %. The exact amount will depend on the

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nature of the fibers and the amount of wet strength required in the product. As in the case of the temporary wet strength agent, these resins are generally recommended for use within a specific pH range depending upon the nature of the resin. For example, the Amres resins are typically used at a pH of about 4.5 to 9.

Temporary wet strength agents are also useful in the method of this invention. Suitable cationic temporary wet strength agents can be selected from agents known in the art such as dialdehyde starch, polyethylene imine, mannogalactan gum, glyoxal, and dialdehyde mannogalactan. Also useful are cationic glyoxylated vinylamide wet strength resins as described in U.S. Pat. No. 3,558,932 issued to Coscia et al. on Jan. 19, 1971, and in U.S. Pat. No. 5,466,337, "Repulpable Wet Strength Paper," issued to William B. Darlington and William G. Lanier on Nov. 14, 1995. Useful water-soluble cation resins include polyacrylamide resins such as those sold under the Parex trademark, such as Parex 831NC, by American Cyanamid Company of Stamford, Conn., generally described in the above-mentioned patent issued to Coscia et al. and in U.S. Pat. No. 3,558,933 issued to Williams et al. on Jan. 19, 1971. U.S. Pat. No. 4,805,702, Guerro et al., issued August 12, 1988, discloses temporary wet strength resin made by reacting a vinylamide polymer with glyoxal, and then subjecting the polymer to an aqueous base treatment. The product is said to provide tissue paper which loses a part of its wet strength when soaked in water at neutral pH. U.S. Pat. No. 4,803,176, Bjorkquist and Schmidt, issued July 29, 1986, discloses related temporary wet strength resins. Generally, the cationic temporary wet strength agent is provided by the manufacturer as an aqueous solution and is added to the pulp in an amount of about 0.05 to 0.4 wt % and more typically in an amount of about 0.1 to 0.2 wt %. Depending on the nature of the resin, the pH of the pulp is adjusted prior to adding the resin. The manufacturer of the resin will usually recommend a pH range for use with the resin. The Parex 831NC resin can be used at a pH of about 4 to 8.



The fifth step is depositing said papermaking furnish on a foraminous surface to form an embryonic web. This step may further comprise dewatering and other operations known in the art prior to drying of the web.

The sixth and final step is drying the web. Any of the techniques known to those skilled in the papermaking art for drying wet fibrous webs can be used. Typically, the web is dried by heat supplied by air moving around, over, or through the web; by contact with a heated surface; by infrared radiation; by exposure to superheated steam, or by a combination of such methods. The exact point at which the wet strength agent begins to cure during the drying of the wet fibrous web is an indistinct one. What is required in the

present invention is that the fibrous web be substantially dried and that the wet strength bonds of whatever nature as provided by the wet strength resin begin to form. The extent of formation of these bonds must have proceeded to such an extent that subsequent process steps will not appreciably interfere with their ultimate completion and the corresponding wet strength development. In general, though not necessarily in all cases, it is desired that the temperature of said web be sufficiently elevated to effectively cure the wet strength agent (i.e., drying may or may not require high temperature curing). The wet:dry tensile strength ratio of the dried web should be at least 0.1, preferably at least about 0.2, and more preferably at least about 0.3 when the process has been properly executed. As used herein, the "wet:dry ratio" is the ratio of the geometric mean wet tensile strength divided by the geometric mean dry tensile strength. Geometric mean tensile strength (GMT) is the square root of the product of the machine direction tensile strength and the cross-machine direction tensile strength of the web. Tensile strengths are measured with standard Instron test devices having a 4-inch jaw span using 3-inch wide strips of tissue, conditioned at 50% relative humidity and 72°F for at least 24 hours, with the tensile test run at a crosshead speed of 10 in/min.

The final wet strength of the paper for a given dose of wet strength agent should be at least 10% higher than is achieved by the use of the wet strength agent without addition of the reactive anionic compound.

The present invention offers multiple advantages over prior art techniques for enhancing wet strength. The present invention requires no coloration or dyeing of the fibers, and requires no bleaching or discharging of chromophores to maintain a white sheet. The present invention requires no addition of NaCl or other chlorides to drive the reaction of the reactive anionic compound with the fiber. Further, the present invention does not require highly dilute fiber slurries in the fiber pretreatment step but has been demonstrated successfully at fiber consistencies as high as 30%. Further, the present invention does not rely on ionic bonds to enhance strength, but takes advantage of reactive wet strength agents that form covalent bonds with the cellulose surface, though ionic bonds do provide the initial attachment of the cationic polymer with the sulfonic groups of the reactive anionic compound.

The novel use of fiber reactive anionic compounds in the present invention can also be coupled with chemical debonder agents to make paper with relatively high wet strength and low dry strength. One or more fiber reactive anionic compounds are used with cationic wet strength resins to establish water-resistant covalent bonds, while chemical debonders are used to reduce the number of hydrogen bonds between fibers,

thus reducing the dry strength of the paper. This is best done by first increasing anionic sites on the cellulose fibers with said fiber reactive anionic compound, according to steps one through three as previously described, followed by addition of a chemical debonder agent and a cationic wet strength agent. The debonder agent may be applied to the fibers after step three while the fibers are in solution, followed by addition of the cationic wet strength agent as in step four, whereafter the paper is formed, dewatered, and dried according to steps five and six above. In this case, wherein the debonder agent is added to the fibers while they are in slurry form, it is desirable that the cationic wet strength resin be added after the debonder agent has been added to the slurry. Otherwise, the cationic wet strength agent may occupy most anionic sites on the fibers and interfere with retention of the chemical debonder agent. Chemical debonder agents typically have a single cationic site, such as a quaternary ammonium salt, with fatty acid chains.

Alternatively, the debonder agent may be applied to the dried or partially dried paper web during step six through known means such as spraying, printing, coating, and the like. Preferably, the web has been dried enough to begin formation of covalent bonds in the web. The web should then be at a solids level of preferably at least 40%, more preferably at least 60%, more preferably still at least 70%, most preferably at least 80%, and desirably between 80 and 90%. The debonder may be applied at other times, but for best results it should be either between steps 3 and 4 or during step 6 of the process described above.

When properly applied, the debonder agent interferes with hydrogen bond formation between the fibers, thus reducing the dry strength of the paper, while having relatively little effect on covalent bond formation. The result is a paper with an increased wet/dry tensile strength ratio. Such paper can have reduced stiffness and improved softness due to the reduced extent of hydrogen bonding, while still having high wet strength.

Desirable chemical debonder agents have less than five cationic sites per molecule and preferably no more than one cationic site which can bond with the anionic sites on the cellulose fiber surface. Large numbers of cationic sites could interfere with the anionic sites provided by the fiber reactive anionic compound if the debonder is applied to the fibers before covalent bonds have formed. Examples of useful chemical debonder agents include fatty chain quaternary ammonium salts (QAS) such as Berocell 584, an ethoxylated QAS made by Eka Nobel, Inc. (Marietta, Georgia), or compounds made by Witco Corp., Melrose Park, Illinois, including C-6027, an imidazoline QAS, Adogen 444, a cetyl trimethyl QAS, Varisoft 3690PG, an imidazoline QAS, or Arosurf

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PA 801, a blended QAS. Agents known as softeners in the art of tissue making are also likely to be suitable as chemical debonder agents. Relative to the dry mass of the fibers, debonder may be added at a level in the range of 0.1% to 2%, preferably 0.2% to 1.5%, and more preferably 0.5% to 1%.

Examples

Example 1.

100 gm of a dried bleached virgin northern softwood kraft pulp (Kimberly-Clark LL-19 pulp) was saturated with 1200 ml of water and dispersed into a slurry through agitation in a Hobart mixer. The slurry was dewatered to a fiber consistency of about 25%. This was repeated several times to obtain multiple batches of high consistency pulp. For each batch of pulp, between 1 and 4 grams of Sandospace S (Clariant Corp., Charlotte, NC) was prepared and diluted with 5 parts of water per part of reagent (thus, the amount of dilution water ranged from 5 to 20 grams of water). Each batch of fiber slurry, comprising 100 gm of fiber per batch, was then reloaded into the Hobart mixer and a Sandospace S solution, containing between 1 and 4 gm of Sandospace S was added during agitation of the pulp. The mixture was thoroughly blended at 25°C for 25 minutes. Then NaHCO₃ was added to each batch at a dose of 0.5 gm of NaHCO₃ per gm of Sandospace S (for a range of 0.5 to 2 gm of NaHCO₃), with the NaHCO₃ having been first dispersed in 5-10 ml of water prior to addition to the mixture of fiber, water, and Sandospace S. Following addition of NaHCO₃, the mixture was further blended in the Hobart mixer for 20 min at 25°C. Thereafter, the mixture was heated to 100°C in an oven and maintained at said temperature for 2 hours without mixing. After cooling the slurry to 25°C, without post-washing of the slurry, the slurry was formed into 60 gsm handsheets using standard Tappi procedures. Kymene 557LX wet strength agent was added to the diluted handsheet slurry at a level of 1% Kymene on a dry fiber basis. The properties of these handsheets are shown in Figures 2-5. Sheet wet strength is shown to have increased substantially as the level of Sandospace S was increased, even though the amount of wet strength agent was constant. This demonstrates the ability of the fiber reactive anionic compound to improve the efficiency and substantivity of the Kymene, which is a cationic wet strength agent.

Untreated LL19 fiber handsheets with 1% Kymene had a wet strength of 1411 grams/in and a wet:dry tensile strength ratio of 24.6%. With pretreatment by the Sandospace S fiber reactive anionic compound, the same level of Kymene resulted in a wet strength of 2374 g/in and a wet:dry tensile strength ratio of 30.1% when 1% of the

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Sandospace S was applied. Results from tensile testing are shown in Table 1. Up to a 68% increase in wet strength was possible with fiber reactive anionic compound relative to the use of 1% Kymene alone.

Table 1: Results from Example 1 (post-alkalization)

%RAC/%Kymene (dry fiber basis)	0/0	0/1	1/1	2/1	3/1	4/1	5/1
wet strength	236	1411	2374	2100	2242	2290	2348
dry strength	4952	5723	7881	7147	7679	7361	8258
Wet TEA	2.24	3.21	8.49	6.52	7.11	7.51	8.39
Dry TEA	25.45	41.05	95	90.42	92	92.43	95.68

Example 2

All steps were conducted as in Example 1 except that the NaHCO_3 solution was added prior to the addition of the Sandospace S solution, resulting in pre-alkalization rather than post alkalkization. Up to a 46% increase in wet strength with fiber reactive anionic compound was possible relative to paper made with the Kymene alone. Note that at 1% RAC (reactive anionic compound), a wet strength of 1606 g was achieved with pre-alkalization compared to 2374 g with post-alkalization.

Table 2: Results from Example 2 (pre-alkalization)

%RAC/%Kymene (dry fiber basis)	0/0	0/1	1/1	2/1	3/1	4/1	5/1
wet strength	236	1594	1606	1872	2115	2334	2330
dry strength	4953	5889	6934	7651	7609	7821	7832
Wet TEA	2.24	6.28	9.03	11.29	12.8	14.13	14.4
Dry TEA	25.45	33.25	64.72	79.64	75.1	74.2	75

Example 3

45 kg of a bleached northern softwood kraft pulp was pulped at 25°C for 20 minutes in a high consistency pulper at a consistency of 8%. 3.6 kg (8% relative to the fiber mass) of Sandospace S paste, as received from Clariant Corp., was added to the slurry in the pulper and mixed for an additional 20 minutes. 0.9 kg of sodium carbonate powder was added to the slurry in the pulper and mixed for another 20 minutes. The slurry was then

heated to 60°C and maintained at that temperature for 2 hours and then dewatered with a centrifuge to 35% consistency. The fibers were then ready for use in papermaking without any washing.

The 35% consistency fibers were then diluted with water to make handsheets according to Tappi procedures for handsheet making. Then Berocell 584 liquid (Eka Nobel Corp., Marietta, Georgia) was added to the dilute slurry at a dose of 1 gram of Berocell liquid per 100 grams of fiber (1% Berocell on a dry fiber basis) and stirred for 20 minutes. Thereafter, 1% Kymene 557LX on a dry fiber basis was also added to the slurry and stirred for 20 minutes. Then 60 gsm handsheets were formed according to Tappi procedures and tested for dry and wet tensile strength properties.

The 60 gsm handsheets had a mean wet strength of 2160 g/inch and a mean dry strength of 4929 g/inch. The wet:dry tensile strength ratio for the handsheets of this example was 43.8%, in contrast to typical values of 30-35% for sheets with Kymene but without debonder, as in Example 1. A handsheet made according to this Example but without any added debonder had a wet:dry tensile strength ratio of 35.1%.

Example 4

Handsheets were prepared as described in Example 3, except that no debonder was added to the fibrous slurry. A 1% by weight aqueous solution of Berocell liquid was prepared and sprayed onto the dried handsheets using a common household hand sprayer. Spray was applied evenly to both sides of the handsheets until the added liquid mass was approximately 100% of the dry handsheet mass, resulting in a total application of 1% pure Berocell to the fibers on a dry fiber basis (1 gram of added Berocell per 100 grams of fiber). Then the handsheets were dried at 105°C for 20 minutes and then cooled, conditioned, and tested for tensile strength. The mean wet strength was 2897 g/inch and the dry strength was 6551 g/inch, yielding a wet:dry tensile ratio of 44.3%.

It will be appreciated that the foregoing examples, given for purposes of illustration, are not to be construed as limiting the scope of this invention, which is defined by the following claims and all equivalents thereto.

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We claim:

1. A method for making wet strength paper comprising the steps of:
 - (a) providing an aqueous slurry of cellulosic papermaking fibers;
 - (b) adding a substantially colorless reactive anionic compound to said aqueous slurry, said reactive anionic compound having the formula:



wherein:

W is sulfonyl or carboxyl or salts thereof;

R is an aliphatic, an aromatic, an inertly or essentially inertly substituted aromatic, a cyclic, a heterocyclic, or an inertly or essentially inertly substituted heterocyclic radical, characterized by low absorption of visible light;

Y signifies NH or $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—NH—}$;

X is a moiety suitable for forming a covalent bond to a hydroxyl group on cellulose, selected from the group consisting of monohalotriazine, dihalotriazine, trihalopyrimidine, dihalopyridazinone, dihaloquinoxaline, dihalophthalazine, halobenzothiazole, acrylamide, vinylsulfone, β -sulfoethylsulfonamide, β -chloroethylsulfone, and methylol;

B is hydrogen, a group of the formula Y-R, wherein Y and R are defined as above; or a group of the formula Y-R-W, wherein Y, R, and W are defined as above;

- (c) adjusting the pH and temperature of said aqueous slurry to promote reaction of the reactive anionic compound with the cellulosic fibers;
- (d) adding a cationic wet strength agent and water to said aqueous slurry to create a papermaking furnish;
- (e) depositing said papermaking furnish on a foraminous surface to form an embryonic web; and

(f) drying the web.

2. The method of Claim 1, wherein the amount of the reactive anionic compound is from about 0.01 to about 4 dry weight percent of the dry fiber mass of the web.
3. The method of Claim 1, wherein the amount of the cationic wet strength agent is from about 0.02 to about 1.5 dry weight percent of the dry fiber mass of said web.
4. The method of Claim 1, wherein the consistency of fiber in said aqueous slurry is about 5% or greater during the step of adding the reactive anionic compound.
5. The method of Claim 1, wherein the consistency of fiber in said aqueous slurry is about 20% or greater during the step of adding the reactive anionic compound.
6. The method of Claim 1, wherein group X of the reactive anionic compound is a moiety selected from the group consisting of dichlorotriazine, trichloropyrimidine, and dichloropyridazinone.
7. The method of Claim 1, wherein the amount of sodium chloride present in the aqueous slurry of step (c) is less than 0.01 g per gram of fiber.
8. The method of Claim 1, wherein the step of adjusting the pH of said slurry is achieved through the addition of an alkaline agent selected from the group consisting of NaHCO_3 , Na_2CO_3 , Na_3PO_4 and NaOH .
9. The method of Claim 1, wherein the cationic wet strength agent is a crosslinkable agent.
10. The method of Claim 1, wherein the cationic wet strength agent is a permanent wet strength agent.
11. The method of Claim 1, wherein the cationic wet strength agent is a permanent wet strength agent.
12. The method of Claim 1, wherein the wet strength of the dried web is greater than 2000 grams per inch based on a 60 gsm Tappi handsheet.

13. The method of Claim 1, wherein the wet strength of the dried web is at least 20% greater than the wet strength of an otherwise identical web made without the addition of the reactive anionic compound.
14. The method of Claim 1, wherein the wet:dry strength ratio of the dried web is 0.2 or greater.
15. The method of Claim 1, wherein the wet:dry strength ratio of the dried web is 0.4 or greater.
16. The method of Claim 1, wherein the pH in step (c) is adjusted to be in the range of from about 8 to about 11.
17. The dried web made according to the method of any one of Claims 1-12 having a wet:dry strength ratio of about 0.2 or greater.
18. The method of Claim 1, further comprising the steps of adding a chemical debonder agent to said aqueous slurry prior to the step of adding a cationic wet strength agent.
19. The method of Claim 1, further comprising the step of adding a chemical debonder agent to said aqueous slurry after the step of adding a cationic wet strength agent.
20. The method of Claim 19, wherein said chemical debonder agent is applied to said web during the step of drying the web, such that the web is at least partially dried prior to application of said chemical debonder agent.
21. The dried web made by the method of Claim 18 or 19 having a wet:dry strength ratio of 0.3 or greater.
22. A paper web comprising:
 - (a) cellulosic papermaking fibers;
 - (b) from 0.02 to about 1.5 dry weight percent, based on dry fiber, of a cationic wet strength additive; and

- (c) from 0.01 to about 4 dry weight percent, based on dry fiber, of a substantially colorless reactive anionic compound, said reactive anionic compound having the formula:



wherein:

W is sulfonyl or carboxyl or salts thereof;

R is an aliphatic, an aromatic, an inertly or essentially inertly substituted aromatic, a cyclic, a heterocyclic, or an inertly or essentially inertly substituted heterocyclic radical, characterized by low absorption of visible light;

Y signifies —NH— or $\text{—}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{—NH—}$;

X is a moiety suitable for forming a covalent bond to a hydroxyl group on cellulose, selected from the group consisting of monohalotriazine, dihalotriazine, trihalopyrimidine, dihalopyridazinone, dihaloquinoxaline, dihalophthalazine, halobenzothiazole, acrylamide, vinylsulfone, β -sulfatoethylsulfonamide, β -chloroethylsulfone, and methylol;

B is hydrogen, a group of the formula Y-R, wherein Y and R are defined as above; or a group of the formula Y-R-W, wherein Y, R, and W are defined as above.

23. The paper web of Claim 22, further comprising 0.1% to 2.0% of a chemical debonder agent.

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(54) **PROCESS FOR PREPARING HYDROLYZABLE SHEET**

(57) The invention relates to a process to improve wet tensile strength as well as water-swelling property of a water-disintegrable sheet to be used as a wet wipe for cleaning in household.

A mixture of water-swelling or water-insoluble carboxymethyl cellulose and/or salt thereof having a degree of substitution = 0.30 - 0.60 and pH $\geq$ 5.0 and water-dispersible fibers is subjected to a foliating step of a process to obtain the water-disintegrable sheet and, before or after the foliating step of the process, the mixture is added with a base.

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Description

FIELD OF THE INVENTION

5 The present invention relates to a process for manufacturing a water-disintegrable sheet adapted to be dispersed or dissolved in water.

BACKGROUND ART

10 Wet wipes for cleaning use in household etc. are well known. Water-dispersible or water-disintegrable sheet-like articles typically as wet wipes are also well known, which are rapidly dispersed or disintegrated in water so that they can be directly thrown away into water, for example, in a flush toilet, and flushed down a drain. It should be understood that terms used herein "water-dispersible" and "water-disintegrable" are synonymous with each other. Generally, wet wipes having such characteristics are required to have a high strength exhibited while they are used in a wet condition and
15 also a rapid integration when they are thrown away into a large quantity of water. To assure that these strength and integration should be compatible with each other, Japanese Laid-open Patent Application No. Hei1-168999 discloses use of water-insoluble sodium/calcium salt of carboxymethyl cellulose or sodium salt of carboxymethyl cellulose. Japanese Patent Publication No. Sho48-27805 discloses a process for paper making wherein a wet paper sheet obtained from water-insoluble carboxymethyl cellulose is sprayed with aqueous solution of alkaline metal. Japanese Laid-Open Patent
20 Application No. Hei3-167400 discloses a process for paper making including a step of mixing a water dispersion of paper making stuff with water-insoluble alkaline salt of carboxymethyl cellulose. Furthermore, Japanese Laid-Open Patent Application No. Hei5-25782 discloses a process for paper making wherein a paper sheet obtained from a mixture of water dispersion of paper making stuff and alkaline salt of carboxymethyl cellulose is impregnated with hydrated organic solvent containing multivalent metal ion.

25 Carboxymethyl cellulose and/or salt thereof conventionally used by the above-mentioned prior arts generally lose their initial water-insolubility, then show a tendency to swell and finally become water-soluble as degree of substitution (D.S.) and pH thereof increase. When these carboxymethyl cellulose and/or salt thereof are used as binders for paper making, the tendency to swell of the binders will make it difficult to get a uniform mixture of the binders with fibers dispersed in water. On the other hand, the binders having become water-soluble will be prohibited from being deposited
30 on a sheet as an intermediate product, strength of the sheet will be not so improved as expected from an actual quantity of the binders mixed in a water dispersion of paper making stuff. Although an aqueous solution of the binders could be sprayed to a sheet obtained from paper making stuff, swollen carboxymethyl cellulose makes an aqueous solution thereof too viscous to be sprayed in a uniform condition.

35 SUMMARY OF THE INVENTION

In view of problems as has been described above, it is a principal object of the invention to provide an improved manufacturing process for making a disintegrable sheet for wet wipes or the like to be used for cleaning sheet materials in household etc. wherein a good quantity of carboxymethyl cellulose and/or salt thereof can be efficiently
40 deposited on the sheet.

The object set forth above is achieved, according to the invention, by a process for manufacturing a water-disintegrable sheet from carboxymethyl cellulose and/or salt thereof and water-dispersible fibers, said process being characterized in that a mixture of water-swelling or water-insoluble carboxymethyl cellulose and/or salt thereof having a degree of substitution (D.S.) = 0.30 - 0.80 and pH $\geq$ 5.0 and water-dispersible fibers is subjected to a step of foliating to obtain
45 said water-disintegrable sheet and, before or after said step of foliating of said process, said mixture is added with a base.

Said base is preferably sodium carbonate. The process according to the invention may further comprise a step of impregnating said water-disintegrable sheet with aqueous solution to obtain a wet wipe from said sheet.

50 DESCRIPTION OF PREFERRED EMBODIMENTS

Materials used in a manufacturing process of the present invention include water-dispersible fibers which can be foliated in the presence of carboxymethyl cellulose and/or salt thereof. While it is preferred to use pulp fiber, it is also possible to use natural fibers such as wool, regenerated fiber such as rayon fiber, semi-synthetic fiber such as acetate,
55 or synthetic fiber such as nylon, polyester etc. For such fibers, low water-swelling or water-insoluble carboxymethyl cellulose and/or salt thereof having D.S. = 0.30 - 0.80 and pH $\geq$ 5.0 is used as binders. In order to provide such binders with a high water-swelling property or a high water-solubility, a base is added to the binders before or after a foliating step of a sheet making process. The base can be added during the foliating step if needed. While any appropriate base and combination of bases can be applied, it is preferred to use sodium carbonate for the present invention. Preferably,

well known paper making techniques are used to foliate a mixture of fibers and binders. It is also possible to use a so-called wet or dry method for manufacturing nonwoven fabric or a method for manufacturing nonwoven fabric using water jet streams. The invention will be described more in detail.

5 Examples 1 - 5

Coniferous pulp for paper making (NBKP) and carboxymethyl cellulose and/or salt thereof were mixed together and dispersed in city water followed by adding a necessary quantity of sodium carbonate to the water dispersion for preparation of a paper making stuff. After the stuff had been settled for a time, it was subjected to a small-sized paper machine used exclusively for testing to obtain a wet paper sheet which was then dried at a temperature of 110°C for 90 seconds using a dryer of rotary drum type to obtain a dried sheet having a basis weight of 40g/m². Then, the dried sheet was sprayed and impregnated with aqueous solution of propylene glycol/calcium chloride/deionized water mixed together at a ratio of 30/0.5/69.5 (by weight) so as to obtain a quantity corresponding to 2.5 times a weight of the dried sheets. The impregnated sheet was settled for 24 hours at a temperature of 20°C to obtain a wet wipe. Water-dispersibility and wet tensile strength of the wet wipe were tested under measuring conditions which will be described below. Test results for evaluating wet wipe examples prepared in accordance with the present invention (Example) and wet wipes for control (Control) are summarized in Table 1. Relationships between a series of Examples and a series of Controls are as follows:

20 (1) Example 1 and Control 1

The test results of Example 1 and Control 1 show effects of sodium carbonate (% by weight) added to carboxymethyl cellulose and/or salt thereof as measured in a dried state during a paper making process.

25 (2) Example 2 and Control 2

The test results of Example 2 and Control 2 show effects of a degree of substitution (D.S.) as well as pH of carboxymethyl cellulose and/or salt thereof.

30 (3) Example 3 and Control 3

The test results of Example 3 and Control 3 show effects of a total quantity (% by weight) of pulp and carboxymethyl cellulose and/or salt thereof.

35 (4) Example 4 and Control 4

The test results of Example 4 and Control 4 show effects of a period for which a water dispersion of pulp and carboxymethyl cellulose and/or salt thereof should be settled after an addition of sodium carbonate during a paper making process.

40 (5) Example 5 and Control 5

The test results of Example 5 and Control 5 show effects of a mixture ratio of pulp and carboxymethyl cellulose and/or salt thereof.

45 Evaluation of water-dispersion

A 10cm X 10cm sample sheet of wet wipe was immersed in 300ml of deionized water contained in a 300ml glass beaker followed by stirring by means of a magnetic stirrer (at 800rpm) and an extent of dispersion of the sample was observed. Observation results were classified as follows:

A: A sample sheet was disintegrated within 100 seconds.

B: A sample sheet was disintegrated within 200 seconds.

C: A sample sheet was not disintegrated within 200 seconds.

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55 Evaluation of wet tensile strength

A sample sheet of wet wipe of 25mm wide and 150mm long was elongated at a chucking distance of 100mm and at an elongation rate of 100mm/min to get tensile strength. It was found that tensile strength of a wet wipe of at least 300g

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is sufficient for its practical use.

Results of the evaluations for Examples and Controls are shown by TABLE 1. From the results it is concluded that:

(1) carboxymethyl cellulose and/or salt thereof should present D.S. = 0.30 - 0.60 and pH $\approx$ 5.0 (Example 2); (2) a quantity of sodium carbonate should correspond to 10 - 400% by weight of carboxymethyl cellulose and/or salt thereof (Example 1); (3) a weight ratio of pulp : carboxymethyl cellulose and/or salt thereof should range from 98 : 2 to 55 : 45; (4) concentration of pulp and carboxymethyl cellulose and/or salt thereof in a paper making stuff should range from 0.5 to 5% by weight; and (5) a settling period after addition of sodium carbonate should be 30 minutes or longer.

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[TABLE 1]

Test No.	Mix. ratio pulp/CMC	CMC		Pulp/CMC Concentration in stuff (%)	Quantity of Na ₂ CO ₃ (% by weight of CMC)	Settling period for stuff (s)	Result of evaluation		Remarks
		D.S.	pH				Water - dispersion	Tensile strength (g/25mm width)	
Ex.1 (1)	87.5/12.5	0.43	6.1	1	80	2	B	486	
Ex.1 (2)	87.5/12.5	0.43	6.1	1	180	2	A	704	
Ex.1 (3)	87.5/12.5	0.43	6.1	1	400	2	B	737	
Control 1 (1)	87.5/12.5	0.43	6.1	1	2	2	C	448	
Control 1 (2)	87.5/12.5	0.43	6.1	1	0	2	C	326	
Ex.2 (1)	87.5/12.5	0.58	6.0	1	80	2	A	517	
Control 2 (1)	87.5/12.5	0.43	4.7	1	80	2	B	195	
Control 2 (2)	87.5/12.5	0.88	6.9	1	80	2	A	253	
Ex.3 (1)	87.5/12.5	0.43	6.1	3	180	2	A	589	
Control 3 (1)	87.5/12.5	0.43	6.1	0.04	180	2	A	271	
Control 3 (2)	87.5/12.5	0.43	6.1	10	180	2	-	-	Impossible to foliate
Ex.4 (1)	87.5/12.5	0.43	6.1	2	180	1	B	486	
Control 4 (1)	87.5/12.5	0.43	6.1	2	180	0.15	C	428	
Ex.5 (1)	95/5	0.43	6.1	2	80	2	A	320	
Control 5 (1)	98.5/0.5	0.43	6.1	2	80	2	A	63	
Control 5 (2)	60/40	0.43	6.1	2	80	2	-	-	Inseparable from dryer

(Note) CMC : carboxymethyl cellulose and/or salt thereof

Examples 6 - 7

Coniferous pulp for paper making (NBKP) and carboxymethyl cellulose and/or salt thereof were mixed together and

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dispersed in city water to obtain a paper making stuff which was foliated by a small-sized paper machine used exclusively for testing. A wet sheet thus obtained was sprayed and impregnated with a quantity of aqueous solution of sodium carbonate corresponding to 2.4 - 8% by weight of carboxymethyl cellulose and/or salt thereof wherein said quantity of aqueous solution corresponded to 2.5 times a weight of the sheet as measured in its dry condition. Then, the sheet was dried at a temperature of 110°C for 90 seconds using a rotary drum type dryer and thereby a dried sheet having a basis weight of 40g/m² was obtained. The dried sheet was sprayed and impregnated with aqueous liquid consisting of propylene glycol/calcium chloride/deionized water mixed together at a ratio of 30/0.5/89.5 (by weight). The impregnated sheet was settled for 24 hours at a temperature of 20°C to obtain a wet wipe. Extent of water-dispersion as well as wet tensile strength of the wet wipe were evaluated under the same condition as Examples 1 - 5. Relationships between Examples and Controls are as follows:

(1) Example 6 and Control 6

The test results of Example 6 and Control 6 show effects of a quantity of sodium carbonate (% by weight) added to carboxymethyl cellulose and/or salt thereof as measured in a dried state during a paper making process.

(2) Example 7 and Control 7

The test results of Example 7 and Control 7 show effects of degree of substitution (D.S.) as well as pH of carboxymethyl cellulose and/or salt thereof.

Result of the evaluations for the respective Examples and Controls are shown by TABLE 2.

(TABLE 2)

Test No.	Mix. ratio pulp/ CMC	CMC		Quantity of Na ₂ CO ₃ (% by weight of CMC)	Result of evaluation	
		D.S.	pH		Water-dispersion	Tensile strength (g/25mm width)
EX.1 (1)	87.5/12.5	* 0.50	7.9	2.4	A	475
Ex.1 (2)	87.5/12.5	* 0.50	7.3	4.0	A	418
Ex.1 (3)	87.5/12.5	* 0.50	7.3	8.0	A	380
Control 1 (1)	87.5/12.5	* 0.50	7.3	0.0	C	438
Ex.2 (1)	87.5/12.5	* 0.43	8.1	8.0	A	401
Ex.2 (2)	87.5/12.5	* 0.50	7.3	8.0	A	380
Control 2 (1)	87.5/12.5	* * 0.64	3.9	8.0	A	133
Control 2 (2)	87.5/12.5	* 0.88	8.9	8.0	A	83
(Note) 1. CMC : carboxymethyl cellulose and/or salt thereof 2. * : sodium carboxymethyl cellulose 3. * * : acid type carboxymethyl cellulose						

Effect of the invention

According to the process of the present invention, water-dispersible fibers are mixed with binders comprising carboxymethyl cellulose and/or salt thereof having low swelling tendency or water-insolubility so that a large quantity of binders can be deposited on a sheet obtained from the mixture of the fibers and the binders. Such binders are denaturalized by addition of a base to water-swelling or water-soluble ones. These binders contribute to improvement of tensile strength of the sheet. And the sheet is thrown away into a large quantity of water after use, the binders can be rapidly dissolved in the water, allowing the sheet to be rapidly disintegrated and dispersed in the water.

Claims

1. A process for manufacturing a water-disintegrable sheet from carboxymethyl cellulose and/or salt thereof and water-dispersible fibers, said process being characterized in that:

a mixture of water-swelling or water-insoluble carboxymethyl cellulose and/or salt thereof having a degree of substitution = 0.30 - 0.60 and pH $\approx$ 5.0 and water-dispersible fibers is subjected to a foliating step to obtain said water-disintegrable sheet and, before or after said foliating step of the process, said mixture is added with a base.

2. The process according to Claim 1, wherein said base is sodium carbonate.

3. The process according to Claim 1 or 2, further comprising a step of impregnating said water-disintegrable sheet with an aqueous solution to obtain a wet wipe from said sheet.

4. The process for manufacturing a water-disintegrable sheet from carboxymethyl cellulose and/or salt thereof, said process being characterized by that:

a mixture of water-swelling or water-insoluble carboxymethyl cellulose and/or salt thereof having a degree of substitution = 0.3 - 0.60 and pH $\approx$ 5.0, water-dispersible fibers and a base is foliated to obtain said water-disintegrable sheet.

5. The process according to Claim 4, wherein said base is sodium carbonate.

6. The process according to Claim 4 or 5, further comprising a step of impregnating said water-disintegrable sheet with an aqueous solution to obtain a wet wipe from said sheet.

7. The process for making a water-disintegrable sheet from carboxymethyl cellulose and/or salt thereof and water-dispersible fibers, said process being characterized in that:

a sheet foliated from a mixture of water-swelling or water-insoluble carboxymethyl cellulose and/or salt thereof having a degree of substitution = 0.30 - 0.60 and pH $\approx$ 5.0 and water-dispersible fibers is added with a base to obtain said water-disintegrable sheet.

8. The process according to Claim 7, wherein said base is sodium carbonate.

9. The process according to Claim 7 or 8, further comprising a step of impregnating said water-disintegrable sheet with an aqueous solution to obtain a wet wipe from said sheet.



US005830317A

United States Patent [19]
Vinson et al.

[11] **Patent Number:** **5,830,317**
[45] **Date of Patent:** ***Nov. 3, 1998**

- [54] **SOFT TISSUE PAPER WITH BIASED SURFACE PROPERTIES CONTAINING FINE PARTICULATE FILLERS**
- [75] **Inventors:** Kenneth Douglas Vinson, Cincinnati, Ohio; Jonathan Andrew Ficke, Lawrenceburg, Ind.; Bart Steven Hersko, Cincinnati, Ohio
- [73] **Assignee:** The Procter & Gamble Company, Cincinnati, Ohio
- [*] **Notice:** The term of this patent shall not extend beyond the expiration date of Pat. No. 5,611,890.

- [21] **Appl. No.:** 771,062
[22] **Filed:** Dec. 20, 1996

Related U.S. Application Data

- [63] **Continuation-in-part of Ser. No. 418,990, Apr. 7, 1995, Pat. No. 5,611,890, and Ser. No. 553,167, Nov. 7, 1995, abandoned.**
- [51] **Int. Cl.⁴** D21H 15/04
- [52] **U.S. Cl.** 162/125; 162/109; 162/112; 162/113; 162/127; 162/128; 162/129; 162/130; 162/158; 162/164.1; 162/168.1; 162/175; 162/181.1; 162/183
- [58] **Field of Search** 162/111, 112, 162/113, 109, 127, 129, 130, 128, 181.1, 183, 158, 123, 125, 164.1, 168.1, 175

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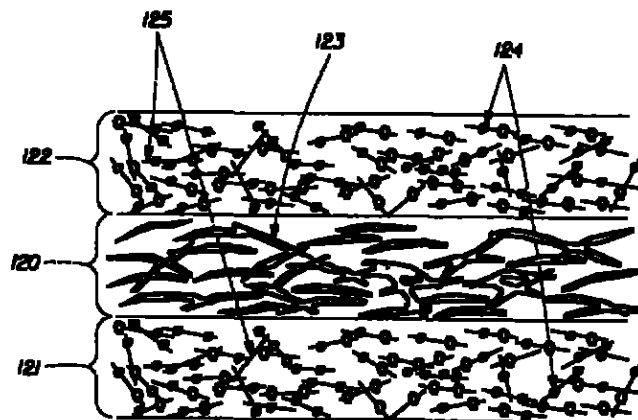
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Attorney, Agent, or Firm—Edward J. Milbrada; Bart S. Hersko; E. Kelly Linman

- [57] **ABSTRACT**

Soft, strong, and low dusting tissue paper webs useful in the manufacture of soft, absorbent sanitary products such as bath tissue, facial tissue, and absorbent towels are disclosed. The tissue papers comprise fibers such as wood pulp and a non-cellulosic, water insoluble particulate filler such as kaolin clay and possess biased surface properties.

18 Claims, 5 Drawing Sheets



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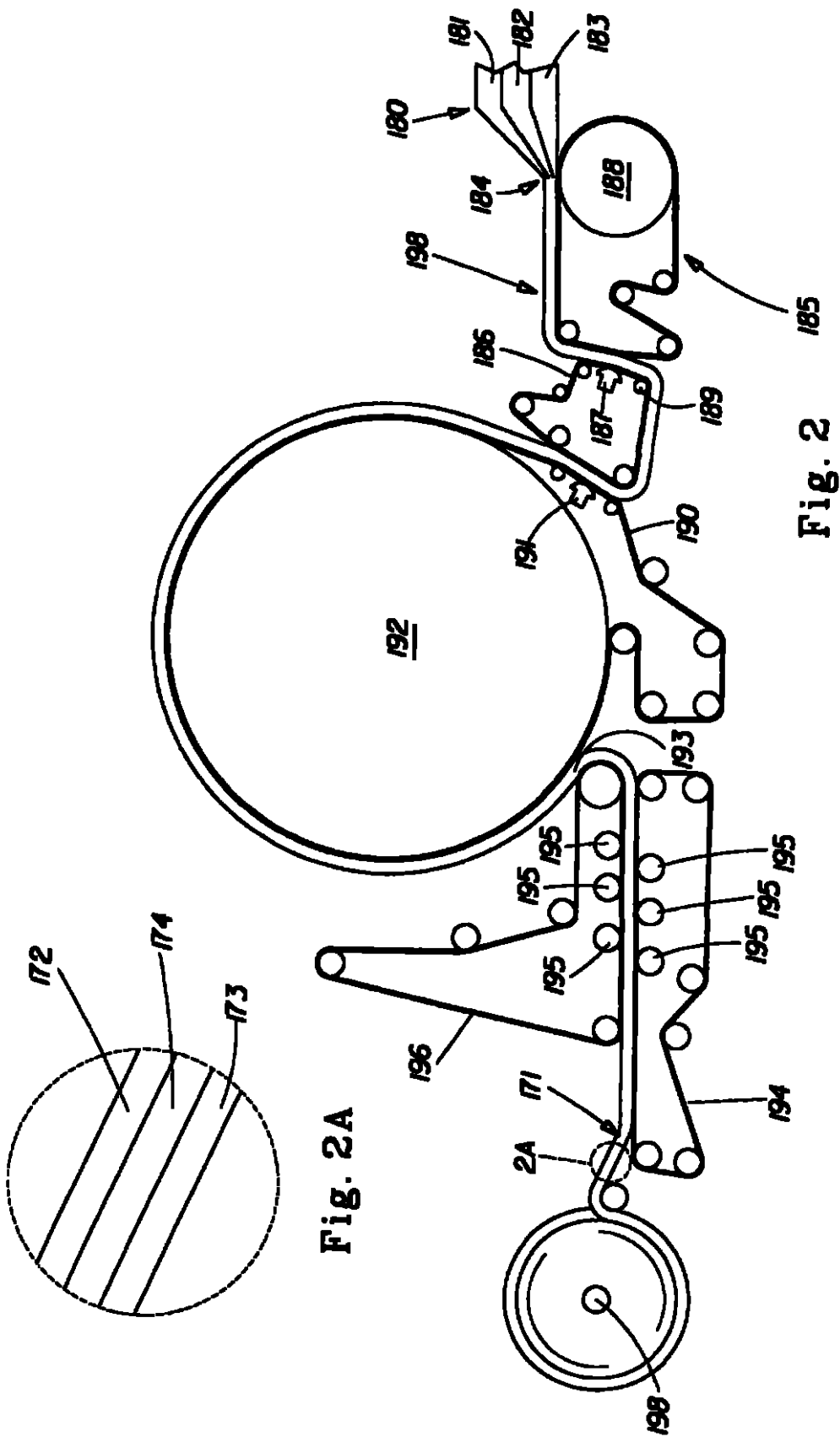
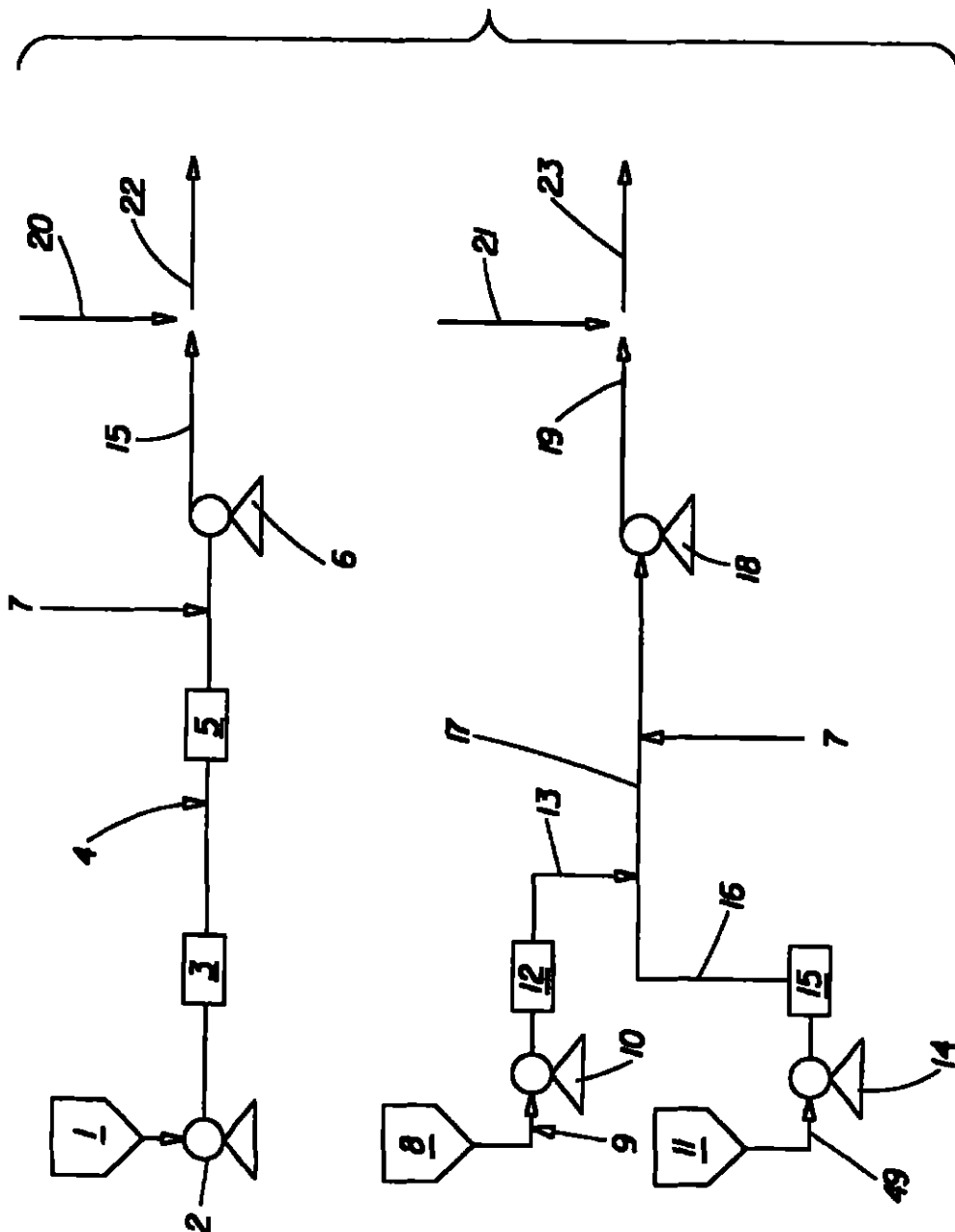


Fig. 2A

Fig. 2

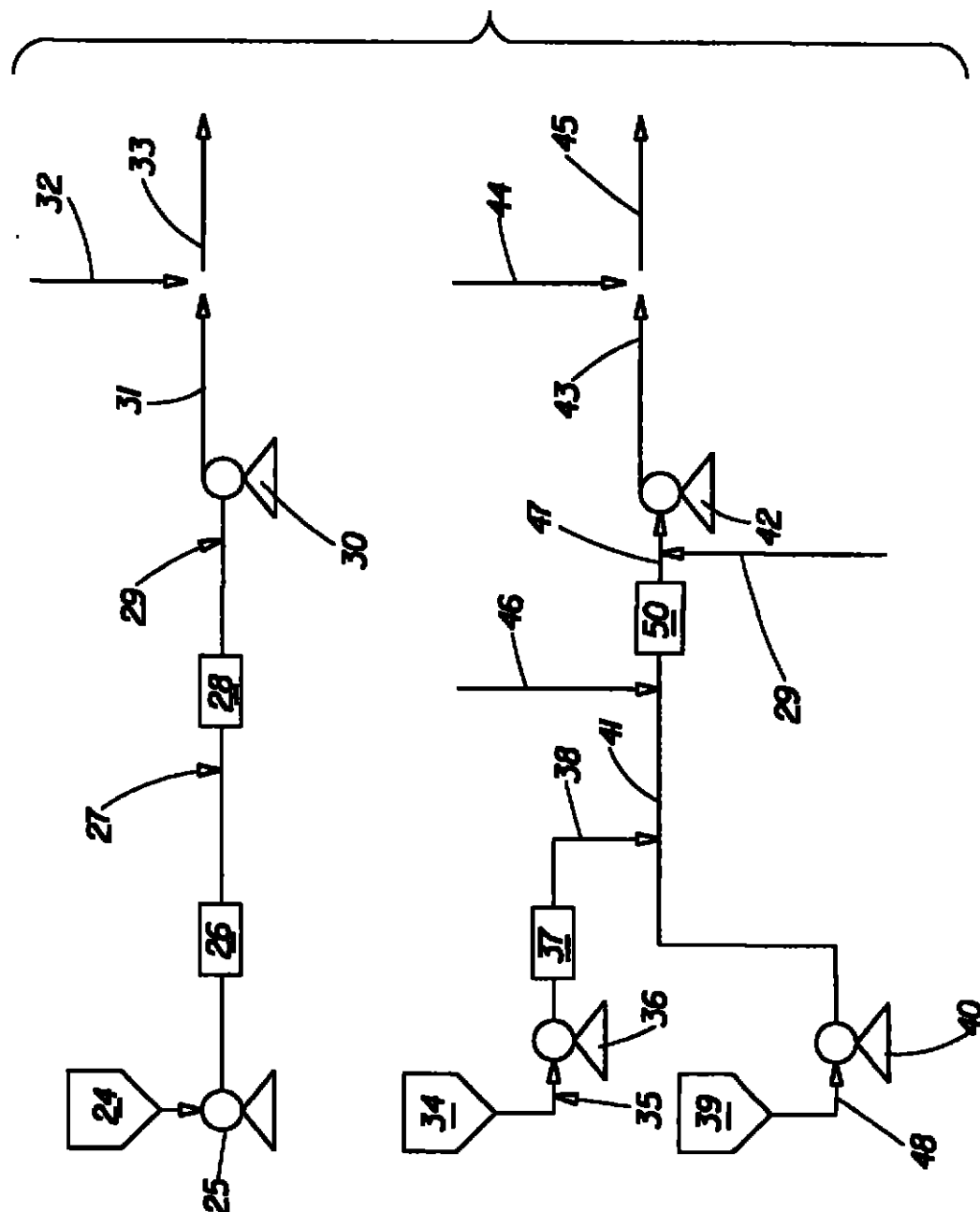
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Fig. 3



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Fig. 4



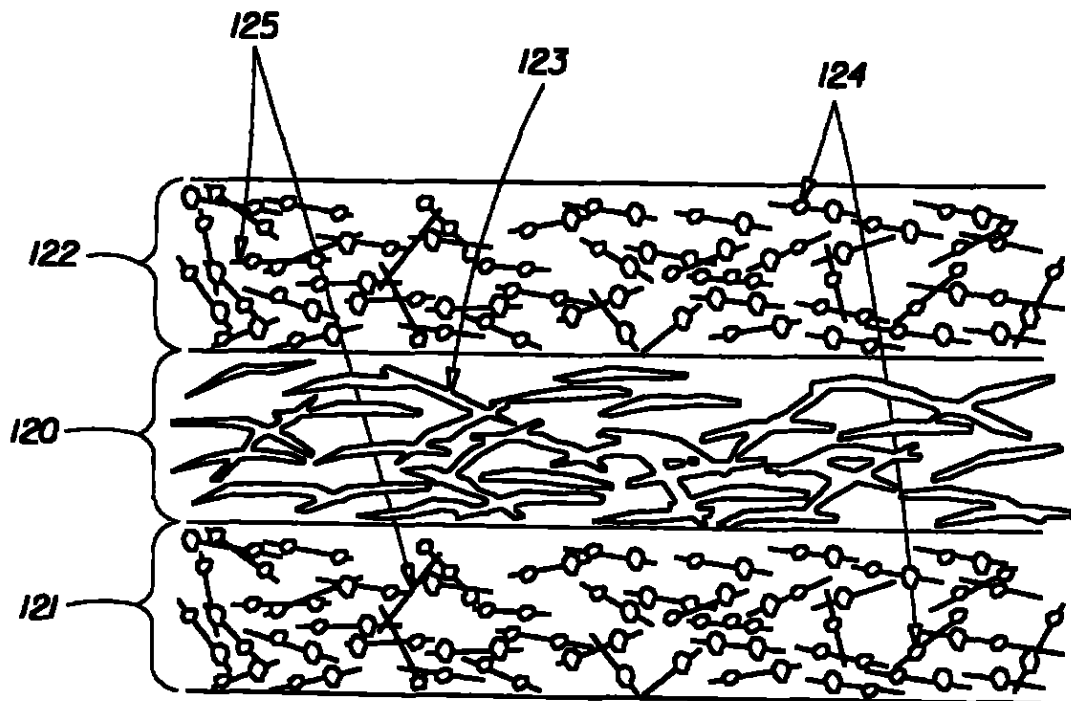


Fig. 5

SOFT TISSUE PAPER WITH BIASED SURFACE PROPERTIES CONTAINING FINE PARTICULATE FILLERS

This application is a continuation-in-part of application Ser. No. 08/418,990, filed Apr. 7, 1995, now U.S. Pat. No. 5,611,890 and application Ser. No. 08/553,167, filed Nov. 7, 1995 now abandoned.

TECHNICAL FIELD

This invention relates, in general, to tissue paper products and processes. More specifically, it relates to tissue paper products made from cellulose pulps and non-cellulosic water insoluble particulate fillers.

BACKGROUND OF THE INVENTION

Sanitary paper tissue products are widely used. Such items are commercially offered in formats tailored for a variety of uses such as facial tissues, toilet tissues and absorbent towels. The formats, i.e. basis weight, thickness, strength, sheet size, dispensing medium, etc. of these products often differ widely. Predominantly, they share in common the process by which they originate, the so-called creped papermaking process. However, it is possible to alternatively produce such products without creping, and tissue paper webs made by such processes are within the scope of the present invention.

Creping is a means of mechanically compacting paper in the machine direction. The result is an increase in basis weight (mass per unit area) as well as dramatic changes in many physical properties, particularly when measured in the machine direction. Creping is generally accomplished with a flexible blade, a so-called doctor blade, against a Yankee dryer in an on machine operation.

A Yankee dryer is a large diameter, generally 8-20 foot drum which is designed to be pressurized with steam to provide a hot surface for completing the drying of papermaking webs at the end of the papermaking process. The paper web which is first formed on a foraminous forming carrier, such as a Fourdrinier wire, where it is freed of the copious water needed to disperse the fibrous slurry is generally transferred to a felt or fabric in a so-called press section where de-watering is continued either by mechanically compacting the paper or by some other de-watering method such as through-drying with hot air, before finally being transferred in the semi-dry condition to the surface of the Yankee for the drying to be completed.

To produce comparable tissue paper webs without creping, an embryonic web is transferred from the foraminous forming carrier upon which it is laid, to a slower moving, high fiber support transfer fabric carrier. The web is then transferred to a drying fabric upon which it is dried to a final dryness. Such webs can offer some advantages in surface smoothness compared to creped paper webs.

The techniques to produce uncreped tissue in this manner are taught in the prior art. For example, Wendi, et. al. in European Patent Application 0 677 612A2, published Oct. 18, 1995 and incorporated herein by reference, teach a method of making soft tissue products without creping. In another case, Hyland, et. al. in European Patent Application 0 617 164 A1, published Sep. 28, 1994 and incorporated herein by reference, teach a method of making smooth uncreped throughdried sheets.

Tissue paper products are linked by common consumer demand for a generally conflicting set of physical properties:

a pleasing tactile impression, i.e. softness while, at the same time having a high strength and a resistance to linting and dusting.

Softness is the tactile sensation perceived by the consumer as he/she holds a particular product, rubs it across his/her skin, or crumples it within his/her hand. This tactile sensation is provided by a combination of several physical properties. One of the most important physical properties related to softness is generally considered by those skilled in the art to be the stiffness of the paper web from which the product is made. Stiffness, in turn, is usually considered to be directly dependent on the strength of the web.

Strength is the ability of the product, and its constituent webs, to maintain physical integrity and to resist tearing, bursting, and shredding under use conditions.

Linting and dusting refers to the tendency of a web its release unbound or loosely bound fibers or particulate fillers during handling or use.

Tissue papers are generally comprised essentially of papermaking fibers. Small amounts of chemical functional agents such as wet strength or dry strength binders, retention aids, surfactants, size, chemical softeners, crepe facilitating compositions are frequently included but these are typically only used in minor amounts. The papermaking fibers most frequently used in tissue papers are virgin chemical wood pulps.

As the world's supply of natural resources comes under increasing economic and environmental scrutiny, pressure is mounting to reduce consumption of forest products such as virgin chemical wood pulps in products such as sanitary tissues. One way to extend the supply of wood pulp without sacrificing product mass is to replace virgin chemical pulp fibers with high yield fibers such as mechanical or chemi-mechanical pulps or to use fibers which have been recycled. Unfortunately, comparatively severe deterioration in performance usually accompanies such changes. Such fibers are prone to have a high coarseness and this contributes to the loss of the velvety feel which is imparted by prime fibers selected because of their slaccidness. In the case of the mechanical or chemi-mechanical liberated fiber, high coarseness is due to the retention of the non-cellulosic components of the original wood substance, such components including lignin and so-called hemicelluloses. This makes each fiber weigh more without increasing its length. Recycled paper can also tend to have a high mechanical pulp content, but, even when all due care is exercised in selecting the wastepaper grade to minimize this, a high coarseness still often occurs. This is thought to be due to the impure mixture of fiber morphologies which naturally occurs when paper from many sources is blended to make a recycled pulp. For example, a certain wastepaper might be selected because it is primarily North American hardwood in nature; however, one will often find extensive contamination from coarser softwood fibers, even of the most deleterious species such as variations of Southern U.S. pine. U.S. Pat. No. 4,300,981, Carstens, issued Nov. 17, 1981, and incorporated herein by reference, explains the textural and surface qualities which are imparted by prime fibers. U.S. Pat. No. 5,228,954, Vinson, issued Jul. 20, 1993, and U.S. Pat. No. 5,405,499, Vinson, to issue Apr. 11, 1995, both incorporated herein by reference, disclose methods for upgrading such fiber sources so that they have less deleterious effects, but still the level of replacement is limited and the new fiber sources themselves are in limited supply and this often limits their use.

Another method of limiting the use of wood pulp in sanitary tissue paper is to replace part of it with a lower cost,

readily available filling material such as kaolin clay or calcium carbonate. While those skilled in the art will recognize that this practice has been common in some parts of the paper industry for many years, they will also appreciate that extending this approach to sanitary tissue products has involved particular difficulties which have prevented it from being practiced up to now.

One major restriction is the retention of the filling agent during the papermaking process. Among paper products, sanitary tissues are at an extreme of low basis weight. The basis weight of a tissue web as it is wound on a reel from a Yankee machine is typically only about 15 g/m² and because of foreshortening the dry fiber basis weight in the forming section of the machine is actually lower than the finished dry basis weight by from about 10% to about 20% or more. To compound the difficulties in retention caused by the low basis weight, tissue webs occupy an extreme of low density, often having an apparent density as wound on the reel of only about 0.1 g/cm³ or less. While it is recognized that some of this loft can be introduced at the creping blade, those skilled in the art will recognize that tissue webs are generally formed from relatively free stock which means that the fibers of which they are comprised are not rendered flaccid from heating. Tissue machines are required to operate at very high speeds to be practical; thus free stock is needed to prevent excessive forming pressures and drying load. The relatively stiff fibers comprising the free stock retain their ability to prop open the embryonic web as it is forming. Those skilled in the art will at once recognize that such light weight, low density structures do not afford any significant opportunity to filter fine particulates as the web is forming. Filler particles not substantively affixed to fiber surfaces will be torn away by the torrent of the high speed approach flow systems, hurled into the liquid phase, and driven through the embryonic web into the water drained from the forming web. Only with repeated recycling of the water used to form the web does the concentration of particulate build to a point where the filler begins to exit with the paper. Such concentrations of solids in water effluent are impractical.

A second major limitation is the general failure of particulate fillers to naturally bond to papermaking fibers in the fashion that papermaking fibers tend to bond to each other as the formed web is dried. This reduces the strength of the product. Filler inclusion causes a reduction in strength, which if left uncorrected, severely limits products which are already quite weak. Steps required to restore strength such as increased fiber heating or the use of chemical strengthening agents is often restricted as well.

The deleterious effects of filler on sheet integrity also often cause hygiene problems by plugging press felts or by transferring poorly from the press section to the Yankee dryer.

Finally, tissue products containing fillers are prone to lint or dust. This is not only because the fillers themselves can be poorly trapped within the web, but also because they have the before mentioned bond inhibiting effect which causes a localized weakening of fiber anchoring into the structure. This tendency can cause operational difficulties papermaking processes and in subsequent converting operations, because of excessive dust created when the paper is handled. Another consideration is that the users of the sanitary tissue products made from the filled tissue demand that they be relatively free of lint and dust. Attempts to overcome this tendency to lint or dust by using chemical binders or mechanical refining invariably cause the tissue product to become harsh.

Consequently, the use of fillers in tissue papers has been severely limited. U.S. Pat. No. 2,216,143, issued to Thiele on Oct. 1, 1940, and incorporated herein by reference discusses the limitations of fillers on Yankee machines and discloses a method of incorporation which overcomes those limitations. Unfortunately, the method requires a cumbersome unit operation to coat a layer of adhesively bound particles onto the felt side of the sheet while it is in contact with the Yankee dryer. This operation is not practical for modern high speed Yankee machines and, those skilled in the art will recognize that the Thiele method would produce a coated rather than filled tissue product. A "filled tissue paper" is distinguished from "coated tissue paper" essentially by the methods practiced to produce them, i.e. a "filled tissue paper" is one which has the particulate matter added to the fibers prior to their assembly into a web while a "coated tissue paper" is one which has the particulate matter added after the web has been essentially assembled. As a result of this difference, a filled tissue paper product can be described as a relatively lightweight, low density tissue paper which contains a filler dispersed throughout the thickness of at least one layer of a multi-layer tissue paper, or throughout the entire thickness of a single-layered tissue paper. The term "dispersed throughout" means that essentially all portions of a particular layer of a filled tissue product contain filler particles, but, it specifically does not imply that such dispersion necessarily be uniform in that layer. In fact, certain advantages can be anticipated by achieving a difference in filler concentration as a function of thickness in a filled layer of tissue.

Finally, applicants have found that the corrective actions required to overcome the before mentioned retention and strength limitations can cause a reduction in softness.

Therefore, it is the object of the present invention to provide for a tissue paper comprising a fine particulate filler which overcomes the before mentioned limitations of the prior art. Specifically, the tissue paper of the present invention comprises a filler and is soft while maintaining a high level of tensile strength and a low level of lint and dust.

This and other objects are obtained using the present invention as will be taught in the following disclosure.

SUMMARY OF THE INVENTION

The invention is a strong, soft filled tissue paper, low in lint and dust, and having biased surface bonding characteristics. The filled tissue paper with biased surface bonding comprises papermaking fibers and a noncellulosic particulate filler, said filler preferably comprising from about 5% to about 50% by weight of said tissue. The surface properties of the tissue product are biased to a degree that the lint ratio is less than about 0.8, and more preferably less than about 0.6. Unexpected combinations of softness, strength, and resistance to dusting have been obtained via biased surface properties in tissue papers filled with these levels of particulate fillers.

In its preferred embodiment, the filled tissue paper of the present invention has a basis weight between about 10 g/m² and about 50 g/m² and, more preferably, between about 10 g/m² and about 30 g/m². It has a density between about 0.03 g/cm³ and about 0.6 g/cm³ and, more preferably, between about 0.05 g/cm³ and 0.2 g/cm³.

The preferred embodiment further comprises papermaking fibers of both hardwood and softwood types wherein at least about 50% of the papermaking fibers are hardwood and at least about 10% are softwood. The hardwood and softwood fibers are most preferably isolated by providing sepa-

rate layers wherein the fraction of softwood fibers relative to hardwood fibers differ by different layers. Preferably, the tissue comprises an inner layer and two outer layers wherein the inner layer fiber content is predominantly softwood and the outer layer fiber content is predominately hardwood.

The preferred tissue paper of the present invention is pattern densified such that zones of relatively high density are dispersed within a high bulk field, including pattern densified tissue wherein zones of relatively high density are continuous and the high bulk field is discrete. Most preferably, the tissue paper is through air dried.

The invention provides for a tissue paper comprising papermaking fibers and a particulate filler. In its preferred embodiment, the particulate filler is selected from the group consisting of clay, calcium carbonate, titanium dioxide, talc, aluminum silicate, calcium silicate, alumina trihydrate, activated carbon, pearl starch, calcium sulfate, glass microspheres, diatomaceous earth, and mixtures thereof. When selecting a filler from the above group several factors need to be evaluated. These include cost, availability, ease of retaining into the tissue paper, color, scattering potential, refractive index, and chemical compatibility with the selected papermaking environment.

Preferably the fillers are inorganic materials such as clay and calcium carbonate. A particularly suitable filler is kaolin clay. Most preferably the so called "hydrous aluminum silicate" form of kaolin clay is preferred as contrasted to the kaolins which are further processed by calcining.

The morphology of kaolin is naturally platy or blocky, but it is preferable to use clays which have not been subjected to mechanical delamination treatments as this tends to reduce the mean particle size. It is common to refer to the mean particle size in terms of equivalent spherical diameter. An average equivalent spherical diameter greater than about 0.2 micron, more preferably greater than about 0.5 micron is preferred in the practice of the present invention. Most preferably, an equivalent spherical diameter greater than about 1.0 micron is preferred.

The preferred embodiment of the present invention employs a bond inhibiting agent. Preferred bond inhibiting agents comprise the well known dialkyldimethylammonium salts such as ditallowdimethylammonium chloride, ditallowdimethylammonium methyl sulfate, di(hydrogenated) tallow dimethyl ammonium chloride; with di(hydrogenated) tallow dimethyl ammonium methyl sulfate being particularly preferred. In its most preferred form, the present invention employs the bond inhibiting agent preferentially biased toward the fabric-side surface.

Tissue paper webs are characterized by having often widely disparate properties from one surface to the other. If the tissue web is made on a Yankee machine, the differences are believed to primarily be an artifact of having one of the surfaces adhesively secured to the relatively smooth Yankee surface, while the other surface, so-called herein the "fabric-side" surface, is pressed or deflected into a felt or a fabric. In an analogous fashion, an uncreped tissue by nature of having one of its surfaces being deflected when it is transferred from its foraminous forming carrier upon which it is laid to a slower moving high fiber support transfer fabric carrier, will have one relatively textured surface, also referred to as a "fabric-side" surface, compared to the other surface.

All percentages, ratios and proportions herein are by weight unless otherwise specified.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation illustrating a creped papermaking process of the present invention for producing

a strong, soft, and low lint creped tissue paper comprising papermaking fibers and particulate fillers.

FIG. 2 is a schematic representation illustrating an uncreped papermaking process of the present invention for producing a strong, soft, and low lint uncreped tissue paper comprising papermaking fibers and particulate fillers.

FIG. 2A is an illustration revealing the layered structure of the tissue paper webs prepared by the uncreped papermaking process of FIG. 2.

FIG. 3 is a schematic representation illustrating the steps for preparing the aqueous papermaking furnish for the papermaking process, according to one embodiment of the present invention based on cationic flocculant.

FIG. 4 is a schematic representation illustrating the steps for preparing the aqueous papermaking furnish for the papermaking process, according to another embodiment of the present invention based on anionic flocculant.

FIG. 5 is a cross-sectional view illustrating a three-layered single-ply tissue paper according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

While this specification concludes with claims particularly pointing out and distinctly claiming the subject matter regarded as the invention, it is believed that the invention can be better understood from a reading of the following detailed description and of the appended examples.

As used herein, the term "comprising" means that the various components, ingredients, or steps, can be conjointly employed in practicing the present invention. Accordingly, the term "comprising" encompasses the more restrictive terms "consisting essentially of" and "consisting of."

As used herein, the term "predominantly" means more than one-half by weight.

As used herein, the term "water soluble" refers to materials that are soluble in water to at least 3%, by weight, at 25° C.

As used herein, the terms "tissue paper web, paper web, web, paper sheet and paper product" all refer to sheets of paper made by a process comprising the steps of forming an aqueous papermaking furnish, depositing this furnish on a foraminous surface, such as a Fourdrinier wire, and removing the water from the furnish as by gravity or vacuum-assisted drainage, with or without pressing, and by evaporation. In one embodiment of the present invention the process comprises the final steps of adhering the sheet in a semi-dry condition to the surface of a Yankee dryer, completing the water removal by evaporation to an essentially dry state, removal of the web from the Yankee dryer by means of a flexible creping blade, and winding the resultant sheet onto a reel. In another embodiment of the present invention, the embryonic web formed when the furnish is deposited on a foraminous surface is transferred from the foraminous forming carrier upon which it is laid, to a slower moving, high fiber support transfer fabric carrier. The web is then transferred to a drying fabric upon which it is dried to a final dryness.

As used herein, the term "filled tissue paper" means a paper product that can be described as a relatively lightweight, low density tissue paper which contains a filler dispersed throughout the thickness of at least one layer of a multi-layer tissue paper. The term "dispersed throughout" means that essentially all portions of a particular layer of a filled tissue product contain filler particles, but, it specifically does not imply that such dispersion necessarily be

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uniform in that layer. In fact, certain advantages can be anticipated by achieving a difference in filler concentration as a function of thickness in a filled layer of tissue.

The terms "multi-layered tissue paper web, multi-layered paper web, multi-layered web, multi-layered paper sheet and multi-layered paper product" are all used interchangeably in the art to refer to sheets of paper prepared from two or more layers of aqueous paper making furnish which are preferably comprised of different fiber types, the fibers typically being relatively long softwood and relatively short hardwood fibers as used in tissue paper making. The layers are preferably formed from the deposition of separate streams of dilute fiber slurries upon one or more endless foraminous surfaces. If the individual layers are initially formed on separate foraminous surfaces, the layers can be subsequently combined when wet to form a multi-layered tissue paper web.

As used herein, the term "single-ply tissue product" means that it is comprised of one ply of tissue; the ply can be substantially homogeneous in nature or it can be a multi-layered tissue paper web. As used herein, the term "multi-ply tissue product" means that it is comprised of more than one ply of tissue. The plies of a multi-ply tissue product can be substantially homogeneous in nature or they can be multi-layered tissue paper webs.

The first step in the process of this invention is the forming of at least one "aqueous papermaking furnish", a term which, as used herein, refers to a suspension of papermaking fibers, usually comprised of wood pulp, and particulate fillers, along with the additives which are essential to provide the retention of the particulate filler and any other functional properties by optionally including modifying chemicals as described hereinafter. Some typical components of the papermaking furnish are described in the following section.

Ingredients of the Papermaking Furnish

The Papermaking Fibers

It is anticipated that wood pulp in all its varieties will normally comprise the papermaking fibers used in this invention. However, other cellulose fibrous pulps, such as cotton linters, bagasse, rayon, etc., can be used and none are disclaimed. Wood pulps useful herein include chemical pulps such as sulfite and sulfate (sometimes called Kraft) pulp as well as mechanical pulps including for example, ground wood, ThermoMechanical Pulp (TMP) and Chemi-ThermoMechanical Pulp (CTMP). Pulps derived from both deciduous and coniferous trees can be used.

Both hardwood pulps and softwood pulps as well as combinations of the two may be employed as papermaking fibers for the tissue paper of the present invention. The term "hardwood pulps" as used herein refers to fibrous pulp derived from the woody substance of deciduous trees (angiosperms), whereas "softwood pulps" are fibrous pulps derived from the woody substance of coniferous trees (gymnosperms). Blends of hardwood Kraft pulps, especially eucalyptus, and northern softwood Kraft (NSK) pulps are particularly suitable for making the tissue webs of the present invention.

A preferred embodiment of the present invention comprises layered tissue webs wherein, most preferably, hardwood pulps such as eucalyptus are used for outer layer(s) and wherein northern softwood Kraft (NSK) pulps are used for the inner layer(s). Also applicable to the present invention are fibers derived from recycled paper, which may contain any or all of the above categories of fibers.

The Particulate Filler

The invention provides for a tissue paper comprising papermaking fibers and a particulate filler. In its preferred embodiment, the particulate filler is selected from the group consisting of clay, calcium carbonate, titanium dioxide, talc, aluminum silicate, calcium silicate, alumina trihydrate, activated carbon, pearl starch, calcium sulfate, glass microspheres, diatomaceous earth, and mixtures thereof. When selecting a filler from the above group several factors need to be evaluated. These include cost, availability, ease of retaining into the tissue paper, color, scattering potential, refractive index, and chemical compatibility with the selected papermaking environment. Preferably the fillers are inorganic materials such as clay and calcium carbonate.

It has now been found that a particularly suitable particulate filler is kaolin clay. Kaolin clay is the common name for a class of naturally occurring aluminum silicate mineral beneficiated as a particulate.

With respect to terminology, it is noted that it is common in the industry, as well as in the prior art patent literature, when referring to kaolin products or processing, to use the term "hydrous" to refer to kaolin which has not been subject to calcination. Calcination subjects the clay to temperatures above 450° C., which temperatures serve to alter the basic crystal structure of kaolin. The so-called "hydrous" kaolins may have been produced from crude kaolins, which have been subjected to beneficiation, as, for example, to froth flotation, to magnetic separation, to mechanical delamination, grinding, or similar comminution, but not to the mentioned heating as would impair the crystal structure.

To be accurate in a technical sense, the description of these materials as "hydrous" is inappropriate. More specifically, there is no molecular water actually present in the kaolinite structure. Thus although the composition can be, and often is, arbitrarily written in the form $2H_2O \cdot Al_2O_3 \cdot 2SiO_2$, it has long been known that kaolinite is an aluminum hydroxide silicate of approximate composition $Al_2(OH)_4Si_2O_5$, which equates to the hydrated formula just cited. Once kaolin is subjected to calcination, which for the purposes of this specification refers to subjecting a kaolin to temperatures exceeding 450° C., for a period sufficient to eliminate the hydroxyl groups, the original crystalline structure of the kaolinite is destroyed. Therefore, although technically such calcined clays are no longer "kaolin", it is common in the industry to refer to these as calcined kaolin, and, for the purposes of this specification, the calcined materials are included when the class of materials "kaolin" is cited. Accordingly, the term "hydrous aluminum silicate" refers to natural kaolin, which has not been subjected to calcination.

Hydrous aluminum silicate is the kaolin form most preferred in the practice of the present invention. It is therefore characterized by the before mentioned approximate 13% by weight loss as water vapor at temperatures exceeding 450° C.

The morphology of kaolin is naturally platy or blocky, because it naturally occurs in the form of thin platelets which adhere together to form "stacks" or "flocs". The stacks separate to some degree into the individual platelets during processing, but it is preferable to use clays which have not been subjected to extensive mechanical delamination treatments as this tends to reduce the mean particle size. It is common to refer to the mean particle size in terms of equivalent spherical diameter. An average equivalent spherical diameter greater than about 0.2 micron, more preferably greater than about 0.5 micron is preferred in the practice of

the present invention. Most preferably, an equivalent spherical diameter greater than about 1.0 micron is preferred.

Most mined clay is subjected to wet processing. Aqueous suspending of the crude clay allows the coarse impurities to be removed by centrifugation and provides a media for chemical bleaching. A polyacrylate polymer or phosphate salt is sometimes added to such slurries to reduce viscosity and slow settling. Resultant clays are normally shipped without drying at about 70% solids suspensions, or they can be spray dried.

Treatments to the clay, such as air floating, froth flotation, washing, bleaching, spray drying, the addition of agents as slurry stabilizers and viscosity modifiers, are generally acceptable and should be selected based upon the specific commercial considerations at hand in a particular circumstance.

Each clay platelet is itself a multi-layered structure of aluminum polysilicates. A continuous array of oxygen atoms forms one face of each basic layer. The polysilicate sheet structure edges are united by these oxygen atoms. A continuous array of hydroxyl groups of joined octahedral alumina structures forms the other face forming a two-dimensional polyaluminum oxide structure. The oxygen atoms sharing the tetrahedral and octahedral structures bind the aluminum atoms to the silicon atoms.

Imperfections in the assembly are primarily responsible for the natural clay particles possessing an anionic charge in suspension. This happens because other di-, tri-, and tetra-valent cations substitute for aluminum. The consequence is that some of the oxygen atoms on the surface become anionic and become weakly dissociable hydroxyl groups.

Natural clay also has a cationic character capable of exchanging their anions for others that are preferred. This happens because aluminum atoms lacking a full complement of bonds occur at some frequency around the peripheral edge of the platelet. They must satisfy their remaining valencies by attracting anions from the aqueous suspension that they occupy. If these cationic sites are not satisfied with anions from solutions, the clay can satisfy its own charge balance by orienting itself edge to face assembling a "card house" structure which forms thick dispersions. Polyacrylate dispersants ion exchange with the cationic sites providing a repulsive character to the clay preventing these assemblies and simplifying the production, shipping, and use of the clay.

A kaolin grade WW fill slurry is a slurry kaolin marketed by Dry Branch Kaolin Company of Dry Branch, Ga. suitable to make tissue paper webs of the present invention.

Starch

In some aspects of the invention, it is useful to include starch as one of the ingredients of the papermaking furnish. A starch that has limited solubility in water in the presence of particulate fillers and fibers is particularly useful in certain aspects of the invention to be detailed later. A common means of achieving this is to use a so called "cationic starch".

As used herein the term "cationic starch" is defined as starch, as naturally derived, which has been further chemically modified to impart a cationic constituent moiety. Preferably the starch is derived from corn or potatoes, but can be derived from other sources such as rice, wheat, or tapioca. Starch from waxy maize also known industrially as amioca starch is particularly preferred. Amioca starch differs from common dent corn starch in that it is entirely amylopectin, whereas common corn starch contains both amylopectin and amylose. Various unique characteristics of

amioca starch are further described in "Amioca—The Starch from Waxy Corn", H. H. Schopmeyer, Food Industries, December 1945, pp. 106-108. The starch can be in granular form, pre-gelatinized granular form, or dispersed form. The dispersed form is preferred. If in granular pre-gelatinized form, it need only be dispersed in cold water prior to its use, with the only pre-caution being to use equipment which overcomes any tendency to gel-block in forming the dispersion. Suitable dispersers known as eductors are common in the industry. If the starch is in granular form and has not been pre-gelatinized, it is necessary to cook the starch to induce swelling of the granules. Preferably, such starch granules are swollen, as by cooking, to a point just prior to dispersion of the starch granule. Such highly swollen starch granules shall be referred to as being "fully cooked". The conditions for dispersion in general can vary depending upon the size of the starch granules, the degree of crystallinity of the granules, and the amount of amylose present. Fully cooked amioca starch, for example, can be prepared by heating an aqueous slurry of about 4% consistency of starch granules at about 190° F. (about 88° C.) for between about 30 and about 40 minutes.

Cationic starches can be divided into the following general classifications: (1) tertiary aminoalkyl ethers, (2) onium starch ethers including quaternary amines, phosphonium, and sulfonium derivatives, (3) primary and secondary aminoalkyl starches, and (4) miscellaneous (e.g., imino starches). New cationic products continue to be developed, but the tertiary aminoalkyl ethers and quaternary ammonium alkyl ethers are the main commercial types. Preferably, the cationic starch has a degree of substitution ranging from about 0.01 to about 0.1 cationic substituent per anhydroglucose units of starch; the substituents preferably chosen from the above mentioned types. Suitable starches are produced by National Starch and Chemical Company, (Bridgewater, N.J.) under the tradename, RediBOND®. Grades with cationic moieties only such as RediBOND 5320® and RediBOND 5327® are suitable, and grades with additional anionic functionality such as RediBOND 2(M5®) are also suitable.

While not wishing to be bound by theory, it is believed that the cationic starch which is initially dissolved in water, becomes insoluble in the presence of filler because of its attraction for the anionic sites on the filler surface. This causes the filler to be covered with the bushy starch molecules which provide an attractive surface for more filler particles, ultimately resulting in agglomeration of the filler. The essential element of this step is believed to be the size and shape of the starch molecule rather than the charge characteristics of the starch. For example, inferior results would be expected by substituting a charge biasing species such as synthetic linear polyelectrolyte for the cationic starch.

In one embodiment of the present invention, cationic starch is preferably added to the particulate filler. In this case, the amount of cationic starch added is from about 0.1% to about 2%, but most preferably from about 0.25% to about 0.75%, by weight based on the weight of the particulate filler. In this aspect of the invention, it is preferable to use a cationic flocculant as a retention aid.

In another embodiment of the present invention, it is preferred to add cationic starch to an entire aqueous papermaking furnish, preferably at a point before the final dilution at the fan pump. This aspect of the invention makes use of an anionic flocculant as a retention aid. In this aspect of the invention, it is preferable to add cationic starch at a rate from about five to about twenty times the rate of the anionic flocculant.

The cationic and anionic flocculants mentioned in the above are described in detail in the following sections.

Retention Aids

A number of materials are marketed as so-called "retention aids", a term as used herein, referring to additives used to increase the retention of the fine furnish solids in the web during the papermaking process. Without adequate retention of the fine solids, they are either lost to the process effluent or accumulate to excessively high concentrations in the recirculating white water loop and cause production difficulties including deposit build-up and impaired drainage. Chapter 17 entitled "Retention Chemistry" of "Pulp and Paper, Chemistry and Chemical Technology", 3rd ed. Vol. 3, by J. E. Unbehend and K. W. Britt, A Wiley Interscience Publication, incorporated herein by reference, provides the essential understanding of the types and mechanisms by which polymeric retention aids function. A flocculant agglomerates suspended particles generally by a bridging mechanism. While certain multivalent cations are considered common flocculants, they are generally being replaced in practice by superior acting polymers which carry many charge sites along the polymer chain.

Cationic Flocculant

Tissue products according to the present invention can be effectively produced using as a retention aid a "cationic flocculant", a term which, as used herein, refers to a class of polyelectrolyte. These polymers generally originate from copolymerization of one or more ethylenically unsaturated monomers, generally acrylic monomers, that consist of or include cationic monomer.

Suitable cationic monomers are dialkyl amino alkyl-(meth)acrylates or -(meth)acrylamides, either as acid salts or quaternary ammonium salts. Suitable alkyl groups include dialkylaminoethyl(meth)acrylates, dialkylaminoethyl(meth)acrylamides and dialkylaminomethyl(meth)acrylamides and dialkylamino-1,3-propyl(meth)acrylamides. These cationic monomers are preferably copolymerized with a nonionic monomer, preferably acrylamide. Other suitable polymers are polyethylene imines, polyamide epichlorohydrin polymers, and homopolymers or copolymers, generally with acrylamide, of monomers such as diallyl dimethyl ammonium chloride.

Any conventional cationic synthetic polymeric flocculant suitable for use on paper as a retention aid can be usefully employed to make products according to the present invention.

The polymer is preferably substantially linear in comparison to the globular structure of cationized starches.

A wide range of charge densities is useful, although a medium density is preferred. Polymers useful to make products of the present invention contain cationic functional groups at a frequency ranging from as low as about 0.2 to as high as 2.5, but more preferably in a range of about 1 to about 1.5 milliequivalents per gram of polymer. Polymers useful to make tissue products according to the present invention should have a molecular weight of at least about 500,000, and preferably a molecular weight above about 1,000,000, and, may advantageously have a molecular weight above 5,000,000.

Examples of acceptable materials are RETEN 1232® and Microform 2321®, both emulsion polymerized cationic polyacrylamides and RETEN 157®, which is delivered as a solid granule; all are products of Hercules, Inc. of Wilmington, Del. Another acceptable cationic flocculant is Accurac 91, a product of Cytec, Inc. of Stamford, Conn.

Those skilled in the art will recognize that the desired usage rates of these polymers will vary widely. Amounts as

low as about 0.005% polymer by weight based on the dry weight of the polymer and the dry finished weight of tissue paper will deliver useful results, but normally the usage rate would be expected to be higher; even higher for the purposes of the present invention than commonly practiced as application of these materials. Amounts as high as about 0.5% might be employed, but normally about 0.1% is optimum.

Anionic Flocculant

In another aspect of the present invention, an "anionic flocculant" is an useful ingredient. An "anionic flocculant" as used herein refers to a high molecular weight polymer having pendant anionic groups.

Anionic polymers often have a carboxylic acid (—COOH) moiety. These can be immediately pendant to the polymer backbone or pendant through typically, an alkalene group, particularly an alkalene group of a few carbons. In aqueous medium, except at low pH, such carboxylic acid groups ionize to provide to the polymer a negative charge.

Anionic polymers suitable for anionic flocculants do not wholly or essentially consist of monomeric units prone to yield a carboxylic acid group upon polymerization, instead they are comprised of a combination of monomers yielding both nonionic and anionic functionality. Monomers yielding nonionic functionality, especially if possessing a polar character, often exhibit the same flocculating tendencies as ionic functionality. The incorporation of such monomers is often practiced for this reason. An often used nonionic unit is (meth)acrylamide.

Anionic polyacrylamides having relatively high molecular weights are satisfactory flocculating agents. Such anionic polyacrylamides contain a combination of (meth)acrylamide and (meth)acrylic acid, the latter of which can be derived from the incorporation of (meth)acrylic acid monomer during the polymerization step or by the hydrolysis of some (meth)acrylamide units after the polymerization, or combined methods.

The polymer is preferably substantially linear in comparison to the globular structure of anionic starch.

A wide range of charge densities is useful, although a medium density is preferred. Polymers useful to make products of the present invention contain anionic functional groups at a frequency ranging from as low as about 0.2 to as high as about 7 or higher, but more preferably in a range of about 2 to about 4 milliequivalents per gram of polymer.

Polymers useful to make tissue products according to the present invention should have a molecular weight of at least about 500,000, and preferably a molecular weight above about 1,000,000, and, may advantageously have a molecular weight above 5,000,000.

An example of an acceptable material is RETEN 235®, which is delivered as a solid granule; a product of Hercules, Inc. of Wilmington, Del. Another acceptable anionic flocculant is Accurac 62®, a product of Cytec, Inc. of Stamford, Conn.

Those skilled in the art will recognize that the desired usage rates of these polymers will vary widely. Amounts as low as about 0.005% polymer by weight based on the finished dry weight of tissue paper will deliver useful results, but normally the usage rate would be expected to be higher; even higher for the purposes of the present invention than commonly practiced as application of these materials. Amounts as high as about 0.5% might be employed, but normally about 0.1% is optimum.

Bond Inhibiting Agents

Bond inhibiting agents are expressly included in the present invention. Acceptable bond inhibiting agents com-

prise the well known dialkyldimethylammonium salts such as ditallowdimethylammonium chloride, ditallowdimethylammonium methyl sulfate, di(hydrogenated)tallow dimethyl ammonium chloride; with di(hydrogenated)tallow dimethyl ammonium methyl sulfate being preferred. This particular material is available commercially from Witco Chemical Company Inc. of Dublin, Ohio under the tradename Varisoft 1370. Bond inhibiting agents act to disrupt the natural fiber to fiber bonding that occurs during the papermaking process. The level of bond inhibiting agent, if used, is preferably from about 0.02% to about 0.5%, by weight based on the dry weight of the tissue paper.

Other Additives

Other materials can be added to the aqueous papermaking furnish or the embryonic web to impart other characteristics to the product or improve the papermaking process so long as they are compatible with the chemistry of the selected particulate filler and do not significantly and adversely affect the softness, strength, or low dusting character of the present invention. The following materials are expressly included, but their inclusion is not offered to be all-inclusive. Other materials can be included as well so long as they do not interfere or counteract the advantages of the present invention.

It is common to add a cationic charge biasing species to the papermaking process to control the zeta potential of the aqueous papermaking furnish as it is delivered to the papermaking process. These materials are used because most of the solids in nature have negative surface charges, including the surfaces of cellulosic fibers and fines and most inorganic fillers. Many experts in the field believe that a cationic charge biasing species is desirable as it partially neutralizes these solids, making them more easily flocculated by cationic flocculants such as the before mentioned cationic starch and cationic polyelectrolyte. One traditionally used cationic charge biasing species is alum. More recently in the art, charge biasing is done by use of relatively low molecular weight cationic synthetic polymers preferably having a molecular weight of no more than about 500,000 and more preferably no more than about 200,000, or even about 100,000. The charge densities of such low molecular weight cationic synthetic polymers are relatively high. These charge densities range from about 4 to about 8 equivalents of cationic nitrogen per kilogram of polymer. One suitable material is Cypro 5140, a product of Cytec, Inc. of Stamford, Conn. The use of such materials is expressly allowed within the practice of the present invention. Caution should be used in their application, however. It is well known that while a small amount of such agents can actually aid retention by neutralizing anionic centers inaccessible to the larger flocculant molecules and thereby lowering the particle repulsion; however, since such materials can compete with cationic flocculants for anionic anchoring sites, they can actually have an effect opposite to the intended one by negatively impacting retention when anionic sites are limited.

The use of high surface area, high anionic charge micro-particles for the purposes of improving formation, drainage, strength, and retention is well taught in the art. See, for example, U.S. Pat. No. 5,221,435, issued to Smith on Jun. 22, 1993, incorporated herein by reference. Common materials for this purpose are silica colloid, or bentonite clay. The incorporation of such materials is expressly included within the scope of the present invention.

If permanent wet strength is desired, the group of chemicals including polyamide-epichlorohydrin,

polyacrylamides, styrene-butadiene latices; insolubilized polyvinyl alcohol; urea-formaldehyde; polyethyleneimine; chitosan polymers and mixtures thereof can be added to the papermaking furnish or to the embryonic web. Polyamide-epichlorohydrin resins are cationic wet strength resins which have been found to be of particular utility. Suitable types of such resins are described in U.S. Pat. No. 3,700,623, issued on Oct. 24, 1972, and U.S. Pat. No. 3,772,076, issued on Nov. 13, 1973, both issued to Keim and both being hereby incorporated by reference. One commercial source of a useful polyamide-epichlorohydrin resins is Hercules, Inc. of Wilmington, Del., which markets such resin under the mark Kymene 557H0.

Many tissue paper products must have limited strength when wet because of the need to dispose of them through toilets into septic or sewer systems. If wet strength is imparted to these products, it is preferred to be fugitive wet strength characterized by a decay of part or all of its potency upon standing in presence of water. If fugitive wet strength is desired, the binder materials can be chosen from the group consisting of dialdehyde starch or other resins with aldehyde functionality such as Co-Bond 10000 offered by National Starch and Chemical Company, Parex 7500 offered by Cytec of Stamford, Conn. and the resin described in U.S. Pat. No. 4,981,557 issued on Jan. 1, 1991, to Bjorkquist and incorporated herein by reference.

If enhanced absorbency is needed, surfactants may be used to treat the tissue paper webs of the present invention. The level of surfactant, if used, is preferably from about 0.01% to about 2.0% by weight, based on the dry fiber weight of the tissue paper. The surfactants preferably have alkyl chains with eight or more carbon atoms. Exemplary anionic surfactants are linear alkyl sulfonates, and alkylbenzene sulfonates. Exemplary nonionic surfactants are alkylglycosides including alkylglycoside esters such as Crodasta SL-400 which is available from Croda, Inc. (New York, N.Y.); alkylglycoside ethers as described in U.S. Pat. No. 4,011,389, issued to W. K. Langdon, et al. on Mar. 8, 1977; and alkylpolyethoxylated esters such as Pegperse 200 ML available from Glyco Chemicals, Inc. (Greenwich, Conn.) and IGEPAL RC-5200 available from Rhone Poulenc Corporation (Cranbury, N.J.).

The present invention can also be used in conjunction with adhesives and coatings designed to be sprayed onto the surface of the web or onto the Yankee dryer, such products designed for controlling adhesion to the Yankee dryer. For example, U.S. Pat. No. 3,926,716, Bates, incorporated here by reference, discloses a process using an aqueous dispersion of polyvinyl alcohol of certain degree of hydrolysis and viscosity for improving the adhesion of paper webs to Yankee dryers. Such polyvinyl alcohols, sold under the tradename Airvol0 by Air Products and Chemicals, Inc. of Allentown, Pa. can be used in conjunction with the present invention. Other Yankee coatings similarly recommended for use directly on the Yankee or on the surface of the sheet are cationic polyamide or polyamine resins such as those made under the tradename Rezonol0 and Unikraft0 by Houghton International of Valley Forge, Pa. and the Cupretol0 tradenames by Hercules, Inc. of Wilmington, Del. These can also be used with the present invention. Preferably the web is secured to the Yankee dryer by means of an adhesive selected from the group consisting of partially hydrolyzed polyvinyl alcohol resin, polyamide resin, polyamine resin, mineral oil, and mixtures thereof. More preferably, the adhesive is selected from the group consisting of polyamide epichlorohydrin resin, mineral oil, and mixtures thereof.

The above listings of optional chemical additives is intended to be merely exemplary in nature, and are not meant to limit the scope of the invention.

Preparation of the Aqueous Papermaking Furnish

Those skilled in the art will recognize that not only the qualitative chemical composition of the papermaking furnish is important to the tissue papermaking process, but also the relative amounts of each component, and the sequence and timing of addition, among other factors. It has now been found that the following techniques are suitable in preparing the aqueous papermaking furnish, but its delineation should not be regarded as limiting the scope of the present invention, which is defined by the claims set forth at the end of this specification.

Papermaking fibers are first prepared by liberating the individual fibers into a aqueous slurry by any of the common pulping methods adequately described in the prior art. Refining, if necessary, is then carried out on the selected parts of the papermaking furnish. It has been found that there is an advantage in retention, if the aqueous slurry which will later be used to adsorb the particulate filler is refined at least to the equivalent of a Canadian Standard Freeness of about 600 ml, but, more preferably 550 ml or below. Dilution generally favors the absorption of polymers and retention aids; consequently, the slurry or slurries of papermaking fibers at this point in the preparation is preferably no more than from about 3-5% solids by weight.

The selected particulate filler is first prepared by also dispersing it into an aqueous slurry. Dilution generally favors the absorption of polymers and retention aids onto solids surfaces; consequently, the slurry or slurries of particulate fillers at this point in the preparation is preferably no more than from about 1-5% solids by weight.

One aspect of the invention is based on a cationic flocculant retention chemistry. It involves first the addition of a starch with a limited water solubility in the presence of the particulate filler. Preferably, the starch is cationic and it is added as an aqueous dispersion in an amount ranging from about 0.3% by weight to 1.0% by weight, based on the dry weight of the starch and the dry weight of the particulate filler, strictly to the dilute aqueous slurry of particulate filler.

While not wishing to be bound by theory, it is believed that the starch acts as an agglomerating agent onto the filler and results in agglomeration of the particles. Agglomerating the filler in this manner makes it more effectively adsorbed onto the surfaces of the papermaking fibers. Adsorption of the filler onto the fiber surfaces can be accomplished by combining the slurry of agglomerates with at least one slurry of papermaking fibers and adding a cationic flocculant to the resultant mixture. Again, while not wishing to be bound by theory, the action of the flocculant is thought to be effective at this point by bridging between anionic sites on the papermaking fibers and anionic sites on the filler agglomerates.

The cationic flocculant can be added at any suitable point in the approach flow of the stock preparation system of the papermaking process. It is particularly preferred to add the cationic flocculant after the fan pump in which the final dilution with the recycled machine water returned from the process is made. It is well known in the papermaking field that shear stages break down bridges formed by flocculating agents, and hence it is general practice to add the flocculating agent after as many shear stages encountered by the aqueous papermaking slurry as feasible.

A second aspect of the invention is based on an anionic flocculant. In this aspect, the anionic flocculant is preferably

added at least to an aqueous slurry of the particulate filler while it is essentially isolated from the remainder of the aqueous papermaking furnish. The combination of anionic flocculant and particulate filler is then combined with at least a portion of the papermaking fibers and cationic starch is added to the mixture; this combination and starch addition is preferably accomplished prior to the final dilution of the process wherein the recycled machine water is combined with the aqueous papermaking furnish and conveyed to a headbox by a fan pump.

Advantageously, there is provided an additional dose of flocculant after the starch is added. While it is essential in this aspect of the invention that the initial dose of flocculant be of the anionic type, the portion of flocculant added after the fan pump can be of either the anionic type or cationic type. Most preferably, this second dose of flocculant occurs after the final dilution with the recycled machine water, i.e. after the fan pump. It is well known in the papermaking field that shear stages break down the flocs formed by flocculating agents, and hence it is general practice to add the flocculating agent after as many shear stages encountered by the aqueous papermaking slurry as feasible.

Those skilled in the art will recognize that the before mentioned recommended addition of flocculant directly to the particulate filler is an exception to minimum shear stage approach; thus this aspect of the present invention yields an unexpected advantage when at least a portion of the anionic flocculant is added to the particulate filler while it is essentially free of the other components of the aqueous papermaking furnish and the flocculant treated particulate filler is added to the papermaking fibers prior to the final dilution stage. A suitable ratio for point of addition of the anionic flocculant is about 4:1, i.e. for each 1 part of the total flocculant dosage that is added after the fan pump, about 4 parts are advantageously added directly to the particulate filler. This ratio can vary considerably, and it is anticipated that ratios from about 0.5:1 to 10:1 might be appropriate depending on varying circumstances.

In preparing products representing either of the before mentioned retention regimens, if multiple slurries of papermaking fibers are prepared, one or more of the slurries can be used to adsorb particulate fillers in accordance with the present invention. Even if one or more aqueous slurries of papermaking fibers in the papermaking process is maintained relatively free of particulate fillers prior to reaching its fan pump, it is preferred to add a cationic or anionic flocculant after the fan pump of such slurries. This is because the recycled water used in that fan pump contains filler agglomerates which failed to retain in previous passes over the foraminous screen. When multiple dilute fiber slurries are used in the creped papermaking process, the flow of cationic or anionic flocculant is preferably added to all dilute fiber slurries and it should be added in a manner which approximately proportions it to the flow of solids in the aqueous papermaking furnish of each dilute fiber slurry.

In a preferred arrangement, a slurry of relatively short papermaking fibers, comprising hardwood pulp, is prepared and used to adsorb fine particulate fillers, while a slurry of relatively long papermaking fibers, comprising softwood pulp, is prepared and left essentially free of fine particulates. The fate of the resultant short fibered slurry is to be directed to the outer chambers of a three layered headbox to form surface layers of a three layered tissue in which a long fibered inner layer is formed out of a inner chamber in the headbox in which the slurry of relatively long papermaking fibers is directed. The resultant filled tissue web is particularly suitable for converting into a single-ply tissue product.

In an alternate preferred arrangement, a slurry of relatively short papermaking fibers, comprising hardwood pulp, is prepared and used to adsorb fine particulate fibers, while a slurry of short papermaking fibers, comprising hardwood pulp, is prepared and left relatively free of fine particulates, and a slurry of relatively long papermaking fibers, comprising softwood pulp, is prepared and left essentially free of fine particulates. The fate of the resultant short fibered slurry containing fine particulate fillers is to be directed to one chamber of a multi-chambered headbox, while the resultant short fibered slurry maintained relatively free of particulates is directed to another chamber and the resultant long fibered slurry is directed to a third chamber. Preferably the chambers are disposed such that the chamber to which the relatively long fibered slurry is directed is disposed between the other two chambers and the chamber carrying the relatively short fibered slurry being relatively free of fine particulate fillers deposits its slurry directly upon the foraminous surface, while the chamber carrying the relatively short fibered slurry containing the fine particulate filler deposits its slurry on the upper surface furthest from the foraminous carrier.

Those skilled in the art will also recognize that the apparent number of chambers of a headbox can be reduced by directing the same type of aqueous papermaking furnish to adjacent chambers.

In all arrangements, it is essential to compose the furnish directed to each layer to achieve the lint ratio prescribed by the present invention. This is preferably accomplished by preferentially adding starch to the furnish which is the genesis of the opposite-side surface and thereby reducing the starch added to the furnish which is the genesis of the fabric-side surface. The lint ratio can also be increased by adding a bond inhibiting agent preferentially into the layer which will ultimately yield the fabric-side surface.

While not wishing to be bound by theory, it is believed that the fabric-side surface of a filled tissue paper without having biased surface properties to achieve the lint ratio prescribed herein is more textured than a similarly made tissue web which does not contain fillers. This is believed to arise from the necessity to bond the fibers more tightly to overcome the strength loss associated with the displacement of fibers with fine particulate. Consequently, the fine-detail of the felt or fabric into which the web is deflected is reproduced with greater clarity imparting more roughness to the web. This difference is not noticeable on the other surface because this surface is not molded into a felt or fabric and consequently possesses a surface texture of an entirely different magnitude. Consequently, reducing the bonding on the felt-side surface has a positive effect which outweighs the negatives associated with further increasing the bonding on the other surface.

Further insight into preparation methods for the aqueous papermaking furnish can be gained by reference to FIG. 3, which is a schematic representation illustrating a preparation of the aqueous papermaking furnish for a papermaking operation yielding a product according to the aspect of the invention based on cationic flocculant and FIG. 4, which is a schematic representation illustrating a preparation of the aqueous papermaking furnish for the creped papermaking operation yielding a product according to another aspect of the invention based on anionic flocculant. The following discussion refers to FIG. 3:

A storage vessel 1 is provided for staging an aqueous slurry of relatively long papermaking fibers. The slurry is conveyed by means of a pump 2 and optionally through a refiner 3 to fully develop the strength potential of the long

papermaking fibers. Additive pipe 4 conveys a resin to provide for wet or dry strength, as desired in the finished product. The slurry is then further conditioned in mixer 5 to aid in absorption of the resin. The suitably conditioned slurry is then diluted with white water 7 in a fan pump 6 forming a dilute long papermaking fiber slurry 15. Pipe 20 adds a cationic flocculant to the slurry 15, producing a flocculated long fibered slurry 22.

Still referring to FIG. 3, a storage vessel 8 is a repository for a fine particulate filler slurry. Additive pipe 9 conveys an aqueous dispersion of a cationic starch additive. Pump 10 acts to convey the fine particulate slurry as well as provide for dispersion of the starch. The slurry is conditioned in a mixer 12 to aid in absorption of the additives. Resultant slurry 13 is conveyed to a point where it is mixed with an aqueous dispersion of refined short fiber papermaking fibers.

Still referring to FIG. 3, short papermaking fiber slurry originates from a repository 11, from which it is conveyed through pipe 49 by pump 14 through a refiner 15 where it becomes a refined slurry of short papermaking fibers 16. After mixing with the conditioned slurry of fine particulate filler 13, it becomes the short fiber based aqueous papermaking slurry 17. White water 7 is mixed with slurry 17 in a fan pump 18 at which point the slurry becomes a dilute aqueous papermaking slurry 19. Pipe 21 directs a cationic flocculant into slurry 19, after which the slurry becomes a flocculated aqueous papermaking slurry 23.

Preferably, the flocculated short-fiber based aqueous papermaking slurry 23 is directed to the preferred creped papermaking process illustrated in FIG. 1 and is divided into two approximately equal streams which are then directed into headbox chambers 82 and 83 ultimately evolving into fabric-side surface layer 75 and the opposite-side surface layer 71, respectively of the strong, soft, low dusting, filled tissue paper. Similarly, the aqueous flocculated long papermaking fiber slurry 22, referring to FIG. 3, is preferably directed into headbox chamber 82b ultimately evolving into center layer 73 of the strong, soft, low dusting, filled tissue paper.

In an alternate arrangement, the flocculated short-fiber based aqueous papermaking slurry 23 of FIG. 3 is directed to the papermaking process illustrated in FIG. 2 and is divided into two approximately equal streams which are then directed into headbox chambers 181 and 183 ultimately evolving into fabric-side surface layer 172 and the opposite-side surface layer 173, respectively of the strong, soft, low dusting, filled tissue paper. Similarly, the aqueous flocculated long papermaking fiber slurry 22, referring to FIG. 3, is preferably directed into headbox chamber 182 ultimately evolving into center layer 174 of the strong, soft, low dusting, filled tissue paper.

The following discussion refers to FIG. 4:

A storage vessel 24 is provided for staging an aqueous slurry of relatively long papermaking fibers. The slurry is conveyed by means of a pump 25 and optionally through a refiner 26 to fully develop the strength potential of the long papermaking fibers. Additive pipe 27 conveys a resin to provide for wet or dry strength, as desired in the finished product. The slurry is then further conditioned in mixer 28 to aid in absorption of the resin. The suitably conditioned slurry is then diluted with white water 29 in a fan pump 30 forming a dilute long papermaking fiber slurry 31. Optionally, pipe 32 conveys an flocculant to mix with slurry 31, forming an aqueous flocculated long fiber papermaking slurry 33.

Still referring to FIG. 4, a storage vessel 34 is a repository for a fine particulate filler slurry. Additive pipe 35 conveys

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an aqueous dispersion of a anionic flocculant. Pump 36 acts to convey the fine particulate slurry as well as provide for dispersion of the flocculant. The slurry is conditioned in a mixer 37 to aid in absorption of the additive. Resultant slurry 38 is conveyed to a point where it is mixed with an aqueous dispersion of short papermaking fibers.

Still referring to FIG. 4, a short papermaking fiber slurry originates from a repository 39, from which it is conveyed through pipe 48 by pump 40 to a point where it mixes with the conditioned fine particulate filler slurry 38 to become the short fiber based aqueous papermaking slurry 41. Pipe 46 conveys an aqueous dispersion of cationic starch which mixes with slurry 41, aided by in line mixer 50, to form flocculated slurry 47. White water 29 is directed into the flocculated slurry which mixes in fan pump 42 to become the dilute flocculated short fiber based aqueous papermaking slurry 43. Optionally, pipe 44 conveys additional flocculant to increase the level of flocculation of dilute slurry 43 forming slurry 45.

Preferably, the short papermaking fiber slurry 45 from FIG. 4 is directed to the preferred papermaking process illustrated in FIG. 1 and is divided into two streams which are then directed into headbox chambers 82 and 83 ultimately evolving into felt-side surface layer 75 and opposite-side surface layer 71, respectively of the strong, soft, low dusting, filled tissue paper. Similarly, the long papermaking fiber slurry 33, referring to FIG. 4, is preferably directed into headbox chamber 82b ultimately evolving into center layer 73 of the strong, soft, low dusting, filled tissue paper.

The Creped Papermaking Process

FIG. 1 is a schematic representation illustrating a creped papermaking process for producing a strong, soft, and low dusting filled creped tissue paper with biased surface bonding properties. These preferred embodiments are described in the following discussion, wherein reference is made to FIG. 1.

FIG. 1 is a side elevational view of a preferred papermaking machine 80 for manufacturing paper according to the present invention. Referring to FIG. 1, papermaking machine 80 comprises a layered headbox 81 having a top chamber 82 a center chamber 82b, and a bottom chamber 83, a slice roof 84, and a Fourdrinier wire 85 which is looped over and about breast roll 86, deflector 90, vacuum suction boxes 91, couch roll 92, and a plurality of turning rolls 94. In operation, one papermaking furnish is pumped through top chamber 82 a second papermaking furnish is pumped through center chamber 82b, while a third furnish is pumped through bottom chamber 83 and thence out of the slice roof 84 in over and under relation onto Fourdrinier wire 85 to form thereon an embryonic web 88 comprising layers 88a, and 88b, and 88c. Dewatering occurs through the Fourdrinier wire 85 and is assisted by deflector 90 and vacuum boxes 91. As the Fourdrinier wire makes its return run in the direction shown by the arrow, showers 95 clean it prior to its commencing another pass over breast roll 86. At web transfer zone 93, the embryonic web 88 is transferred to a foraminous carrier fabric 96 by the action of vacuum transfer box 97. Carrier fabric 96 carries the web from the transfer zone 93 past vacuum dewatering box 98, through blow-through predryers 100 and past two turning rolls 101 after which the web is transferred to a Yankee dryer 108 by the action of pressure roll 102. The carrier fabric 96 is then cleaned and dewatered as it completes its loop by passing over and around additional turning rolls 101, showers 103, and vacuum dewatering box 105. The predried paper web is

adhesively secured to the cylindrical surface of Yankee dryer 108 aided by adhesive applied by spray applicator 109. Drying is completed on the steam heated Yankee dryer 108 and by hot air which is heated and circulated through drying hood 110 by means not shown. The web is then dry creped from the Yankee dryer 108 by doctor blade 111 after which it is designated paper sheet 70 comprising a Yankee-side layer 71 a center layer 73, and an off-Yankee-side layer 75. Paper sheet 70 then passes between calendar rolls 112 and 113, about a circumferential portion of reel 115, and thence is wound into a roll 116 on a core 117 disposed on shaft 118.

Still referring to FIG. 1, the genesis of Yankee-side layer 71 of paper sheet 70 is the furnish pumped through bottom chamber 83 of headbox 81, and which furnish is applied directly to the Fourdrinier wire 85 whereupon it becomes layer 88c of embryonic web 88. The genesis of the center layer 73 of paper sheet 70 is the furnish delivered through chamber 82.5 of headbox 81, and which furnish forms layer 88b on top of layer 88c. The genesis of the off-Yankee-side layer 75 of paper sheet 70 is the furnish delivered through top chamber 82 of headbox 81, and which furnish forms layer 88a on top of layer 88b of embryonic web 88. Although FIG. 1 shows papermachine 80 having headbox 81 adapted to make a three-layer web, headbox 81 may alternatively be adapted to make other multi-layered tissue webs having different numbers of layers. One embodiment of the present invention is achieved by relegating the fine particulate filler to the furnish resulting in layer 88c; thereby increasing the retentive efficiency of the papermaking process.

Further, with respect to making paper sheet 70 embodying the present invention on papermaking machine 80, FIG. 1, the Fourdrinier wire 85 must be of a fine mesh having relatively small spans with respect to the average lengths of the fibers constituting the short fiber furnish so that good formation will occur; and the foraminous carrier fabric 96 should have a fine mesh having relatively small opening spans with respect to the average lengths of the fibers constituting the long fiber furnish to substantially obviate bulking the fabric side of the embryonic web into the inter-filamentary spaces of the fabric 96. Also, with respect to the process conditions for making exemplary paper sheet 70, the paper web is preferably dried to about 80% fiber consistency, and more preferably to about 95% fiber consistency prior to creping.

The present invention is applicable to creped tissue paper in general, including but not limited to conventionally felt-pressed creped tissue paper; high bulk pattern densified creped tissue paper; and high bulk, uncompacted creped tissue paper.

The Uncreped Tissue Papermaking Process

FIG. 2 is a schematic representation illustrating an uncreped papermaking process for producing a strong, soft, and low dust filled uncreped tissue paper. These preferred embodiments are described in the following discussion, wherein reference is made to FIG. 2.

FIG. 2 is a side elevational view of a preferred papermaking machine for manufacturing uncreped tissue paper webs according to the present invention. Referring to FIG. 2, the papermaking machine comprises a layered headbox 180 having a top chamber 181 a center chamber 182, and a bottom chamber 183, a slice roof 184, and a foraminous forming fabric (e.g. a Fourdrinier wire) 185 which is looped over and about breast roll 188 and a plurality of turning rolls shown but not numbered for simplicity. In operation, one

papermaking furnish is pumped through top chamber 181 a second papermaking furnish is pumped through center chamber 182, while a third furnish is pumped through bottom chamber 183 and thence out of the slice roof 184 in over and under relation onto Fourdrinier wire 185 to form thereon a multi-layered embryonic web 194. Dewatering occurs through the Fourdrinier wire 185 and can be assisted by deflectors or vacuum boxes which for simplicity are not shown. As the Fourdrinier wire makes its return, showers, not shown, clean it prior to its commencing another pass over breast roll 188. The embryonic web supported by Fourdrinier wire 185 is transferred to a foraminous transfer (i.e. carrier) fabric 186 by the action of vacuum transfer box 187. Carrier fabric 186 travels at a slower speed than Fourdrinier wire 185. The purpose of carrier fabric 186 is therefore to shorten the embryonic web 194 relative to its length while being supported on Fourdrinier wire 185. A further purpose of carrier fabric 186 is to transport the embryonic web to a blow through dryer fabric 190. During this travel, the embryonic web can optionally be further dewatered by means of vacuum boxes not shown. The path of carrier fabric 186 is controlled by a plurality of turning rolls shown but not numbered for simplicity. The transfer to the blow through dryer fabric 190 is effected by means of a vacuum box 191. Carrier fabric 186 is preferably showered by means not shown prior to its return to the web transfer zone promoted by vacuum box 187. After transfer to the blow through dryer fabric 190, the wet web is transported through blow through dryer 192, whereupon, hot air generated by means not shown is propelled through the dryer fabric and consequently the embryonic web which resides thereupon. The dried web 193 is dislodged from the dryer fabric 190 at the exit of the predryer. At this point, dried web 193 can optionally be directed between two, relatively smooth, dry and carrying fabrics, an upper fabric 196 and a lower fabric 194. While secured between fabrics 196 and 194, the dried web 193 can be calendered by a series of fixed gap calendering nips formed between opposing pairs of rollers 195. These nips smooth the surface and control the thickness of the tissue paper.

Still referring to FIG. 2, the finished calendered web 171 emerges from the space between opposing carrier fabrics 196 and 194 still supported by carrier fabric 194 after which it is wound upon reel 198. The finished web 171 is comprised of three layers as revealed in the detailed drawing inset of FIG. 2A. The detail drawing inset FIG. 2A reveals outer layers 173 and 172 consisting of a felt-side surface layer 172 and an opposite-side surface layer 173 and an inner layer 174 between the outer layers 173 and 172. The genesis of layers 173, 172 and 174 are the furnishes of headbox chambers 183, 181 and 182 respectively. Although FIG. 2 shows a papermachine having headbox 180 adapted to make a three-layer web, headbox 180 can alternatively be adapted to make unlayered, two layer or other multi-layer webs.

Further, with respect to making paper sheet 171 embodying the present invention: the papermaking machine of FIG. 2 must possess a Fourdrinier wire 185 of a fine mesh having relatively small spans with respect to the average lengths of the fibers constituting the short fiber furnish so that good formation will occur. The preferred characteristics of the clothing elements 186, 190, 194, and 196 specific to this class of papermaking are adequately discussed in the prior art. For example, Hyland, in European Patent Application 0 617 164 A1, published Sep. 28, 1994 and incorporated herein by reference discusses the preferred characteristics of the beforementioned clothing.

The filled tissue paper webs of the present invention have a basis weight of between 10 g/m² and about 100 g/m². In

its preferred embodiment, the filled tissue paper of the present invention has a basis weight between about 10 g/m² and about 50 g/m² and, most preferably, between about 10 g/m² and about 30 g/m². Tissue paper webs suitable for the present invention possess a density of about 0.60 g/cm³ or less. In its preferred embodiment, the filled tissue paper of the present invention has a density between about 0.03 g/cm³ and about 0.6 g/cm³ and, most preferably, between about 0.05 g/cm³ and 0.2 g/cm³.

The present invention is further applicable to multi-layered tissue paper webs. Tissue structures formed from layered paper webs are described in U.S. Pat. No. 3,994,771, Morgan, Jr. et al. issued Nov. 30, 1976, U.S. Pat. No. 4,340,981, Carstens, issued Nov. 17, 1981, U.S. Pat. No. 4,166,001, Dunning et al., issued Aug. 28, 1979, and European Patent Publication No. 0 613 979 A1, Edwards et al., published Sep. 7, 1994, all of which are incorporated herein by reference. The layers are preferably comprised of different fiber types, the fibers typically being relatively long softwood and relatively short hardwood fibers as used in multi-layered tissue paper making. Multi-layered tissue paper webs suitable for the present invention comprise at least two superposed layers, an inner layer and at least one outer layer contiguous with the inner layer. Preferably, the multi-layered tissue papers comprise three superposed layers, an inner or center layer, and two outer layers, a Yankee side outer layer and an off-Yankee side outer layer with the inner layer located between the two outer layers. The Yankee side outer layer is so named because it forms the surface which contacts the Yankee dryer surface. The two outer layers preferably comprise a primary filamentary constituent of relatively short paper making fibers having an average fiber length between about 0.5 and about 1.5 mm, preferably less than about 1.0 mm. These short paper making fibers typically comprise hardwood fibers, preferably hardwood Kraft fibers, and most preferably derived from eucalyptus. The inner layer preferably comprises a primary filamentary constituent of relatively long paper making fibers having an average fiber length of least about 2.0 mm. These long paper making fibers are typically softwood fibers, preferably, northern softwood Kraft fibers.

Preferably, the majority of the particulate filler of the present invention is contained in at least one of the outer layers of the multi-layered tissue paper web of the present invention. In one embodiment of the present invention, the majority of the particulate filler of the present invention is contained in both of the outer layers. In another embodiment of the present invention, the majority of the particulate filler is contained in one of the outer layers; specifically, in the outer layer originating at the farthest distance from the foraminous surface, i.e., the fabric-side surface outer layer. The other outside layer is referred to herein as the opposite-side surface layer. The inner layer is located between the two outer layers (i.e. fabric-side surface layer and opposite-side surface layer). While not wishing to be bound by theory, directing the filler material to this layer is believed to result in greater retention owing to the build up of an initial fiber layer prior to the drainage of the furnish containing the filler material. In addition, the presence of the filler in the surface layer designed to have the higher lint of the two surface layers aids in achieving the desired lint ratio prescribed in the present invention.

The tissue paper products made from multi-layered tissue paper webs can be single-ply tissue products or multi-ply tissue products. The advantages of the present invention will be most pronounced when the multi-layered tissue paper webs of the present invention are used in single-ply tissue paper products.

The equipment and methods are well known to those skilled in the art. In a typical process, a low consistency pulp furnish is provided in a pressurized headbox. The headbox has an opening for delivering a thin deposit of pulp furnish onto the Fourdrinier wire to form a wet web. The web is then typically dewatered to a fiber consistency of between about 7% and about 25% (total web weight basis) by vacuum dewatering.

To prepare filled tissue paper products according to those disclosed in the present invention, an aqueous papermaking furnish is deposited on a foraminous surface to form an embryonic web. The scope of the invention also includes tissue paper products resultant from the formation of multiple paper layers in which two or more layers of furnish are preferably formed from the deposition of separate streams of dilute fiber slurries for example in a multi-channelled headbox. The layers are preferably comprised of different fiber types, the fibers typically being relatively long softwood and relatively short hardwood fibers as used in multi-layered tissue paper making. If the individual layers are initially formed on separate wires, the layers are subsequently combined when wet to form a multi-layered tissue paper web. The papermaking fibers are preferably comprised of different fiber types, the fibers typically being relatively long softwood and relatively short hardwood fibers. More preferably, the hardwood fibers comprise at least about 50% and said softwood fibers comprise at least about 10% of said papermaking fibers.

In the papermaking process used to make filled tissue products according to the present invention, the step comprising the transfer of the web to a felt or fabric, e.g., conventionally felt pressing tissue paper, well known in the art, is expressly included within the scope of this invention. In this process step, the web is dewatered by transferring to a dewatering felt and pressing the web so that water is removed from the web into the felt by pressing operations wherein the web is subjected to pressure developed by opposing mechanical members, for example, cylindrical rolls. Because of the substantial pressures needed to de-water the web in this fashion, the resultant webs made by conventional felt pressing are relatively high in density and are characterized by having a uniform density throughout the web structure.

In the papermaking process used to make filled tissue products according to the present invention, the step comprising the transfer of the semi-dry web to a Yankee dryer, the web is pressed during transfer to the cylindrical steam drum apparatus known in the art as a Yankee dryer. The side of web pressed against the Yankee dryer is referred to herein as the "opposite-side" surface outer layer, whereas the side facing away from the Yankee dryer is referred to herein as the "fabric-side" surface outer layer. The transfer is effected by mechanical means such as an opposing cylindrical drum pressing against the web. Vacuum may also be applied to the web as it is pressed against the Yankee surface. Multiple Yankee dryer drums can be employed.

More preferable variations of the creped papermaking processes for making filled tissue papers include the so-called pattern densified methods in which the resultant structure is characterized by having a relatively high bulk field of relatively low fiber density and an array of densified zones of relatively high fiber density dispersed within the high bulk field. The high bulk field is alternatively characterized as a field of pillow regions. The densified zones are alternatively referred to as knuckle regions. The densified zones may be discretely spaced within the high bulk field or may be interconnected, either fully or partially, within the high

bulk field. Preferably, the zones of relatively high density are continuous and the high bulk field is discrete. Preferred processes for making pattern densified tissue webs are disclosed in U.S. Pat. No. 3,301,746, issued to Sanford and Sisson on Jan. 31, 1967, U.S. Pat. No. 3,974,025, issued to Peter G. Ayers on Aug. 10, 1976, and U.S. Pat. No. 4,191,609, issued to Paul D. Trokhan on Mar. 4, 1980, and U.S. Pat. No. 4,637,859, issued to Paul D. Trokhan on Jan. 20, 1987, U.S. Pat. No. 4,942,077 issued to Wendi et al. on Jul. 17, 1990, European Patent Publication No. 0 617 164 A1, Hyland et al., published Sep. 28, 1994, European Patent Publication No. 0 616 174 A1, Hermans et al., published Sep. 21, 1994; all of which are incorporated herein by reference.

To form pattern densified creped tissue webs, the web transfer step immediately after forming the web is to a forming fabric rather than a felt. The web is juxtaposed against an array of supports comprising the forming fabric. The web is pressed against the array of supports, thereby resulting in densified zones in the web at the locations geographically corresponding to the points of contact between the array of supports and the wet web. The remainder of the web not compressed during this operation is referred to as the high bulk field. This high bulk field can be further dedensified by application of fluid pressure, such as with a vacuum type device or a blow-through dryer. The web is dewatered, and optionally predried, in such a manner as to substantially avoid compression of the high bulk field. This is preferably accomplished by fluid pressure, such as with a vacuum type device or blow-through dryer, or alternately by mechanically pressing the web against an array of supports wherein the high bulk field is not compressed. The operations of dewatering, optional predrying and formation of the densified zones may be integrated or partially integrated to reduce the total number of processing steps performed. The moisture content of the semi-dry web at the point of transfer to the Yankee surface is less than about 40% and the hot air is forced through said semi-dry web while the semi-dry web is on said forming fabric to form a low density structure.

The pattern densified web is transferred to the Yankee dryer and dried to completion, preferably still avoiding mechanical pressing. In the present invention, preferably from about 8% to about 55% of the creped tissue paper surface comprises densified knuckles having a relative density of at least 125% of the density of the high bulk field.

The array of supports is preferably an imprinting carrier fabric having a patterned displacement of knuckles which operate as the array of supports which facilitate the formation of the densified zones upon application of pressure. The pattern of knuckles constitutes the array of supports previously referred to. Imprinting carrier fabrics are disclosed in U.S. Pat. No. 3,301,746, Sanford and Sisson, issued Jan. 31, 1967, U.S. Pat. No. 3,821,008, Salvucci, Jr. et al., issued May 21, 1974, U.S. Pat. No. 3,974,025, Ayers, issued Aug. 10, 1976, U.S. Pat. No. 3,573,164, Friedberg et al., issued Mar. 30, 1971, U.S. Pat. No. 3,473,576, Amneus, issued Oct. 21, 1969, U.S. Pat. No. 4,239,065, Trokhan, issued Dec. 16, 1980, and U.S. Pat. No. 4,528,239, Trokhan, issued Jul. 9, 1985, all of which are incorporated herein by reference.

Most preferably, the embryonic web is caused to conform to the surface of an open mesh drying/imprinting fabric by the application of a fluid force to the web and thereafter thermally predried on said fabric as part of a low density paper making process.

The advantages of the present invention will be realized to the greatest degree when the drying or imprinting fabric

herein before described in one which is characterized by having continuous high density ("knuckle") areas dispersed within a high bulk field. Preferably, relatively high bulk areas of a differential density structure are discrete regions referred to as "pillows" herein. When the drying or imprinting fabric comprises continuous high density or knuckle areas, the pillows are necessarily discrete. The frequency of pillows in a given area of the tissue paper is significant. It is desirable to maintain as high a level of pillows as possible for maximum bulk and visibility of the imprinting fabric pattern. However, excessive size can detract significantly from softness owing to the negatives of the more grossly textured surface. The present invention is particularly applicable to rather coarsely textured tissue papers. Therefore, one preferred embodiment of the present invention comprises tissue papers with less than about 150 discrete regions (i.e., pillows) per square inch of tissue paper surface, more preferably less than about 100 discrete regions (i.e., pillows) per square inch.

Another variation of the processing steps included within the present invention includes the formation of, so-called uncompacted, non pattern-densified multi-layered tissue paper structures such as are described in U.S. Pat. No. 3,812,100 issued to Joseph L. Salvucci, Jr. and Peter N. Yiannos on May 21, 1974 and U.S. Pat. No. 4,208,459, issued to Henry E. Becker, Albert L. McConnell, and Richard Schutte on Jun. 17, 1980, both of which are incorporated herein by reference. In general uncompacted, non pattern densified multi-layered tissue paper structures are prepared by depositing a paper making furnish on a foraminous forming wire such as a Fourdrinier wire to form a wet web, draining the web and removing additional water without mechanical compression until the web has a fiber consistency of at least 80%, and creping the web. Water is removed from the web by vacuum dewatering and thermal drying. The resulting structure is a soft but weak high bulk sheet of relatively uncompacted fibers. Bonding material is preferably applied to portions of the web prior to creping.

The advantages related to the practice of the present invention include the ability to reduce the amount of paper-making fibers required to produce a given amount of tissue paper product. Further, the optical properties, particularly the opacity, of the tissue product are improved. These advantages are realized in a tissue paper web which is soft while having a high level of strength and low tendency for linting and dusting.

The term "strength" as used herein refers to the specific total tensile strength, the determination method for this measure is included in a later section of this specification. The tissue paper webs according to the present invention are strong. This generally means that their specific total tensile strength is at least about 0.200 meters, more preferably more than about 0.300 meters.

The terms "lint" and "dust" are used interchangeably herein and refer to the tendency of a tissue paper web to release fibers or particulate fillers as measured in a controlled abrasion test, the methodology for which is detailed in a later section of this specification. Lint and dust are related to strength since the tendency to release fibers or particles is directly related to the degree to which such fibers or particles are anchored into the structure. As the overall level of anchoring is increased, the strength will be increased. However, it is possible to have a level of strength which is regarded as acceptable but have an unacceptable level of linting or dusting. This is because linting or dusting can be localized. For example, the surface of a tissue paper web can be prone to linting or dusting, while the degree of

bonding beneath the surface can be sufficient to raise the overall level of strength to quite acceptable levels. In another case, the strength can be derived from a skeleton of relatively long papermaking fibers, while fiber fines or the particulate filler can be insufficiently bound within the structure. The filled tissue paper webs according to the present invention are relatively low in lint. Ultimate lint values, representing the average of lint values of the fabric-side surface and the opposite-side surface, below about 12 are preferable; below about 10 are more preferable.

The multi-layered tissue paper web of this invention can be used in any application where soft, absorbent multi-layered tissue paper webs are required. Particularly advantageous uses of the multi-layered tissue paper web of this invention are in toilet tissue and facial tissue products. Both single-ply and multi-ply tissue paper products can be produced from the webs of the present invention.

The Soft Filled Tissue Paper with Biased Surface Properties

FIG. 5 is a schematic representation of one embodiment of the soft tissue paper of the present invention revealing the structure of the various layers of the creped tissue paper.

Referring to FIG. 5, inner layer 120 is located between fabric-side surface layer 122 and opposite-side surface layer 121. Inner layer 120 predominately contains softwood fibers 123, while each of the outer layers 121 and 122 predominantly contain hardwood fibers, 125.

Fine particulate filler particles 124 are preferably located in outer layers 121 and 122, and, particularly in one aspect of the invention are restricted as far as practical to the layer 122.

The degree of bonding in layer 122 is controlled to be less than in layer 121 such that the lint value when measured with respect to layer 122 is higher than when measured with respect to layer 121. This is accomplished by promoting less bonding in layer 122 relative to layer 121. Those skilled in the art will recognize specific means by which this can be accomplished. Examples of means include refining the furnish composition for layer 122 to less degree, using less binder such as starch in layer 122, adding a higher proportion of all of the filler to layer 122, adding a bond inhibiting agent to layer 122, or altering the ratios of thickness of the layers such that layer 122 contains more mass than layer 121.

Preferably, layer 122 will have from about 1.5 to about 2 times as much mass as layer 121.

Analytical and Testing Procedures

A. Density

The density of multi-layered tissue paper, as that term is used herein, is the average density calculated as the basis weight of that paper divided by the caliper, with the appropriate unit conversions incorporated therein. Caliper of the multi-layered tissue paper, as used herein, is the thickness of the paper when subjected to a compressive load of 95 g/in² (15.5 g/cm²).

B. Molecular Weight Determination

The essential distinguishing characteristic of polymeric materials is their molecular size. The properties which have enabled polymers to be used in a diversity of applications derive almost entirely from their macro-molecular nature. In order to characterize fully these materials it is essential to have some means of defining and determining their molecular weights and molecular weight distributions. It is more correct to use the term relative molecular mass rather the

Filler in Tissue Paper =

$$\frac{\text{Weight of Filler (g)} \times 100}{[(\text{Weight of Platinum Dish \& Paper}) - (\text{Weight of Platinum Dish})]}$$

Determination of Kaolin Clay by XRF

The main advantage of the XRF technique over the muffle furnace ashing technique is speed, but it is not as universally applicable. The XRF spectrometer can quantitate the level of kaolin clay in a paper sample within 5 minutes compared to the hours it takes in the muffle furnace ashing method.

The X-ray Fluorescence technique is based on the bombardment of the sample of interest with X-ray photons from a X-ray tube source. This bombardment by high energy photons causes core level electrons to be photoemitted by the elements present in the sample. These empty core levels are then filled by outer shell electrons. This filling by the outer shell electrons results in the fluorescence process such that additional X-ray photons are emitted by the elements present in the sample. Each element has distinct "finger-print" energies for these X-ray fluorescent transitions. The energy and thus the identity of the element of interest of these emitted X-ray fluorescence photons is determined with a lithium doped silicon semiconductor detector. This detector makes it possible to determine the energy of the impinging photons and thus the identify the elements present in the sample. The elements from sodium to uranium may be identified in most sample matrices.

In the case of the clay fillers, the detected elements are both silicon and aluminum. The particular X-ray Fluorescence instrument used in this clay analysis is a Spectrace 5(X) made by Baker-Hughes Inc. of Mountain View, Calif. The first step in the quantitative analysis of clay is to calibrate the instrument with a set of known clay filled tissue standards, using clay inclusions ranging from 8% to 20%, for example.

The exact clay level in these standard paper samples is determined with the muffle furnace ashing technique described above. A blank paper sample is also included as one of the standards. At least 5 standards bracketing the desired target clay level should be used to calibrate the instrument.

Before the actual calibration process, the X-ray tube is powered to settings of 13 kilovolts and 0.20 milliamps. The instrument is also set up to integrate the detected signals for the aluminum and silicon contained in the clay. The paper sample is prepared by first cutting a 2" by 4" strip. This strip is then folded to make a 2"x2" with the off-Yankee side facing out. This sample is placed on top of the sample cup and held in place with a retaining ring. During sample preparation, care must be taken to keep the sample flat on top of the sample cup. The instrument is then calibrated using this set of known standards.

After calibrating the instrument with the set of known standards, the linear calibration curve is stored in the computer system's memory. This linear calibration curve is used to calculate clay levels in the unknowns. To insure the X-ray Fluorescence system is stable and working properly, a check sample of known clay content is run with every set of unknowns. If the analysis of the check sample results in an inaccurate result (10 to 15% off from its known clay content), the instrument is subjected to trouble-shooting and/or re-calibrated.

For every paper-making condition, the clay content in at least 3 unknown samples is determined. The average and standard deviation is taken for these 3 samples. If the clay application procedure is suspected or intentionally set up to

vary the clay content in either the cross direction (CD) or machine direction (MD) of the paper, more samples should be measured in these CD and MD directions.

E. Measurement of Tissue Paper Lint

The amount of lint generated from a tissue product is determined with a Sutherland Rub Tester. This tester uses a motor to rub a weighted felt 5 times over the stationary toilet tissue. The Hunter Color L value is measured before and after the rub test. The difference between these two Hunter Color L values is calculated as lint.

10 SAMPLE PREPARATION

Prior to the lint rub testing, the paper samples to be tested should be conditioned according to Tappi Method #T402OM-88. Here, samples are preconditioned for 24 hours at a relative humidity level of 10 to 35% and within a temperature range of 22° to 40° C. After this preconditioning step, samples should be conditioned for 24 hours at a relative humidity of 48 to 52%, and within a temperature range of 22° to 24° C. This rub testing should also take place within the confines of the constant temperature and humidity room.

The Sutherland Rub Tester may be obtained from Testing Machines, Inc. (Amityville, N.Y., 1701). The tissue is first prepared by removing and discarding any product which might have been abraded in handling, e.g. on the outside of the roll. For multi-ply finished product, sufficient sections with each section containing two sheets of multi-ply product are removed to yield six sections of two-sheets each when separated. The plies of the multi-ply product are separated forming the six sections with each containing two sheets of single-ply product; the six sections are set on the bench-top. From this point forward, the individual plies of a multi-ply product are treated in the same manner as a single-ply product. For single-ply product, six sections with each containing two sheets of single-ply product are removed and set on the bench-top. Each sample is then folded in half such that the crease is running along the cross direction (CD) of the tissue sample. Make up 3 samples with the fabric-side surface "out" and 3 with the opposite-side surface "out". Keep track of which samples are fabric-side surface "out" and which are opposite-side surface out.

Obtain a 30"x40" piece of Crescent #300 cardboard from Cordage Inc. (8001 E. Ross Road, Cincinnati, Ohio, 45217). Using a paper cutter, cut out six pieces of cardboard of dimensions of 2.5"x6". Puncture two holes into each of the six cards by forcing the cardboard onto the hold down pins of the Sutherland Rub tester.

Center and carefully place each of the 2.5"x6" cardboard pieces on top of the six previously folded samples. Make sure the 6" dimension of the cardboard is running parallel to the machine direction (MD) of each of the tissue samples. Center and carefully place each of the cardboard pieces on top of the three previously folded samples. Once again, make sure the 6" dimension of the cardboard is running parallel to the machine direction (MD) of each of the tissue samples.

55 Fold one edge of the exposed portion of tissue sample onto the back of the cardboard. Secure this edge to the cardboard with adhesive tape obtained from 3M Inc. (1/4" wide Scotch Brand, St. Paul, Minn.). Carefully grasp the other over-hanging tissue edge and snugly fold it over onto the back of the cardboard. While maintaining a snug fit of the paper onto the board, tape this second edge to the back of the cardboard. Repeat this procedure for each sample.

65 Turn over each sample and tape the cross direction edge of the tissue paper to the cardboard. One half of the adhesive tape should contact the tissue paper while the other half is adhering to the cardboard. Repeat this procedure for each of

the samples. If the tissue sample breaks, tears, or becomes frayed at any time during the course of this sample preparation procedure, discard and make up a new sample with a new tissue sample strip.

There will now be 3 fabric-side surface "out" samples on cardboard and 3 opposite-side surface "out" samples on cardboard.

FELT PREPARATION

Obtain a 30"x40" piece of Crescent #300 cardboard from Cordage Inc. (800 E. Ross Road, Cincinnati, Ohio, 45217). Using a paper cutter, cut out six pieces of cardboard of dimensions of 2.25"x7.25". Draw two lines parallel to the short dimension and down 1.125" from the top and bottom most edges on the white side of the cardboard. Carefully score the length of the line with a razor blade using a straight edge as a guide. Score it to a depth about half way through the thickness of the sheet. This scoring allows the cardboard/felt combination to fit tightly around the weight of the Sutherland Rub Tester. Draw an arrow running parallel to the long dimension of the cardboard on this scored side of the cardboard.

Cut the six pieces of black felt (1'-55 or equivalent from New England Gasket, 550 Broad Street, Bristol, Conn. 06010) to the dimensions of 2.25"x8.5"x0.0625". Place the felt on top of the unscored, green side of the cardboard such that the long edges of both the felt and cardboard are parallel and in alignment. Make sure the fluffy side of the felt is facing up. Also allow about 0.5" to overhang the top and bottom most edges of the cardboard. Snugly fold over both overhanging felt edges onto the backside of the cardboard with Scotch brand tape. Prepare a total of six of these felt/cardboard combinations.

For best reproducibility, all samples should be run with the same lot of felt. Obviously, there are occasions where a single lot of felt becomes completely depleted. In those cases where a new lot of felt must be obtained, a correction factor should be determined for the new lot of felt. To determine the correction factor, obtain a representative single tissue sample of interest, and enough felt to make up 24 cardboard/felt samples for the new and old lots.

As described below and before any rubbing has taken place, obtain Hunter L readings for each of the 24 cardboard/felt samples of the new and old lots of felt. Calculate the averages for both the 24 cardboard/felt samples of the old lot and the 24 cardboard/felt samples of the new lot.

Next, rub test the 24 cardboard/felt boards of the new lot and the 24 cardboard/felt boards of the old lot as described below. Make sure the same tissue lot number is used for each of the 24 samples for the old and new lots. In addition, sampling of the paper in the preparation of the cardboard/tissue samples must be done so the new lot of felt and the old lot of felt are exposed to as representative as possible of a tissue sample. Discard any product which might have been damaged or abraded. Next, obtain 48 strips of tissue each two usable units (also termed sheets) long. Place the first two usable unit strip on the far left of the lab bench and the last of the 48 samples on the far right of the bench. Mark the sample to the far left with the number "1" in a 1 cm by 1 cm area of the corner of the sample. Continue to mark the samples consecutively up to 48 such that the last sample to the far right is numbered 48.

Use the 24 odd numbered samples for the new felt and the 24 even numbered samples for the old felt. Order the odd number samples from lowest to highest. Order the even numbered samples from lowest to highest. Now, mark the lowest number for each set with a letter "I." Mark the next highest number with the letter "O." Continue marking the

samples in this alternating "I"/"O" pattern. Use the "I" samples for fabric-side surface "out" lint analyses and the "O" samples for opposite-side surface "out" lint analyses. There are now a total of 24 samples for the new lot of felt and the old lot of felt. Of this 24, twelve are for fabric-side surface "out" lint analysis and 12 are for opposite-side surface "out" lint analysis.

Rub and measure the Hunter Color L values for all 24 samples of the old felt as described below. Record the 12 fabric-side surface Hunter Color L values for the old felt. Average the 12 values. Record the 12 opposite-side surface Hunter Color L values for the old felt. Average the 12 values. Subtract the average initial un-rubbed Hunter Color L felt reading from the average Hunter Color L reading for the fabric-side surface rubbed samples. This is the delta average difference for the fabric-side surface samples. Subtract the average initial un-rubbed Hunter Color L felt reading from the average Hunter Color L reading for the opposite-side surface rubbed samples. This is the delta average difference for the opposite-side surface samples. Calculate the sum of the delta average difference for the fabric-side surface and the delta average difference for the opposite-side surface and divide this sum by 2. This is the uncorrected lint value for the old felt. If there is a current felt correction factor for the old felt, add it to the uncorrected lint value for the old felt. This value is the corrected Lint Value for the old felt.

Rub and measure the Hunter Color L values for all 24 samples of the new felt as described below. Record the 12 fabric-side surface Hunter Color L values for the new felt. Average the 12 values. Record the 12 opposite-side surface Hunter Color L values for the new felt. Average the 12 values. Subtract the average initial un-rubbed Hunter Color L felt reading from the average Hunter Color L reading for the fabric-side surface rubbed samples. This is the delta average difference for the fabric-side surface samples. Subtract the average initial un-rubbed Hunter Color L felt reading from the average Hunter Color L reading for the opposite-side surface rubbed samples. This is the delta average difference for the opposite-side surface samples. Calculate the sum of the delta average difference for the fabric-side surface and the delta average difference for the opposite-side surface and divide this sum by 2. This is the uncorrected lint value for the new felt.

Take the difference between the corrected Lint Value from the old felt and the uncorrected lint value for the new felt. This difference is the felt correction factor for the new lot of felt.

Adding this felt correction factor to the uncorrected lint value for the new felt should be identical to the corrected Lint Value for the old felt.

CARE OF 4 POUND WEIGHT

The four pound weight has four square inches of effective contact area providing a contact pressure of one pound per square inch. Since the contact pressure can be changed by alteration of the rubber pads mounted on the face of the weight, it is important to use only the rubber pads supplied by the manufacturer (Brown Inc., Mechanical Services Department, Kalamazoo, Mich.). These pads must be replaced if they become hard, abraded or chipped off.

When not in use, the weight must be positioned such that the pads are not supporting the full weight of the weight. It is best to store the weight on its side.

RUB TESTER INSTRUMENT CALIBRATION

The Sutherland Rub Tester must first be calibrated prior to use. First, turn on the Sutherland Rub Tester by moving the tester switch to the "on" position. When the tester arm is in its position closest to the user, turn the tester's switch to

the "auto" position. Set the tester to run 5 strokes by moving the pointer arm on the large dial to the "five" position setting. One stroke is a single and complete forward and reverse motion of the weight. The end of the rubbing block should be in the position closest to the operator at the beginning and at the end of each test.

Prepare a tissue paper on cardboard sample as described above. In addition, prepare a felt on cardboard sample as described above. Both of these samples will be used for calibration of the instrument and will not be used in the acquisition of data for the actual samples.

Place this calibration tissue sample on the base plate of the tester by slipping the holes in the board over the hold-down pins. The hold-down pins prevent the sample from moving during the test. Clip the calibration felt/cardboard sample onto the four pound weight with the cardboard side contacting the pads of the weight. Make sure the cardboard/felt combination is resting flat against the weight. Hook this weight onto the tester arm and gently place the tissue sample underneath the weight/felt combination. The end of the weight closest to the operator must be over the cardboard of the tissue sample and not the tissue sample itself. The felt must rest flat on the tissue sample and must be in 100% contact with the tissue surface. Activate the tester by depressing the "push" button.

Keep a count of the number of strokes and observe and make a mental note of the starting and stopping position of the felt covered weight in relationship to the sample. If the total number of strokes is five and if the end of the felt covered weight closest to the operator is over the cardboard of the tissue sample at the beginning and end of this test, the tester is calibrated and ready to use. If the total number of strokes is not five or if the end of the felt covered weight closest to the operator is over the actual paper tissue sample either at the beginning or end of the test, repeat this calibration procedure until 5 strokes are counted the end of the felt covered weight closest to the operator is situated over the cardboard at the both the start and end of the test.

During the actual testing of samples, monitor and observe the stroke count and the starting and stopping point of the felt covered weight. Recalibrate when necessary.

HUNTER COLOR METER CALIBRATION

Adjust the Hunter Color Difference Meter for the black and white standard plates according to the procedures outlined in the operation manual of the instrument. Also run the stability check for standardization as well as the daily color stability check if this has not been done during the past eight hours. In addition, the zero reflectance must be checked and readjusted if necessary.

Place the white standard plate on the sample stage under the instrument port. Release the sample stage and allow the sample plate to be raised beneath the sample port.

Using the "L-Y", "a-X", and "b-Z" standardizing knobs, adjust the instrument to read the Standard White Plate Values of "L", "a", and "b" when the "L", "a", and "b" push buttons are depressed in turn.

MEASUREMENT OF SAMPLES

The first step in the measurement of lint is to measure the Hunter color values of the black felt/cardboard samples prior to being rubbed on the toilet tissue. The first step in this measurement is to lower the standard white plate from under the instrument port of the Hunter color instrument. Center a felt covered cardboard, with the arrow pointing to the back of the color meter, on top of the standard plate. Release the sample stage, allowing the felt covered cardboard to be raised under the sample port.

Since the felt width is only slightly larger than the viewing area diameter, make sure the felt completely covers the

viewing area. After confirming complete coverage, depress the L push button and wait for the reading to stabilize. Read and record this L value to the nearest 0.1 unit.

If a D25D2A head is in use, lower the felt covered cardboard and plate, rotate the felt covered cardboard 90 degrees so the arrow points to the right side of the meter. Next, release the sample stage and check once more to make sure the viewing area is completely covered with felt. Depress the L push button. Read and record this value to the nearest 0.1 unit. For the D25D2M unit, the recorded value is the Hunter Color L value. For the D25D2A head where a rotated sample reading is also recorded, the Hunter Color L value is the average of the two recorded values.

Measure the Hunter Color L values for all of the felt covered cardboards using this technique. If the Hunter Color L values are all within 0.3 units of one another, take the average to obtain the initial L reading. If the Hunter Color L values are not within the 0.3 units, discard these felt/cardboard combinations outside the limit. Prepare new samples and repeat the Hunter Color L measurement until all samples are within 0.3 units of one another.

For the measurement of the actual tissue paper/cardboard combinations, place the tissue sample/cardboard combination on the base plate of the tester by slipping the holes in the board over the hold-down pins. The hold-down pins prevent the sample from moving during the test. Clip the calibration felt/cardboard sample onto the four pound weight with the cardboard side contacting the pads of the weight. Make sure the cardboard/felt combination is resting flat against the weight. Hook this weight onto the tester arm and gently place the tissue sample underneath the weight/felt combination. The end of the weight closest to the operator must be over the cardboard of the tissue sample and not the tissue sample itself. The felt must rest flat on the tissue sample and must be in 100% contact with the tissue surface.

Next, activate the tester by depressing the "push" button. At the end of the five strokes the tester will automatically stop. Note the stopping position of the felt covered weight in relation to the sample. If the end of the felt covered weight toward the operator is over cardboard, the tester is operating properly. If the end of the felt covered weight toward the operator is over sample, disregard this measurement and recalibrate as directed above in the Sutherland Rub Tester Calibration section.

Remove the weight with the felt covered cardboard. Inspect the tissue sample. If torn, discard the felt and tissue and start over. If the tissue sample is intact, remove the felt covered cardboard from the weight. Determine the Hunter Color L value on the felt covered cardboard as described above for the blank felts. Record the Hunter Color L readings for the felt after rubbing. Rub, measure, and record the Hunter Color L values for all remaining samples.

After all tissues have been measured, remove and discard all felt. Felts strips are not used again. Cardboards are used until they are bent, torn, limp, or no longer have a smooth surface.

CALCULATIONS

Determine the delta L values by subtracting the average initial L reading found for the unused felts from each of the measured values for the fabric-side surface and opposite-side surface sides of the sample as follows. Subtract the average initial L reading found for the unused felts from each of the three fabric-side surface L readings and each of the three opposite-side surface L readings. Calculate the average delta for the three fabric-side surface values. Calculate the average delta for the three opposite-side surface side values. Subtract the felt factor from each of these

averages. The final results are termed a lint for the fabric-side surface and a lint for the opposite-side surface of the tissue web. By taking a ratio of the lint value on the opposite-side compared to the value on the fabric-side surface, the "lint ratio" is obtained. In other words, to calculate the lint ratio, the following formula is used:

$$\text{Lint Ratio} = \frac{\text{Lint Value, opposite-side surface}}{\text{Lint Value, fabric-side surface}}$$

By taking the average of the lint value on the fabric-side surface and the opposite-side surface, an ultimate lint is obtained for the overall tissue web. In other words, to calculate the ultimate lint, the following formula is used:

$$\text{Ultimate Lint} = \frac{\text{Lint Value, fabric-side} + \text{Lint Value, opposite-side}}{2}$$

F. Measurement of Panel Softness of Tissue Papers

Ideally, prior to softness testing, the paper samples to be tested should be conditioned according to Tappi Method #1402OM-88. Here, samples are preconditioned for 24 hours at a relative humidity level of 10 to 35% and within a temperature range of 22° to 40° C. After this preconditioning step, samples should be conditioned for 24 hours at a relative humidity of 48 to 52% and within a temperature range of 22° to 24° C.

Ideally, the softness panel testing should take place within the confines of a constant temperature and humidity room. If this is not feasible, all samples, including the controls, should experience identical environmental exposure conditions.

Softness testing is performed as a paired comparison in a form similar to that described in "Manual on Sensory Testing Methods", ASTM Special Technical Publication 434, published by the American Society For Testing and Materials 1968 and is incorporated herein by reference. Softness is evaluated by subjective testing using what is referred to as a Paired Difference Test. The method employs a standard external to the test material itself. For tactile perceived softness two samples are presented such that the subject cannot see the samples, and the subject is required to choose one of them on the basis of tactile softness. The result of the test is reported in what is referred to as Panel Score Unit (PSU). With respect to softness testing to obtain the softness data reported herein in PSU, a number of softness panel tests are performed. In each test ten practiced softness judges are asked to rate the relative softness of three sets of paired samples. The pairs of samples are judged one pair at a time by each judge: one sample of each pair being designated X and the other Y. Briefly, each X sample is graded against its paired Y sample as follows:

1. a grade of plus one is given if X is judged to may be a little softer than Y, and a grade of minus one is given if Y is judged to may be a little softer than X;
2. a grade of plus two is given if X is judged to surely be a little softer than Y, and a grade of minus two is given if Y is judged to surely be a little softer than X;
3. a grade of plus three is given to X if it is judged to be a lot softer than Y, and a grade of minus three is given if Y is judged to be a lot softer than X; and, lastly:
4. a grade of plus four is given to X if it is judged to be a whole lot softer than Y, and a grade of minus 4 is given if Y is judged to be a whole lot softer than X.

The grades are averaged and the resultant value is in units of PSU. The resulting data are considered the results of one

panel test. If more than one sample pair is evaluated then all sample pairs are rank ordered according to their grades by paired statistical analysis. Then, the rank is shifted up or down in value as required to give a zero PSU value in which ever sample is chosen to be the zero-base standard. The other samples then have plus or minus values as determined by their relative grades with respect to the zero base standard. The number of panel tests performed and averaged is such that about 0.2 PSU represents a significant difference in subjectively perceived softness.

G. Measurement of Strength of Tissue Papers DRY TENSILE STRENGTH

The tensile strength is determined on one inch wide strips of sample using a Thwing-Albert Intelect II Standard Tensile Tester (Thwing-Albert Instrument Co., 10960 Dutton Rd., Philadelphia, Pa., 19154). This method is intended for use on finished paper products, reel samples, and unconverted stocks.

SAMPLE CONDITIONING AND PREPARATION

Prior to tensile testing, the paper samples to be tested should be conditioned according to Tappi Method #1402OM-88. All plastic and paper board packaging materials must be carefully removed from the paper samples prior to testing. The paper samples should be conditioned for at least 2 hours at a relative humidity of 48 to 52% and within a temperature range of 22° to 24° C. Sample preparation and all aspects of the tensile testing should also take place within the confines of the constant temperature and humidity room.

For finished product, discard any damaged product. Next, remove 5 strips of four usable units (also termed sheets) and stack one on top to the other to form a long stack with the perforations between the sheets coincident. Identify sheets 1 and 3 for machine direction tensile measurements and sheets 2 and 4 for cross direction tensile measurements. Next, cut through the perforation line using a paper cutter (JDC-1-10 or JDC-1-12 with safety shield from Thwing-Albert Instrument Co., 10960 Dutton Road, Philadelphia, Pa., 19154) to make 4 separate stacks. Make sure stacks 1 and 3 are still identified for machine direction testing and stacks 2 and 4 are identified for cross direction testing.

Cut two 1" wide strips in the machine direction from stacks 1 and 3. Cut two 1" wide strips in the cross direction from stacks 2 and 4. There are now four 1" wide strips for machine direction tensile testing and four 1" wide strips for cross direction tensile testing. For these finished product samples, all eight 1" wide strips are five usable units (also termed sheets) thick.

For unconverted stock and/or reel samples, cut a 15" by 15" sample which is 8 plies thick from a region of interest of the sample using a paper cutter (JDC-1-10 or JDC-1-12 with safety shield from Thwing-Albert Instrument Co., 10960 Dutton Road, Philadelphia, Pa., 19154). Make sure one 15" cut runs parallel to the machine direction while the other runs parallel to the cross direction. Make sure the sample is conditioned for at least 2 hours at a relative humidity of 48 to 52% and within a temperature range of 22° to 24° C. Sample preparation and all aspects of the tensile testing should also take place within the confines of the constant temperature and humidity room.

From this preconditioned 15" by 15" sample which is 8 plies thick, cut four strips 1" by 7" with the long 7" dimension running parallel to the machine direction. Note these samples as machine direction reel or unconverted stock samples. Cut an additional four strips 1" by 7" with the long 7" dimension running parallel to the cross direction. Note these samples as cross direction reel or unconverted stock samples. Make sure all previous cuts are made using

a paper cutter (JDC-1-10 or JDC-1-12 with safety shield from Thwing-Albert Instrument Co., 10960 Dutton Road, Philadelphia, Pa., 19154). There are now a total of eight samples: four 1" by 7" strips which are 8 plies thick with the 7" dimension running parallel to the machine direction and four 1" by 7" strips which are 8 plies thick with the 7" dimension running parallel to the cross direction.

OPERATION OF TENSILE TESTER

For the actual measurement of the tensile strength, use a Thwing-Albert Intelect II Standard Tensile Tester (Thwing-Albert Instrument Co., 10960 Dutton Rd., Philadelphia, Pa., 19154). Insert the flat face clamps into the unit and calibrate the tester according to the instructions given in the operation manual of the Thwing-Albert Intelect II. Set the instrument crosshead speed to 4.00 in/min and the 1st and 2nd gauge lengths to 2.00 inches. The break sensitivity should be set to 20.0 grams and the sample width should be set to 1.00" and the sample thickness at 0.025".

A load cell is selected such that the predicted tensile result for the sample to be tested lies between 25% and 75% of the range in use. For example, a 5000 gram load cell may be used for samples with a predicted tensile range of 1250 grams (25% of 5000 grams) and 3750 grams (75% of 5000 grams). The tensile tester can also be set up in the 10% range with the 5000 gram load cell such that samples with predicted tensiles of 125 grams to 375 grams could be tested.

Take one of the tensile strips and place one end of it in one clamp of the tensile tester. Place the other end of the paper strip in the other clamp. Make sure the long dimension of the strip is running parallel to the sides of the tensile tester. Also make sure the strips are not overhanging to the either side of the two clamps. In addition, the pressure of each of the clamps must be in full contact with the paper sample.

After inserting the paper test strip into the two clamps, the instrument tension can be monitored. If it shows a value of 5 grams or more, the sample is too taut. Conversely, if a period of 2-3 seconds passes after starting the test before any value is recorded, the tensile strip is too slack.

Start the tensile tester as described in the tensile tester instrument manual. The test is complete after the crosshead automatically returns to its initial starting position. Read and record the tensile load in units of grams from the instrument scale or the digital panel meter to the nearest unit.

If the reset condition is not performed automatically by the instrument, perform the necessary adjustment to set the instrument clamps to their initial starting positions. Insert the next paper strip into the two clamps as described above and obtain a tensile reading in units of grams. Obtain tensile readings from all the paper test strips. It should be noted that readings should be rejected if the strip slips or breaks in or at the edge of the clamps while performing the test.

CALCULATIONS

For the four machine direction 1" wide finished product strips, sum the four individual recorded tensile readings. Divide this sum by the number of strips tested. This number should normally be four. Also divide the sum of recorded tensiles by the number of usable units per tensile strip. This is normally five for both 1-ply and 2-ply products.

Repeat this calculation for the cross direction finished product strips.

For the unconverted stock or reel samples cut in the machine direction, sum the four individual recorded tensile readings. Divide this sum by the number of strips tested. This number should normally be four. Also divide the sum of recorded tensiles by the number of usable units per tensile strip. This is normally eight.

Repeat this calculation for the cross direction unconverted or reel sample paper strips.

All results are in units of grams/inch.

For purposes of this specification, the tensile strength should be converted into a "specific total tensile strength" defined as the sum of the tensile strength measured in the machine and cross machine directions, divided by the basis weight, and corrected in units to a value in meters.

EXAMPLES

The following examples are offered to illustrate the practice of the present invention. These examples are intended to aid in the description of the present invention, but, in no way, should be interpreted as limiting the scope thereof. The present invention is bounded only by the appended claims.

Example 1

This comparative Example illustrates a reference process for forming a filled tissue paper, not incorporating the features of the present invention.

This process is illustrated in the following steps:

An aqueous slurry of eucalyptus fibers of about 3% by weight is made up using a conventional repulper. Cypro 514® is added to the slurry at a rate of 0.02% based on the dry weight of the Cypro 514 relative to the finished dry weight of the creped tissue paper. The treated slurry is then carried through a stock pipe toward the paper machine.

The particulate filler is kaolin clay, grade WW Fil Slurry®, made by Dry Branch Kaolin of Dry Branch, Ga. It is delivered as a slurry at 70% solids through a stock pipe where it is mixed with an anionic flocculent, Accurac 62®, which is delivered as a 0.3% dispersion in water. Accurac 62® is conveyed at a rate equivalent to about 0.5% based on the amount of solid weight of the flocculant and finished dry weight of the resultant creped tissue product. The adsorption of the flocculant is promoted by passing the mixture through an in line mixer. This forms a conditioned slurry of filler particles.

The conditioned slurry of filler particles is then mixed into the stock pipe carrying the refined eucalyptus fibers.

The eucalyptus fiber and particulate filler mixture is divided into two separate flows in a proportion such that the flow whose fate will ultimately be to comprise the fabric-side surface contains about twice the mass as the flow whose fate will ultimately be to comprise the opposite side surface. The eucalyptus flows are directed toward the paper machine. Each flow stream is then treated with a cationic starch RediBOND 5320®, which is delivered as a 1% dispersion in water. The flow which will ultimately form the fabric-side surface layer is treated with the starch at a rate of 0.15% based on the dry weight of starch and the finished dry weight of the resultant creped tissue product. The flow which will ultimately form the opposite-side surface layer is treated with the starch at a rate of 0.05% based on the dry weight of starch and the finished dry weight of the resultant creped tissue product.

Absorption of the cationic starch is improved by passing the resultant mixture through an in line mixer. The resultant slurries are then each diluted with white water at the inlet of their respective fan pumps to a consistency of about 0.2% based on the weight of the solid filler particles and eucalyptus fibers. After the fan pumps carrying the combination of agglomerated filler particles and eucalyptus fibers, additional Accurac 62®, diluted to a concentration of about 0.05% solids, is added to each of the mixtures at a rate corresponding to about 0.013% based on the solids weight of the filler and eucalyptus fiber.

A bond inhibiting composition is prepared by melting together a mixture of equal amounts of Varisoft 137® and Polyethylene glycol 400 at a temperature of about 88° C. The melted mixture is then changed into an agitated water-stream at a temperature of about 66° C. to a concentration of about 2%, based on the Varisoft content. The bond inhibiting composition is added to one of the eucalyptus and particulate fiber slurry flows such that it is added to the flow which will ultimately form the layer comprising the fabric-side surface layer. An amount of the bond inhibiting composition is added to comprise approximately 0.2% based on the Varisoft 137® weight compared to the dry weight of the finished tissue.

An aqueous slurry of NSK of about 3% consistency is made up using a conventional pulper and is passed through a stock pipe toward the headbox of the Fourdrinier.

In order to impart a temporary wet strength to the finished product, a 1% dispersion of Parex 750® is prepared and is added to the NSK stock pipe at a rate sufficient to deliver 1.38% Parex 750® based on the dry weight of the NSK fibers. The absorption of the temporary wet strength resin is enhanced by passing the treated slurry through an in-line mixer. To impart additional dry strength, the NSK slurry is also then treated with a cationic starch, RediBOND 5320®, which is delivered as a 1% dispersion in water. The starch is used at a rate of 0.15% based on the dry weight of starch and the finished dry weight of the resultant creped tissue product. The absorption of the temporary wet strength resin is enhanced by passing the treated slurry through an in-line mixer.

The NSK slurry is diluted with white water to about 0.2% consistency at the fan pump. After the fan pump, additional Accurac 62®, diluted to a concentration of about 0.05% solids, is added to the mixture at a rate corresponding to about 0.065% based on the solids weight of the filler and the NSK fiber.

The slurries of NSK and eucalyptus are directed into a multi-chambered headbox suitably equipped with layering leaves to maintain the streams as separate layers until discharge onto a traveling Fourdrinier wire. A three-chambered headbox is used. The combined eucalyptus and particulate filler containing sufficient solids flow to achieve 80% of the dry weight of the ultimate paper is directed to chambers leading to each of the two outer layers, while the NSK slurry comprising sufficient solids flow to achieve 20% of the dry weight of the ultimate paper is directed to a chamber leading to a layer between the two eucalyptus layers. The NSK and eucalyptus slurries are combined at the discharge of the headbox into a composite slurry. The flows to the two outer chambers of the headbox are controlled to cause about twice as much of the mass of the eucalyptus slurry to be directed to the fabric-side surface layer as to the opposite-side surface layer.

The composite slurry is discharged onto the traveling Fourdrinier wire and is dewatered assisted by a deflector and vacuum boxes.

The embryonic wet web is transferred from the Fourdrinier wire, at a fiber consistency of about 15% at the point of transfer, to a patterned drying fabric. The drying fabric is designed to yield a pattern densified tissue with discontinuous low-density deflected areas arranged within a continuous network of high density (knuckle) areas. This drying fabric is formed by casting an impervious resin surface onto a fiber mesh supporting fabric. The supporting fabric is a 45x72 filament, three layer mesh with a fiber support index of 95. The thickness of the resin cast is about 4.5 mil. The

knuckle area is about 35% and the open cells remain at a frequency of about 78 per square inch.

Further de-watering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%.

While remaining in contact with the patterned forming fabric, the patterned web is pre-dried by air blow-through to a fiber consistency of about 62% by weight.

The semi-dry web is then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising a 0.125% aqueous solution of polyvinyl alcohol. The creping adhesive is delivered to the Yankee surface at a rate of 0.1 adhesive solids based on the dry weight of the web.

The fiber consistency is increased to about 96% before the web is dry creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees.

The percent crepe is adjusted to about 18% by operating the Yankee dryer at about 800 fpm (feet per minute) (about 244 meters per minute), while the dry web is formed into roll at a speed of 656 fpm (200 meters per minutes).

The web is converted into a three-layer, single-ply creped patterned densified tissue paper product of about 19 lb per 3000 ft² basis weight.

Example 2

This Example illustrates preparation of a filled tissue paper exhibiting one embodiment of the present invention.

An aqueous slurry of eucalyptus fibers of about 3% by weight is made up using a conventional repulper. Cypro 514® is added to the slurry at a rate of 0.02% based on the dry weight of the Cypro 514 relative to the finished dry weight of the creped tissue paper. The treated slurry is then carried through a stock pipe toward the paper machine.

The particulate filler is kaolin clay, grade WW Fil Slurry®, made by Dry Branch Kaolin of Dry Branch, Ga. It is delivered as a slurry at 70% solids through a stock pipe where it is mixed with an anionic flocculant, Accurac 62, which is delivered as a 0.3% dispersion in water. Accurac 62® is conveyed at a rate equivalent to about 0.05% based on the amount of solid weight of the flocculant and finished dry weight of the resultant creped tissue product. The absorption of the flocculant is promoted by passing the mixture through an in line mixer. This forms a conditioned slurry of filler particles.

The agglomerated slurry of filler particles is then mixed into the stock pipe carrying the refined eucalyptus fibers.

The eucalyptus fiber and particulate filler mixture is divided into two separate flows in a proportion such that the flow whose fate will ultimately be to comprise the fabric-side surface contains about twice the mass as the flow whose fate will ultimately be to comprise the opposite side surface. The eucalyptus flows are directed toward the papermachine. Each flow stream is then treated with a cationic starch RediBOND 5320®, which is delivered as a 1% dispersion in water. The flow which will ultimately form the fabric-side surface layer is treated with the starch at a rate of 0.05% based on the dry weight of starch and the finished dry weight of the resultant creped tissue product. The flow which will ultimately form the opposite-side surface layer is treated with the starch at a rate of 0.05% based on the dry weight of starch and the finished dry weight of the resultant creped tissue product. Absorption of the cationic starch is improved by passing the resultant mixture through an in line mixer. The resultant slurries are then each diluted with white water

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an in line mixer. The resultant slurry is then diluted with white water at the inlet of a fan pump to a consistency of about 0.2% based on the weight of the solid filler particles and eucalyptus fibers. After the fan pump carrying the combination of agglomerated filler particles and eucalyptus fibers, additional Accurac 620, diluted to a concentration of about 0.05% solids, is added to the mixture at a rate corresponding to about 0.013% based on the solids weight of the filler and eucalyptus fiber.

The other stock pipe carrying eucalyptus fibers is treated with a cationic starch, RediBOND 52300, which is delivered as a 1% dispersion in water and at a rate of 0.05% based on the dry weight of starch and the finished dry weight of the resultant creped tissue product. Absorption of the cationic starch is improved by passing the resultant mixture through an in line mixer. The stream is then diluted with white water at the inlet of a fan pump to a consistency of about 0.2% based on the weight of the solid filler particles and eucalyptus fibers. After the fan pump carrying the combination of agglomerated filler particles and eucalyptus fibers, additional Accurac 620, diluted to a concentration of about 0.05% solids, is added to the mixture at a rate corresponding to about 0.065% based on the solids weight of the eucalyptus fiber.

An aqueous slurry of NSK of about 3% consistency is made up using a conventional pulper and is passed through a stock pipe toward the headbox of the Fourdrinier.

In order to impart a temporary wet strength to the finished product, a 1% dispersion of Parex 7500 is prepared and is added to the NSK stock pipe at a rate sufficient to deliver 1.25% Parex 7500 based on the dry weight of the NSK fibers. The absorption of the temporary wet strength resin is enhanced by passing the treated slurry through an in-line mixer. To impart additional dry strength, the NSK slurry is also then treated with a cationic starch, RediBOND 52300, which is delivered as a 1% dispersion in water. The starch is used at a rate of 0.1% based on the dry weight of starch and the finished dry weight of the resultant creped tissue product. The absorption of the temporary wet strength resin is enhanced by passing the treated slurry through an in-line mixer.

The NSK slurry is diluted with white water to about 0.2% consistency at the fan pump. After the fan pump, additional Accurac 620, diluted to a concentration of about 0.05% solids, is added to the mixture at a rate corresponding to about 0.013% based on the solids weight of the filler and the NSK fiber.

The three slurries (NSK, eucalyptus mixed with filler, and eucalyptus without filler) are directed into a multi-channeled headbox suitably equipped with layering leaves to maintain the streams as separate layers until discharge onto a traveling Fourdrinier wire. A three-chambered headbox is used. The slurry of eucalyptus without particulate filler is directed to the chamber discharging closest to the forming wire surface. The slurry containing the NSK is directed to the center chamber, and the slurry of combined eucalyptus and particulate filler is directed to the outer layer chamber furthest away from the forming wire surface. The NSK slurry comprising sufficient solids flow to achieve about 20% of the dry weight of the ultimate paper. The flows to the two outer chambers of the headbox are controlled to direct twice as much of the mass of the eucalyptus slurry containing particulate filler to be directed to the fabric-side surface layer compared to the eucalyptus slurry free of particulate fillers being directed to the opposite-side surface layer. The slurries are combined at the discharge of the headbox into a com-

posite slurry. The composite slurry is discharged onto the traveling Fourdrinier wire and is dewatered assisted by a deflector and vacuum boxes.

The embryonic wet web is transferred from the Fourdrinier wire, at a fiber consistency of about 15% at the point of transfer, to a patterned drying fabric. The drying fabric is designed to yield a pattern densified tissue with discontinuous low-density deflected areas arranged within a continuous network of high density (knuckle) areas. This drying fabric is formed by casting an impervious resin surface onto a fiber mesh supporting fabric. The supporting fabric is a 45x72 filament, three layer mesh with a fiber support index of 95. The thickness of the resin cast is about 4.5 mil. The knuckle area is about 35% and the open cells remain at a frequency of about 78 per square inch.

Further de-watering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%.

While remaining in contact with the patterned forming fabric, the patterned web is pre-dried by air blow-through to a fiber consistency of about 62% by weight.

The semi-dry web is then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising a 0.125% aqueous solution of polyvinyl alcohol. The creping adhesive is delivered to the Yankee surface at a rate of 0.1% adhesive solids based on the dry weight of the web.

The fiber consistency is increased to about 96% before the web is dry creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees.

The percent crepe is adjusted to about 18% by operating the Yankee dryer at about 800 fpm (feet per minute) (about 244 meters per minute), while the dry web is formed into roll at a speed of 656 fpm (200 meters per minutes).

The web is converted into a three-layer, single-ply creped patterned densified tissue paper product of about 19 lb per 3000 ft² basis weight.

	Example 1	Example 2	Example 3
Kaolin content %	8.2%	8.3%	8.7%
Kaolin Retention (Overall) %	85%	85%	95%
Specific Total Tensile Strength (meters)	0.500	0.480	0.490
Opposite-Side Surface Lin	9.2	6.0	6.2
Fabric-Side Surface Lin	9.4	12.0	11.9
Lin Ratio	0.98	0.47	0.52
Ultimate Lin	9.3	9.4	8.9
Number Softness Relative score	0.0	+0.2	+0.2

What is claimed is:

1. A strong, soft and low dusting filled tissue paper having a density less than about 0.60 grams per cubic centimeter and comprising three superposed layers, an inner layer, a fabric-side surface outer layer, and an opposite-side surface outer layer, said inner layer being located between two said outer layers, wherein each of said layers comprises paper-making fibers and a non-cellulosic particulate filler, wherein said particulate filler is selected from the group consisting of clay, calcium carbonate, titanium dioxide, talc, aluminum silicate, calcium silicate, alumina trihydrates, activated carbon, calcium sulfate, glass microspheres, diatomaceous

an in line mixer. The resultant slurry is then diluted with white water at the inlet of a fan pump to a consistency of about 0.2% based on the weight of the solid filler particles and eucalyptus fibers. After the fan pump carrying the combination of agglomerated filler particles and eucalyptus fibers, additional Accurac 620, diluted to a concentration of about 0.05% solids, is added to the mixture at a rate corresponding to about 0.013% based on the solids weight of the filler and eucalyptus fiber.

The other stock pipe carrying eucalyptus fibers is treated with a cationic starch, RediBOND 52300, which is delivered as a 1% dispersion in water and at a rate of 0.05% based on the dry weight of starch and the finished dry weight of the resultant creped tissue product. Absorption of the cationic starch is improved by passing the resultant mixture through an in line mixer. The stream is then diluted with white water at the inlet of a fan pump to a consistency of about 0.2% based on the weight of the solid filler particles and eucalyptus fibers. After the fan pump carrying the combination of agglomerated filler particles and eucalyptus fibers, additional Accurac 620, diluted to a concentration of about 0.05% solids, is added to the mixture at a rate corresponding to about 0.065% based on the solids weight of the eucalyptus fiber.

An aqueous slurry of NSK of about 3% consistency is made up using a conventional pulper and is passed through a stock pipe toward the headbox of the Fourdrinier.

In order to impart a temporary wet strength to the finished product, a 1% dispersion of Parex 7500 is prepared and is added to the NSK stock pipe at a rate sufficient to deliver 1.25% Parex 7500 based on the dry weight of the NSK fibers. The absorption of the temporary wet strength resin is enhanced by passing the treated slurry through an in-line mixer. To impart additional dry strength, the NSK slurry is also then treated with a cationic starch, RediBOND 52300, which is delivered as a 1% dispersion in water. The starch is used at a rate of 0.1% based on the dry weight of starch and the finished dry weight of the resultant creped tissue product. The absorption of the temporary wet strength resin is enhanced by passing the treated slurry through an in-line mixer.

The NSK slurry is diluted with white water to about 0.2% consistency at the fan pump. After the fan pump, additional Accurac 620, diluted to a concentration of about 0.05% solids, is added to the mixture at a rate corresponding to about 0.013% based on the solids weight of the filler and the NSK fiber.

The three slurries (NSK, eucalyptus mixed with filler, and eucalyptus without filler) are directed into a multi-channelled headbox suitably equipped with layering leaves to maintain the streams as separate layers until discharge onto a traveling Fourdrinier wire. A three-chambered headbox is used. The slurry of eucalyptus without particulate filler is directed to the chamber discharging closest to the forming wire surface. The slurry containing the NSK is directed to the center chamber, and the slurry of combined eucalyptus and particulate filler is directed to the outer layer chamber furthest away from the forming wire surface. The NSK slurry comprising sufficient solids flow to achieve about 20% of the dry weight of the ultimate paper. The flows to the two outer chambers of the headbox are controlled to direct twice as much of the mass of the eucalyptus slurry containing particulate filler to be directed to the fabric-side surface layer compared to the eucalyptus slurry free of particulate fillers being directed to the opposite-side surface layer. The slurries are combined at the discharge of the headbox into a com-

posite slurry. The composite slurry is discharged onto the traveling Fourdrinier wire and is dewatered assisted by a deflector and vacuum boxes.

The embryonic wet web is transferred from the Fourdrinier wire, at a fiber consistency of about 15% at the point of transfer, to a patterned drying fabric. The drying fabric is designed to yield a pattern densified tissue with discontinuous low-density deflected areas arranged within a continuous network of high density (knuckle) areas. This drying fabric is formed by casting an impervious resin surface onto a fiber mesh supporting fabric. The supporting fabric is a 45x72 filament, three layer mesh with a fiber support index of 95. The thickness of the resin cast is about 4.5 mil. The knuckle area is about 35% and the open cells remain at a frequency of about 78 per square inch.

Further de-watering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%.

While remaining in contact with the patterned forming fabric, the patterned web is pre-dried by air blow-through to a fiber consistency of about 62% by weight.

The semi-dry web is then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising a 0.125% aqueous solution of polyvinyl alcohol. The creping adhesive is delivered to the Yankee surface at a rate of 0.1% adhesive solids based on the dry weight of the web.

The fiber consistency is increased to about 96% before the web is dry creped from the Yankee with a doctor blade.

The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees.

The percent crepe is adjusted to about 18% by operating the Yankee dryer at about 800 fpm (feet per minute) (about 244 meters per minute), while the dry web is formed into roll at a speed of 656 fpm (200 meters per minutes).

The web is converted into a three-layer, single-ply creped patterned densified tissue paper product of about 19 lb per 3000 ft² basis weight.

	Example 1	Example 2	Example 3
Kaolin content %	8.2%	8.2%	8.7%
Kaolin Retention	89%	85%	93%
(Overall) %			
Specific Total	0.500	0.488	0.490
Tensile Strength			
(meters)			
Opposite-Side	9.2	8.0	6.2
Surface Lin			
Fabric-Side Surface	9.4	12.9	11.0
List			
List Ratio	0.98	0.47	0.52
Ultimate List	9.3	9.4	8.9
Number			
Softness Relative	0.0	+0.2	+0.2
score			

What is claimed is:

1. A strong, soft and low dusting filled tissue paper having a density less than about 0.60 grams per cubic centimeter and comprising three superposed layers, an inner layer, a fabric-side surface outer layer, and an opposite-side surface outer layer, said inner layer being located between two said outer layers, wherein each of said layers comprises paper-making fibers and a non-cellulosic particulate filler, wherein said particulate filler is selected from the group consisting of clay, calcium carbonate, titanium dioxide, talc, aluminum silicate, calcium silicate, alumina trihydrate, activated carbon, calcium sulfate, glass microspheres, diatomaceous

earth, and mixtures thereof and more than about one half of said particulate filler is located in at least one of said outer layers, said outer layers further comprising hardwood fibers having an average length less than about 1.0 mm and one or more retention aids, said retention aids being selected from the group consisting of cationic starches, cationic flocculant polymers, anionic flocculant polymers, and mixtures thereof, said tissue paper having controlled bonding in at least one of said outer layers so as to provide biased surface bonding properties such that the lint ratio is less than about 0.8.

2. The filled tissue paper of claim 1 wherein said tissue paper has a basis weight between about 10 g/m² and about 50 g/m² and a density between about 0.03 g/cm³ and about 0.6 g/cm³.

3. The filled tissue paper of claim 2 wherein said tissue paper has a basis weight between about 10 g/m² and about 30 g/m² and a density between 0.05 g/cm³ and 0.2 g/cm³.

4. The filled tissue paper of claim 3 wherein said particulate filler comprises from about 5% to about 50% by weight of said tissue paper.

5. The tissue paper of claim 3 wherein said papermaking fibers comprise a blend of hardwood fibers and softwood fibers, said hardwood fibers comprising at least about 50% and said softwood fibers comprising at least about 10% of said papermaking fibers.

6. The tissue paper of claim 5 wherein said inner layer comprises softwood fibers having an average length greater than at least about 2.0 mm.

7. The tissue paper of claim 6 wherein the said fabric-side surface outer layer contains from about 50% to about 100% greater mass than said opposite-side surface outer layer.

8. The tissue paper of claim 7 wherein the said fine particulate filler is located predominantly in the fabric-side surface outer layer.

9. The tissue paper of claim 8 wherein the softwood fibers comprise northern softwood Kraft fibers and the hardwood fibers comprise eucalyptus Kraft fibers.

10. The tissue paper of claim 9 wherein said particulate filler is kaolin clay.

11. The tissue paper of claim 1 wherein said lint ratio is less than about 0.6.

12. The tissue paper of claim 11 wherein a bond inhibiting agent is added to the fabric-side surface layer.

13. The tissue paper of claim 12 wherein said bond inhibiting agent is di(hydrogenated)tallow dimethyl ammonium methyl sulfate.

14. The tissue paper of claim 13 wherein the said fabric-side surface outer layer contains from about 50% to about 100% greater mass than said opposite-side surface outer layer.

15. The tissue paper of claim 14 wherein said particulate filler is kaolin clay.

16. The tissue paper of claim 15 wherein said tissue paper is pattern densified paper such that zones of relatively high density are dispersed within a high bulk field.

17. The tissue paper of claim 16 wherein said zones of relatively high density are continuous and the high bulk field is discrete.

18. The tissue paper of claim 17 wherein said discrete high bulk field constitutes less than about 150 discrete regions per square inch of area of said tissue paper.

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

RADICACIÓN: 0-89078

EDICTO No. 2928

LA SECRETARÍA GENERAL AD-HOC HACE SABER:

Que esta Superintendencia profirió Resolución No. 1998 de 31-ENE-2008. Que el contenido de la parte resolutive es como sigue: El Superintendente de Industria y Comercio.

RESUELVE

ARTICULO PRIMERO: Negar el privilegio de patente de invención para la solicitud correspondiente a "PRODUCTOS TISU SANITARIOS CON CAPACIDAD MEJORADA DE ELIMINACION EN EL INODORO".

ARTICULO SEGUNDO: Notificar personalmente el contenido de la presente resolución al doctor Ramiro Castro Duque, o a quien haga sus veces, en su calidad de apoderado de Kimberly-Clark Worldwide, Inc., entregándole copia de la misma, advirtiéndole que contra ella procede el recurso de reposición interpuesto ante el Superintendente de Industria y Comercio, al momento de la notificación o dentro de los 5 días hábiles siguientes a ella.

NOTIFÍQUESE Y CUMPLASE

Dada en Bogotá, D.C., a los 31 ENE 2008

EL SUPERINTENDENTE DE INDUSTRIA Y COMERCIO,


JAIME EMILIO ESCOBAR

Para notificar a los interesados, se fija el presente EDICTO en lugar visible al público en la SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO, por el término de (10) diez días hábiles contados a partir de las 8:30 a.m. de hoy.

Secretaría General Ad-Hoc 21-FEB-2008
Secretaría General Ad-Hoc
EDICTO No. 2928

Este edicto se desfiló hoy 06-MAR-2008 a las cinco (5:00 p.m.)