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SEÑORES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
MINISTERIO DE DESARROLLO ECONOMICO

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REF: EXPEDIENTE : **00083196**
SOLICITANTE: SCA HYGIENE PRODUCTS ZEIST B.V
FECHA DE LA SOLICITUD: NOVIEMBRE 1, 2000
TITULO: PRODUCTOS SUPERABSORBENTES NEUTRALIZANTES
DE ALCALIS

DILIA RODRÍGUEZ D'ALEMAN, en mi condición de apoderada de la Sociedad solicitante, por el presente escrito atentamente solicito a Usted se realice el desglose del recibo No. 03-10.287 correspondiente al pago de examen de patentabilidad, ya que dicha tasa fue anexada por un error involuntario al expediente No. 92228848 con radicación de fecha Marzo 5 de 2003.

Agradezco la atención que se sirva prestar a la presente.

Señor Jefe,


DILIA RODRÍGUEZ D'ALEMAN
T.P.No. 20824 del CSJ

P-369

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

DIVISIÓN DE NUEVAS CREACIONES

2020

Bogotá, D. C., 6 de Septiembre de 2005

Doctora

DILIA RODRÍGUEZ D'ALEMAN

Representante **SCA HYGIENE PRODUCTS ZEIST B. V.**

ASUNTO

Radicación No. 00-83196

Trámite 002

Evento 001

Actuación 430

Oficio 8393

Folios 135

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 4 a 11 de la solicitud en estudio.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 11 reivindicaciones en los folios 12 a 14 de la solicitud en estudio.
- c) 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 3 de noviembre de 1999 y en el momento de la radicación **SI** se reclamo prioridad de la primera solicitud presentada en Europa EP99203622.8

2) Objeto de la invención

- a) Las reivindicaciones 1 a 12 de la solicitud en estudio se refieren a:

- i) (1.-) Un artículo superabsorbente de la invención que tiene control de olores y control microbiano mejorados, que comprende una capa posterior impermeable a líquidos, una capa intermedia absorbente de líquidos que contiene un polímero hidrofílico ácido parcialmente neutralizado, especialmente un poliacrilato con entrecruzamiento en superficie, y una capa superior no absorbente permeable a líquidos, y se caracteriza por comprender un agente neutralizante de alcalinidad que está uniformemente distribuido en dicha capa absorbente intermedia.
 - ii) (12.-) Un proceso para producir un artículo superabsorbente que tiene control de olores y control microbiano mejorados, que comprende mezclar una gente neutralizante de alcalinidad con un polímero hidrofílico ácido altamente neutralizado con entrecruzamiento de superficie, distribuyendo la mezcla en un material transportador fibroso, formando el material transportador en una capa y cubriendo la capa de material transportador con una capa impermeable a líquidos en un lado y con una capa no absorbente permeable a líquidos en el otro lado.
- b) El anterior producto y su procedimiento de fabricación buscan mejorar las propiedades de prevención de crecimiento microbiano y de olor en artículos absorbentes desechables.
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a: A 61 F 13/15

3) 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 **A 61 F 13/15** y las más cercanas a ellas, se encontró que antes del 3 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 artículos absorbentes desechables con neutralizador de álcalis.

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

Nº	Documento	Título	Fecha de Publicación
D1	EP 0761241	Absorbing agent composition, absorbent material and absorbent product containing	1997.03.12
D2	WO 9519191	Method and compositions for enhancing blood absorbence by absorbent materials	1995.07.20
D3	EP 0 745 160	Fibres which can be densified and method for their production	1995.08.24
D4	EP 0 316 518	Hygienischer Zellstoffartikel	1989.05.24
D5	DE 30 30 920	Sanitäre Hygienemittel, die der Aufnahme Harn und Blut enthaltender Sekrete dienen, mit geruchsverhindernden Eigenschaften	1982.04.22
D6	GB 2326348	Absorbent article comprising a pH controlling superabsorbent	1998.12.23
D7	US 3794034	Odor reductant body waste pad	1974.02.26
D8	US 3707148	Impregnated diaper	1972.12.26

4) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial".

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

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".

El art. 21 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los productos o procedimiento ya patentados, comprendidos en el estado de la técnica, no serán objeto de nueva patente, por el simple hecho de atribuirse un uso distinto al originalmente comprendido por la patente inicial."

La presente solicitud comprende un artículo superabsorbente que comprende una capa posterior impermeable a líquidos, una capa intermedia absorbente de líquidos que contiene un polímero hidrofílico ácido parcialmente neutralizado, especialmente un poliacrilato con entrecruzamiento en superficie, y una capa superior no absorbente permeable a líquidos, y se caracteriza por comprender un agente neutralizante de alcalinidad que está uniformemente distribuido en dicha capa absorbente intermedia.

D1 (EP 0761241) revela un artículo absorbente con las mismas partes que la presente solicitud, y donde la composición absorbente puede comprender una resina absorbente con entrecruzamiento de superficie, y donde dicha resina puede ser un poliacrilato. D1 relaciona que a dichos artículos absorbentes pueden contener ácidos y da una serie de ejemplos de posibles ácidos. El proceso de fabricación es prácticamente el mismo de la presente solicitud.

D2 (WO 9519191) también revela el uso de ácidos para neutralizar materiales superabsorbentes en artículos

D3 (EP 0 745 160) igualmente incorpora materiales para artículos absorbentes desechables que muestran el uso de ácidos

Los procesos de D2 y D3 son prácticamente los mismos que la presente solicitud.

D4 (EP 0 316 518) muestra la aplicación de agentes neutralizadores de álcalis para aplicación con artículos absorbentes desechables. Muchos de los ácidos coinciden, al igual que el pH que manejan.

D5 (DE 3030 920) también revela el uso de ácidos para artículos absorbentes desechables.

D6 (GB 2326348) muestra formas de controlar el pH en artículos absorbentes desechables.

D7 (US 3794034) muestra el uso de un ácido para controlar el pH de un material absorbente de un artículo absorbente desechable. En esencia lo mismo que el solicitante quiere proteger. Algo similar ocurre con D8 (US3707148)

En general lo que plantea el solicitante, o ya es conocido del estado de la técnica, o se deriva de forma obvia de cada uno de los documentos citados. No habría no la novedad ni la altura inventiva 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	Requisito que afecta
D1	EP 0761241	1 - 11	Novedad
			Nivel inventivo
D2	WO 9519191	1 - 11	Novedad
			Nivel inventivo
D3	EP 0 745 160	1 - 11	Novedad
			Nivel inventivo
D4	EP 0 316 518	1 - 11	Novedad
			Nivel inventivo
D5	DE 3030 920	1 - 11	Novedad
			Nivel inventivo
D6	GB 2326348	1 - 11	Novedad
			Nivel inventivo
D7	US 3794034	1 - 11	Novedad
			Nivel inventivo
D8	US 3707148	1 - 11	Novedad
			Nivel inventivo

5) 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

15 SET. 2005

Concepto Técnico N°	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
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(11) **EP 0 761 241 A2**

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(54) **Absorbing agent composition, absorbent material, and absorbent product containing absorbent material**

(57) There is provided an absorbing agent exhibiting superior properties for liquid absorbency and absorbed liquid retention under compressional load, making it es-

pecially useful in personal hygiene products such as disposable diapers, sanitary napkins and incontinence pads.

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Description

The present invention relates to an absorbing agent composition suited for use in sanitary goods, such as paper
diapers (disposal diapers), sanitary napkins, incontinence pads, an absorbent material, and an absorbent product
containing the absorbent material.

Recently, an absorbent resin is used extensively in sanitary goods, such as paper diapers, sanitary napkins, in-
continence pads, to absorb body fluids.

Examples of such absorbent resins include: a partially neutralized crosslinked polymer of polyacrylic acid (Japa-
nese Laid-Open Patent Publication Nos. 84304/1980 (Tokukaisho 55-84304), 108407/1980 (Tokukaisho 55-108407),
and 133413/1980 (Tokukaisho 55-133413)); a hydrolyzed graft polymer of starch-acrylonitrile (Japanese Laid-Open
Patent Publication No. 43995/1971 (Tokukaisho 46-43995); a neutralized graft polymer of starch-acrylic acid (Japanese
Laid-Open Patent Publication No. 125468/1976 (Tokukaisho 51-125468)); a saponified copolymer of vinyl acetate-
acrylic ester (Japanese Laid-Open Patent Publication No. 14689/1977 (Tokukaisho 52-14689)); a hydrolyzed copoly-
mer of acrylonitrile or acrylamide, or a crosslinked product thereof (Japanese Laid-Open Patent Publication No.
15959/1978 (Tokukaisho 53-15959)); and a crosslinked polymer of cationic monomer (Japanese Laid-Open Patent
Publication Nos. 154709/1983 (Tokukaisho 58-154709) and 154710/1983 (Tokukaisho 58-154710)).

Notable properties of the absorbent resin include absorbing capacity and absorbency under pressure when it is
in contact with an aqueous liquid like a body fluid, gel strength, and absorbing power of absorbing liquid from a base
material containing an aqueous liquid, etc. Conventionally, the absorbent resins having some of the above-mentioned
properties which show desirable properties (absorption properties) in their applications of paper diaper, sanitary napkin,
etc., as well as absorbent materials and the absorbent product using such absorbent resins have been proposed.

Examples of such absorbent resins, absorbent materials and absorbent products include: an absorbent resin dis-
closing a combination of a specific gel capacity, shear modulus and an extraction polymer content (US Patent No.
4,654,039); an absorbent resin having predetermined ranges of absorbing capacity, absorbing rate, and gel strength,
and paper diapers or sanitary napkins using such an absorbent resin (Japanese Laid-Open Patent Publication Nos.
185550/1985 (Tokukaisho 60-185550), 185551/1985 (Tokukaisho 60-185551), and 185804/1985 (Tokukaisho
60-185804)); paper diapers using an absorbent resin having predetermined ranges of absorbing capacity, absorbing
rate, and gel stability (Japanese Laid-Open Patent Publication No. 185805/1985 (Tokukaisho 60-185805)); an absorb-
ent product containing an absorbent resin having predetermined ranges of absorbing capacity, absorbing power, and
water-soluble content (Japanese Laid-Open Patent Publication No. 21902/1988 (Tokukaisho 63-21902)); absorbent
sanitary goods containing an absorbent resin having predetermined ranges of absorbing capacity, absorbing capacity
under pressure and gel breaking strength (Japanese Laid-Open Patent Publication No. 99861/1988 (Tokukaisho
63-99861)); a paper diaper containing an absorbent resin having predetermined ranges of absorbing capacity and
absorbency under pressure (Japanese Laid-Open Patent Publication No. 34167/1990 (Tokukaisho 2-34167)); an ab-
sorbing agent containing an absorbent resin having predetermined ranges of absorbing capacity under pressure and
particle diameter (European Patent No. 339,461); an absorbent structure including at least a predetermined amount
of absorbent resin having predetermined ranges of absorbing rate and absorbing capacity under pressure in a short
period of time (European Patent No. 443,627); and a synthetic absorbing material having at least a predetermined
amount of absorbent resin having predetermined ranges of deformation under load and wicking index (European Patent
No. 532,002).

Recent sanitary goods, such as paper diapers and sanitary napkins, have been improved in terms of performance
and thinness, and accordingly, an amount of absorbent resin used in the sanitary goods per sheet, or percent by weight
of the absorbent resin based on the weight of the absorbent material mainly composed of the absorbent resin and
hydrophilic fibers (hereinafter simply referred to as a resin concentration) has been increasing. Namely, by reducing
the amount of hydrophilic fiber having a small bulk specific gravity and increasing the amount of the absorbent resin
having a large bulk specific gravity, the ratio of the absorbent resin in the absorbent material is raised, and a thinner
sanitary material can be achieved without reducing the absorbing capacity.

However, earnest researches have been made by the inventors of the present invention in order to increase the
absorbing amount of the sanitary material, for example, by increasing the resin concentration in the absorbent material.
As a result, the inventors have found that the absorbent material having a higher resin concentration than conventional
absorbent material cannot be used without having problems such as leakage of aqueous liquid from the sanitary goods,
etc., only by controlling the described absorbing capacity, absorbency under pressure, gel strength, absorbing capacity,
etc. For example, as to the absorbent resin which has been viewed with interest in which only absorbing capacity under
pressure is large, by raising the resin concentration, the liquid dispersibility of the absorbent material is significantly
reduced.

Further researches have been made by the inventors on absorbing properties of the absorbent material having
higher resin concentration than conventional absorbent material. As a result, they have found that in the case of using
a mixture of a known absorbent resin, a hydrophilic fiber is used as an absorbent material, although when a resin

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concentration is low, the absorbent material shows a predetermined level of absorbing properties, when a resin concentration is above 40 percent by weight, such undesirable conditions that the liquid dispersibility is rapidly lowered, the absorbing capacity of weight per unit of the absorbent material is lowered, etc., would occur. In short, the absorbent material made of a mixture of a known absorbent resin and hydrophilic fibers causes the problems explained above.

5 It is therefore an object of the present invention to provide an absorbing agent composition such that exhibits excellent properties (absorbing properties), such as capabilities of maintaining high liquid diffusion and a constant absorbing capacity per unit weight, even when an absorbent resin is increased in percent by weight based on the absorbing agent composition, as well as an absorbent material containing such an absorbing agent composition and an absorbent product containing the absorbent material.

10 To fulfill the above object, the inventors of the present invention continued the steady and persistent studies on absorbing agent composition, absorbent material, and absorbent product containing the absorbent material. In the meantime, the inventors discovered a unique property value, that is, a diffusing absorbency index under pressure, which is suitably used to measure liquid diffusion when the absorbing agent composition is absorbing an aqueous liquid under predetermined conditions. The absorbing agent composition having a higher diffusing absorbency index
15 under pressure can be obtained by mixing an absorbent resin having at least predetermined diffusing absorbency under pressure and a specific compound, or surface crosslinking such an absorbent resin under specific conditions.

The inventors discovered that an absorbing agent composition having a higher diffusing absorbency index under pressure can steadily absorb an aqueous liquid supplied in bulk even if the absorbent resin is increased in percent by weight, and that such an absorbing agent composition exhibits excellent properties (absorbing properties), such as
20 capabilities of maintaining high liquid diffusion and a constant absorbing capacity per unit weight. The inventors also discovered that using such an absorbing agent composition makes it possible to obtain an absorbent material and an absorbent product with excellent absorbing properties.

To fulfill the above object, the absorbing agent composition of the present invention is characterized by having a diffusing absorbency index under pressure of 1.5g/g-min or higher with respect to a 0.9 weight percent sodium chloride
25 solution under a load of 20g/cm².

According to the above arrangement, the above absorbing agent composition can steadily absorb an aqueous liquid supplied in bulk, and even if the absorbent resin is increased in percent by weight, the absorbing agent composition exhibits excellent properties (absorbing properties), such as capabilities of maintaining high liquid diffusion and a constant absorbing capacity per unit weight.

30 Also, to fulfill the above object, the absorbent material of the present invention is characterized by including at least one of the above-specified absorbing agent compositions.

According to the above arrangement, it has become possible to provide an absorbent material which can steadily absorb an aqueous liquid supplied in bulk while exhibiting excellent absorbing properties, such as capabilities of maintaining high liquid diffusion and a constant absorbing capacity. The absorbent material of the present invention can be
35 used suitably in making further improved and thinner absorbent products, such as sanitary goods including paper diapers, sanitary napkins, incontinence pads, etc.

Further, to fulfill the above object, the absorbent product of the present invention is characterized by comprising an absorbent layer containing the above absorbent material sandwiched by a liquid permeable sheet and a liquid impermeable sheet.

40 According to the above arrangement, it has become possible to provide an absorbent product, such as sanitary goods, which can steadily absorb an aqueous liquid supplied in bulk and exhibits excellent absorbing properties, such as capabilities of maintaining high liquid diffusion and a constant absorbing capacity.

For a fuller understanding of the nature and advantages of the invention, reference should be made to the ensuing detailed description taken in conjunction with the accompanying drawings.

45 Figure 1 is a schematic cross section of a device measuring diffusing absorbency under pressure indicating one of the properties of an absorbing agent composition of the present invention;

Figure 2 is a cross section showing a major portion of the above measuring device:

Figure 3 is a view explaining a diffusing direction of a physiological saline solution in the above measuring device:

50 Figure 4 is a schematic cross section of a device measuring diffusing absorbency under pressure indicating one of the properties of an absorbent material of the present invention;

Figure 5 is a cross section showing a major portion of the measuring device of Figure 4; and

Figure 6 is a view explaining a diffusing direction of a physiological saline solution in the measuring device of Figure 4.

55 The diffusing absorbency index under pressure referred herein is a new property value suitably used to evaluate liquid diffusion of the absorbent resin or absorbing agent composition (hereinafter, the explanation is carried out on the basis of the absorbent resin for the explanation's convenience) while the same is absorbing an aqueous liquid

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when the basis weight of the absorbent resin is high and resin particles are linked tightly to each other by an external force. The diffusing absorbency index under pressure is calculated using maximum absorbency under pressure at which the absorbent resin absorbs an aqueous liquid along the direction of the absorbent resin layer (hereinafter, referred to as the lateral direction) under predetermined conditions, the details of which will be given below.

5 The diffusing absorbent index under pressure indicates how steadily the absorbent resin absorbs the aqueous liquid and how uniform and fast the absorbent resin diffuses the aqueous liquid in the lateral direction. The diffusion (liquid diffusion and liquid transmissivity) of the aqueous liquid in the lateral direction is particularly an important factor in absorbing a great amount of aqueous liquid. This evaluation makes it easier to predict the absorbing behavior of the absorbent resin in an absorbent material, for example, the one mainly composed of the absorbent resin and hydrophilic fibers, especially the one having a high resin concentration. The structure of the absorbent material will be described below.

10 The diffusing absorbency under pressure used herein as a preferable property value for the absorbing agent composition is a property value used to evaluate an absorbing capacity of the absorbing agent composition in consideration of diffusion of the aqueous liquid when the basis weight of the absorbent resin is high and resin particles are linked tightly to each other by an external force. The diffusing absorbency under pressure is calculated using a value measured under predetermined conditions after a predetermined period, for example, 60 minutes, since the absorption started, which will be explained below.

15 Many of the foregoing prior art documents incorporate the evaluation on the absorbing rate. However, none of them includes the evaluation on the maximum absorbing rate under pressure while an aqueous liquid is being diffused in the lateral direction. In other words, the evaluation was carried out only in a direction intersecting with the resin layer direction (hereinafter, referred to as the longitudinal direction) in these documents, that is to say, the evaluation was carried out only in the shorter distance the aqueous liquid moves. Thus, the absorbing behavior of the absorbent material in the diapers, etc. adopting the absorbent material having a high resin concentration, can not be predicted accurately from the result of the conventional evaluations.

20 The absorbing agent composition of the present invention has a diffusing absorbency index under pressure of 1.5g/g·min or higher, and more preferably, 3.0g/g·min or higher, with respect to a 0.9 weight percent sodium chloride solution under a load of 20g/cm². A preferred absorbing agent composition further has diffusing absorbency under pressure of 25g/g or higher with respect to a 0.9 weight percent sodium chloride solution under a load of 20g/cm² after 60 minutes since the absorption started. Further, the absorbing agent composition may include a non-volatile water-soluble compound.

25 To be more specific, the absorbing agent composition of the present invention can be obtained by adding microscopic water-insoluble inorganic powders (hereinafter referred to as water-insoluble inorganic powders) to an absorbent resin having diffusing absorbency under pressure of 25g/g or higher with respect to a 0.9 weight percent sodium chloride solution under a load of 20g/cm² after 60 minutes since the absorption started. Alternatively, the absorbing agent composition of the present invention can be obtained by adding a polyamine compound whose weight average molecular weight (Mw) is 5,000 or greater (hereinafter, referred to as polyamine compound) to an absorbent resin having diffusing absorbency under pressure of 25g/g or higher with respect to a 0.9 weight percent sodium chloride solution under a load of 20g/cm² after 60 minutes since the absorption started. Also, the absorbing agent composition of the present invention can be obtained by adding the water-insoluble inorganic powders and polyamine compound to an absorbent resin having diffusing absorbency under pressure of 25g/g or higher with respect to a 0.9 weight percent sodium chloride solution under a load of 20g/cm² after 60 minutes since the absorption started.

30 Further, the absorbing agent composition of the present invention can be obtained by surface crosslinking an absorbent resin through heat treatment using a surface crosslinking agent made of a mixture of specific crosslinking agents, and mixing the surface crosslinked absorbent resin and the surface crosslinking agent to subject the resulting mixture to heat treatment again. The surface crosslinking agent will be detailed below.

35 A preferred absorbent resin is, for example, an absorbent crosslinked polymer containing a carboxyl group. The absorbent crosslinked polymer is obtained by, for example, letting a hydrophilic unsaturated monomer mainly composed of acrylic acid or the salt thereof undergo (co)polymerization (hereinafter, referred to as polymerization). Of all the preferred absorbent crosslinked polymers, the more preferable is a crosslinked polymer of the salt of polyacrylic acid. It is further preferable that 50-90 mole percent acid radicals of the above crosslinked polymer are neutralized by alkali metal salt, ammonium salt, amine salt, or the like.

40 The above absorbent resin may be known absorbent resins, such as partially neutralized crosslinked polymer of polyacrylic acid (U.S. Patent Nos. 4,625,001, 4,654,039, 5,250,640, and 5,275,773, and Europe Patent No. 456136), a partially neutralized crosslinked graft polymer of starch-acrylonitrile (U.S. Patent No. 4,076,663), a copolymer of isobutylene-maleic acid (U.S. Patent No. 4,389,513), a saponified copolymer of vinyl acetate-acrylic acid (U.S. Patent No. 4,124,748), a hydrolyzed (co)polymer of acrylamide (U.S. Patent No. 3,959,569), and a hydrolyzed polymer of acrylonitrile (U.S. Patent No. 3,935,099).

45 The above hydrophilic unsaturated monomer may optionally contain unsaturated monomers other than acrylic acid

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and the salt thereof (hereinafter referred to as other monomers). Examples of the other monomers include, but are not limited to:

anionic unsaturated monomers, such as methacrylic acid, maleic acid, vinylsulfonic acid, styrenesulfonic acid, 2-(meth)acrylamide-2-methylpropanesulfonic acid, 2-(meth)acryloylethanesulfonic acid, 2-(meth)acryloylpropanesulfonic acid, and salts of these acids;

nonionic unsaturated monomers containing hydrophilic groups, such as acrylamide, methacrylamide, N-ethyl(meth)acrylamide, N-n-propyl(meth)acrylamide, N-isopropyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, methoxypolyethylene glycol (meth)acrylate, polyethylene glycol mono(meth)acrylate, vinylpyridine, N-vinylpyrrolidone, N-acryloylpiperidine, and N-acryloylpyrrolidine;

cationic unsaturated monomers, such as N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylaminoethyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylamide, and quaternary salts thereof; etc.

An amount of use of these monomers is preferably 30 percent by mole or less, and more preferably 10 percent by mole or less, based on the entire hydrophilic unsaturated monomer.

A precursor of the absorbent resin (hereinafter, referred to as the absorbent resin precursor) obtained by polymerizing the hydrophilic unsaturated monomer contains a carboxyl group. When obtaining the absorbent resin precursor, it is preferable to introduce the crosslinking structure inside of the same using an internal crosslinking agent. The internal crosslinking agent is not especially limited and may be any compound having a plurality of polymeric unsaturated groups and/or reactive groups in one molecule. In other words, the internal crosslinking agent may be any compound having a plurality of substituent groups copolymerizable and/or reactive with the hydrophilic unsaturated monomer in one molecule. Alternatively, the hydrophilic unsaturated monomer may be a self-crosslinking compound that forms the crosslinking structure without using the internal crosslinking agent.

Examples of the internal crosslinking agent include, but are not limited to:

N,N'-methylenebis(meth)acrylamide, (poly)ethylene glycol di(meth)acrylate, (poly)propylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane di(meth)acrylate, glycerol tri(meth)acrylate, glycerin acrylate methacrylate, ethylene oxide denatured trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, triallyl cyanurate, triallyl isocyanurate, triallyl phosphate, triallylamine, poly(meth)allyloxyalkane, (poly)ethylene glycol diglycidyl ether, glycerol diglycidyl ether, ethylene glycol, polyethylene glycol, propylene glycol, glycerin, pentaerythritol, ethylenediamine, polyethyleneimine, glycidyl(meth)acrylate, etc. One member or a mixture of two or more members selected from these internal crosslinking agents can be used effectively. Of all these internal crosslinking agents, those having a plurality of polymeric unsaturated groups in one molecule can further improve the absorbing properties of the resulting absorbent resin.

A preferred amount of use of the internal crosslinking agent with respect to the hydrophilic unsaturated monomer is in a range between 0.005 percent by mole and 3 percent by mole, and more preferably, between 0.01 percent by mole and 1.5 percent by mole. Neither an amount less than 0.005 percent by mole nor an amount more than 3 percent by mole may result in an absorbent resin with desired absorbing properties.

When obtaining the absorbent resin precursor by polymerizing the hydrophilic unsaturated monomer, the followings or the like may be added to the reactant:

a hydrophilic polymer, such as starch, a derivative of starch, cellulose, a derivative of cellulose, polyvinyl alcohol, polyacrylate, polyacrylic acid, crosslinked polyacrylate, and crosslinked polyacrylic acid;
a chain transfer agent, such as hypophosphite and hypophosphorous acid; and
water soluble or water dispersible surfactant.

A polymerizing method of the hydrophilic unsaturated monomer is not especially limited. For example, known methods, such as solution polymerization, reverse phase suspension polymerization, bulk polymerization, and precipitation polymerization can be adopted. Of all these polymerization methods, methods in which a water solution of the hydrophilic unsaturated monomer is polymerized, that is, the solution polymerization and reverse phase suspension polymerization, are particularly preferred in terms of readiness in controlling the polymerization reaction and properties of the resulting absorbent resin. The reaction conditions, such as reaction temperature and time, are not especially limited, and can be set arbitrary depending on the kinds of the hydrophilic unsaturated monomers.

The hydrophilic unsaturated monomer can be also polymerized by known methods, for example, those disclosed in U.S. Patent Nos. 4,625,001, 4,769,427, 4,873,299, 4,093,776, 4,367,323, 4,446,261, 4,683,274, 4,690,996, 4,721,647, 4,738,867, and 4,748,076.

When polymerizing the hydrophilic unsaturated monomer, a radical polymerization initiator, such as potassium

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persulfate, ammonium persulfate, sodium persulfate, t-butylhydro peroxide, hydrogen peroxide, 2,2'-azobis(2-amidinopropane)dihydrochloride, activation energy rays, such as UV rays and electron beams, or the like can be used. When the oxidizing radical polymerization initiator is used, the hydrophilic unsaturated monomer may undergo redox polymerization using a reducing agent, such as sodium sulfite, sodium hydrogen sulfite, ferrous sulfate, and L-ascorbic acid. A preferable amount of use of the polymerization initiator is in a range between 0.001 percent by mole and 2 percent by mole, and more preferably, between 0.01 percent by mole and 0.5 percent by mole.

The resulting absorbent resin precursor obtained by any of the above polymerization methods is, for example, sieved to a predetermined particle size. The absorbent resin precursor may be spherical, leaflet, undefined, fibriform, granular, bar-wise, substantially spherical, flat, etc.

The absorbent resin of the present invention, having diffusing absorbency under pressure of 25g/g or higher with respect to a 0.9 weight percent sodium chloride solution under a load of 20g/cm² after 60 minutes since the absorption started, is obtained by surface crosslinking the above absorbent resin precursor in the presence of a specific surface crosslinking agent. An example method of obtaining the absorbent resin is disclosed in U.S. Patent Application Serial No. 08/571,960. To be more specific, the absorbent resin precursor is sieved to have an average particle size between 200μm and 600μm and to contain up to 10 weight percent particles having a diameter smaller than 106μm. Then, the absorbent resin precursor is subject to heat treatment in the presence of a mixture of the first crosslinking agent and second crosslinking agent, which will be described below. According to the above method, the crosslinking density of the absorbent resin is increased on the surface than the inside, thereby making it possible to obtain an absorbent resin having high diffusing absorbency under pressure. When the absorbent resin precursor has an average particle diameter outside of the above range between 200μm and 600μm, or the particles having a diameter smaller than 106μm exceeds 10 percent by weight, it may become difficult to obtain an absorbent resin having high diffusing absorbency under pressure.

The surface crosslinking agent referred herein is a mixture of compounds that can react with carboxyl groups of the absorbent resin precursor, that is to say, a mixture of the first surface crosslinking agent and second surface crosslinking agent having their respective solubility parameter values (SP values). The solubility parameter value is generally used as a factor representing the polarity of a compound. The present invention adopts a solubility parameter $\delta(\text{cal/cm}^3)^{1/2}$ of solvents set forth in pages 527-539 of the Polymer Handbook, the third edition, Wiley Interscience. As to the solvents which are not found in the above pages, the solubility parameter is calculated by substituting a Hoy's condense energy constant set forth in page 525 into a Small's equation set forth in page 524.

A preferable first surface crosslinking agent is a compound capable of reacting with carboxyl groups of the absorbent resin precursor and having solubility parameter of $12.5(\text{cal/cm}^3)^{1/2}$ or higher, and more preferably, $13.0(\text{cal/cm}^3)^{1/2}$ or higher. Examples of the first surface crosslinking agent include, but are not limited to: ethylene glycol, propylene glycol, glycerin, pentaerythritol, sorbitol, ethylenecarbonate(1,3-dioxolane-2-one), propylenecarbonate(4-methyl-1,3-dioxolane-2-one), etc. One member or a mixture of two or more members selected from these first surface crosslinking agents can be used effectively.

A preferable second surface crosslinking agent is a compound capable of reacting with carboxyl groups of the absorbent resin precursor and having solubility parameter below $12.5(\text{cal/cm}^3)^{1/2}$, and more preferably, in a range between $9.5(\text{cal/cm}^3)^{1/2}$ and $12.0(\text{cal/cm}^3)^{1/2}$. Examples of the second crosslinking agent include, but are not limited to: diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2, 4-pentanediol, 1, 6-hexanediol, 2,5-hexanediol, trimethylolpropane, diethanolamine, triethanolamine, ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, ethylenediamine, diethylenetriamine, triethylene tetramine, 2,4-tolylene diisocyanate, hexamethylene diisocyanate, 4,5-dimethyl-1,3-dioxolane-2-one, epichlorohydrin, epibromohydrin, etc. One member or a mixture of two or more members selected from these second surface crosslinking agents can be used effectively.

An amount of use of the surface crosslinking agent varies depending on the kinds of compounds and a combination thereof; however, a preferable amount of the first surface crosslinking agent and that of the second surface crosslinking agent with respect to 100 parts by weight of solid content of the absorbent resin precursor is in a range between 0.01 part by weight and 5 parts by weight, and in a range between 0.001 part by weight and 1 part by weight, respectively, and more preferably, in a range between 0.1 part by weight and 2 parts by weight and in a range between 0.005 part by weight and 0.5 part by weight, respectively. An amount exceeding the above specified ranges is not preferable because it is excessive to enable the absorbent resin to form an optimal crosslinking structure, besides it is not economical. An amount below the above specified ranges is not preferable either, because it is not sufficient to attain appreciable improvement in the properties of the absorbent resin, such as diffusing absorbency under pressure.

It is preferable to use water as a solvent when the absorbent resin precursor and surface crosslinking agent are mixed. An amount of use of water varies depending on the kinds or particle diameter of the absorbent resin precursors; however, a preferred range with respect to 100 parts by weight of solid content of the absorbing agent precursor is between 0 part by weight exclusive and 20 parts by weight inclusive, and more preferably, between 0.5 parts by weight

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and 10 parts by weight.

When the absorbent resin precursor and the surface crosslinking agent are mixed, a hydrophilic organic solvent may be used optionally as a solvent. Examples of the hydrophilic organic solvent include:

- 5 lower alcohols, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, and t-butyl alcohol;
ketons, such as acetone;
ethers, such as dioxane, tetrahydrofuran, alcoxypolyethylene glycol;
amides, such as N,N-dimethylformamide;
10 sulfoxides, such as dimethylsulfoxide; etc.

An amount of use of the hydrophilic organic solvent varies depending on the kinds and particle diameter of the absorbent resin precursor: however, a preferred range with respect to 100 parts by weight of solid content of the absorbing agent precursor is up to 20 parts by weight, and more preferably, between 0.1 part by weight and 10 parts by weight.

- 15 When the absorbent resin precursor and the surface crosslinking agent are mixed, the absorbent resin precursor is, for example, dispersed in any of the above example hydrophilic organic solvents, and after which the crosslinking agent is mixed. However, a method of mixing is not limited to the above. Of all the possible mixing methods, the preferred is a method in which the surface crosslinking agent dissolved into water and/or hydrophilic organic solvent is mixed with the absorbent resin precursor directly or through atomization or dripping.

- 20 A preferred mixing device (hereinafter, referred to as the mixing device a) for mixing the absorbent resin precursor and the surface crosslinking agent has a mixing force large enough to mix these two elements homogeneously in a secure manner. Preferred example of the mixing device a include: a cylindrical mixer, a double wall conical mixer, a V-shaped mixer, a ribbon type mixer, a screw type mixer, a fluidized oven rotary desk mixer, a flash type mixer, a two-arm type kneader, an internal mixer, a grinding kneader, a rotary mixer, a screw type extruder, etc.

- 25 After the absorbent resin precursor and the surface crosslinking agent are mixed, the resulting mixture is subject to heat treatment to surface crosslink the absorbent resin precursor. The temperature of the heat treatment varies depending on the kinds of the surface crosslinking agents; however, a preferable range is between 160°C and 250°C inclusive. The heat treatment at a temperature below 160°C is not preferable because it is not high enough to form a uniform crosslinking structure and therefore the resulting absorbent resin does not exhibit high diffusing absorbency.
30 under pressure, besides, the heat treatment takes too long, which lowers the productivity as a result. The heat treatment at a temperature above 250°C is not preferable either, because the absorbent resin precursor deteriorates and the resulting absorbent resin exhibits poor properties.

The heat treatment is carried out using a typical dryer or furnace. Examples of the dryer include: a channel mixing dryer, a rotary dryer, a desk dryer, a fluidized-bed dryer, a flash type dryer, an infra-red dryer, etc.

- 35 Examples of the water-insoluble inorganic powders contained in the absorbing agent composition of the present invention optionally include, but are not limited to: silicon dioxide, titanium dioxide, aluminium oxide, magnesium oxide, zinc oxide, talc, calcium phosphate, barium phosphate, silicic acid, silicate, clay, diatom earth, zeolite, bentonite, kaolin, hydrotalcite, activated clay, etc. One member or a mixture of two or more members selected from these water-insoluble inorganic powders can be used effectively. Of all these examples, microscopic noncrystal silicon dioxide is preferred.
40 Further, a preferred particle diameter of the noncrystal silicon dioxide is 1,000µm or smaller, and more preferably 100µm or smaller, further preferably 50µm or smaller, and most preferably 10µm or smaller.

An amount of use of the water-insoluble inorganic powders varies depending on the use of the absorbing agent composition or the like: however, a preferred range with respect to 100 parts by weight of the absorbent resin is between 0.05 part by weight and 2 parts by weight, and more preferably between 0.1 part by weight and 1 part by weight. If the used amount is less than 0.05 part by weight, the resulting absorbing agent composition may not exhibit a desired diffusing absorbency index under pressure. On the other hand, using an amount exceeding 2 parts by weight does not necessarily attain appreciable effects for the increased amount, meaning that it is not economical.

- 45 Preferred examples of a mixing device (hereinafter referred to as the mixing device b) for mixing absorbent resin and water-insoluble inorganic powders include: a cylindrical mixer, a screw type mixer, a screw type extruder, a turbulizer, a nauter type mixer, a V-shaped mixer, a ribbon type mixer, a two-arm type kneader, a fluidized mixer, a flash type mixer, a rotary disk mixer, a roll mixer, a rotary mixer, etc. The mixing speed can be either high or low. Note that it is preferable to mix the water-insoluble inorganic powders and the absorbent resin without using a solvent, which is known as dry blend. However, if a solvent is used, emulsion of water-insoluble inorganic powders may be mixed with the absorbent resin.
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- 55 The polyamine compound optionally contained in the absorbing agent composition of the present invention is not especially limited as long as the same has a weight average molecular weight of 5,000 or more. The polyamine compound is not especially limited, but must contain at least one kind of amino group selected from a group consisting of a primary amino group, a secondary amino group, and a tertiary amino group in one molecule.

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Examples of the polyamine compound include:

- (1) a homopolymer of a monoallylamine derivative and a homopolymer of a diallylamine derivative;
- (2) a copolymer of more than one kind of monoallylamine derivatives, a copolymer of more than one kind of diallylamine derivatives, a copolymer of a monoallylamine derivative and a diallylamine derivative;
- (3) a copolymer of a monoallylamine derivative and/or diallylamine derivative, and a dialkyldiallylammonium salt;
- (4) a homopolymer of an unsaturated carboxylic acid derivative containing a tertiary amino group (hereinafter referred to as the unsaturated carboxylic acid derivative *a*);
- (5) a copolymer of more than one kind of the unsaturated carboxylic acid derivatives *a*;
- (6) a copolymer of the unsaturated carboxylic acid derivative *a*, and an unsaturated carboxylic acid derivative containing quaternary ammonium salt which is in effect a protonic and/or alkylated tertiary amino group, and/or a dialkyldiallylammonium salt as a substituent group (hereinafter referred to as the unsaturated carboxylic acid derivative *b*);
- (7) a ternary copolymer of the unsaturated carboxylic acid derivatives *a* and *b*, and a vinyl monomer copolymerizable with the unsaturated carboxylic acid derivatives *a* and *b*;
- (8) a polymer produced by copolymerizing an unsaturated carboxylic acid and an unsaturated monomer copolymerizable with the unsaturated carboxylic acid first, and thence reacting alkyleneimine with a carboxyl group of the resulting copolymer;
- (9) polyalkyleneimine;
- (10) a polyalkyleneimine-epihalohydrin resin;
- (11) polyalkylenepolyamino;
- (12) a polymer of (2-methacryloyloxyethyl) ethyleneimine, and a copolymer of (2-methacryloyloxyethyl)ethyleneimine and an unsaturated monomer copolymerizable with (2-methacryloyloxyethyl) ethyleneimine;
- (13) polyamidepolyamine;
- (14) polyamideamine-epihalohydrin resin;
- (15) denaturated polyacrylamide as a result of Mannich reaction and denaturated polymethacrylamide as a result of Mannich reaction;
- (16) polyvinylamine, and a copolymer of vinylamine and an unsaturated monomer copolymerizable with vinylamine;
- (17) a condensation polymer of dicyandiamide-diethylenetriamine; etc.

To be more specific, examples of the polyamine compound include:

polyallylamine, polydiallylamine, poly(N-alkyldiallylamine), poly(alkyldiallylamine), a copolymer of monoallylamine-diallylamine, a copolymer of N-alkyldiallylamine-monoallylamine, a copolymer of monoallylamine-dialkyldiallylammonium salt, a copolymer of diallylamine-dialkyldiallylammonium salt, polydimethylaminoethyl acrylate, polydiethylaminoethyl acrylate, polydimethylaminoethyl acrylamide, straight-chain polyethyleneimine, branched-chain polyethyleneimine, polyethylenepolyamine, polypropylenepolyamine, polyamidepolyamine, polyetherpolyamine, polyvinylamine, polyamidepolyamine-epichlorohydrin resin, polyamidine, etc. The examples also include amino denaturated products produced by reacting formaldehyde and diethylamine with polyacrylamide or polymethacrylamide.

The polyamino compound may be neutralized by an acid compound, either entirely or partially. The acid compound may be any compound capable of neutralizing the polyamine compound, that is to say, any inorganic acid and organic acid. Example of inorganic acid include:

carbonic acid;
hydroacids, such as hydrochloric acid and hydrofluoric acid;
oxygen acids, such as sulfuric acid, sulfurous acid, nitric acid, hypophosphorous acid, phosphorous acid, orthophosphoric acid, metaphosphoric acid, polyphosphoric acid including pyrophosphoric acid, triphosphoric acid, ultraphosphoric acid (acid metaphosphoric acid), perchloric acid;
salts of the above oxygen acids; etc.

Examples of the organic acid include compounds containing an acid functional group, such as carboxylic acid, sulfinic acid, sulfonic acid, phenolic acid, enol (a tautomer of a carbonyl compound), mercaptan, imide (acid imide), oxime, sulfonamide, etc. To be more specific, examples of the organic acid include:

hydroxy acids, such as glycolic acid, lactic acid, trichlorolactic acid, glyceric acid, malic acid, tartaric acid, citric acid, tartronic acid, and gallic acid;
amino acids, such as aspartic acid; etc. One member or a mixture of two or more members selected from these acid compounds can be used effectively.

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The polyamine compound has a weight average molecular weight of 5,000 or higher, and a preferred range of the same is between 10,000 and 10,000,000. Using a polyamine compound having a weight average molecular weight below 5,000 is not preferable, because the resulting absorbing agent composition often fails to exhibit a desired diffusing absorbency index under pressure. An amount of use of the polyamine compound varies depending on the use of the resulting absorbing agent composition: however, a preferred range with respect to 100 parts by weight of the absorbent resin is between 0.1 part by weight and 10 parts by weight.

In a suitable method of mixing the absorbent resin and polyamine compound, a solution or dispersion liquid is prepared by dissolving or dispersing the polyamine compound into water and/or any of the aforementioned hydrophilic organic solvents, and the solution or dispersion liquid is mixed with the absorbent resin through atomization or dripping. The absorbent resin and polyamine compound are mixed with each other by any of the above-mentioned mixing devices. The mixing speed can be either high or low.

The water-insoluble inorganic powders and polyamine compound may be used separately or together. The mixing order of the absorbent resin, water-insoluble inorganic powders, and polyamine compound is not especially limited.

As previously mentioned, the absorbing agent composition of the present invention can be obtained by another method, which will be described below.

In the first place, the absorbent resin precursor is adjusted in such a manner to contain carboxyl groups, have an average particle diameter in a range between 200 μ m and 600 μ m, and contain up to 10 weight percent particles having a diameter smaller than 106 μ m. Then, the absorbent resin precursor is subject to heat treatment under the presence of the first and second surface crosslinking agents reactive with the carboxyl group at 160°C or higher to produce an absorbent resin: the first surface crosslinking agent has a solubility parameter of 12.5(cal/cm³)^{1/2} or higher while the second surface crosslinking agent has a solubility parameter below 12.5(cal/cm³)^{1/2}.

In the second place, the surface crosslinking agent, preferably, the first surface crosslinking agent having a solubility parameter of 12.5(cal/cm³)^{1/2} or higher and the second surface crosslinking agent having a solubility parameter below 12.5(cal/cm³)^{1/2}, is added to the resulting absorbent resin and mixed, after which the resulting mixture is subject to heat treatment at 160°C or higher.

The non-volatile water-soluble compound optionally contained in the absorbing agent composition of the present invention has a boiling point of 150°C or higher under normal pressure, remains in a solid state at room temperature, and at least 1g of which dissolves into 100g of water at room temperature. A compound that remains in a solid state at room temperature, or has a boiling point of 200°C or higher under normal pressure is preferable. More preferable is a compound at least 10g of which dissolves into 100g of water at room temperature, and further preferable is a compound at least 100g of which dissolves into 100g of water at room temperature. When the absorbing agent composition is used in the absorbent product, such as paper diapers, using the above non-volatile water-soluble compound makes it possible to improve urine resistance while reducing an amount of wet back of an aqueous liquid (an amount of the absorbed aqueous liquid seeps back from the absorbing agent composition).

Examples of the non-volatile water-soluble compound include organic compounds containing at least one functional group selected from a group consisting of hydroxyl group, carboxyl group, amide group and amino group, and inorganic compounds exhibiting basic properties to the absorbent resin. The inorganic compounds exhibiting basic properties to the absorbent resin referred herein is a compound having a higher pH than the absorbent resin. A compound preferred as such inorganic compounds has a pH of 8.5 or higher, more preferably 9.0 or higher, and most preferably in a range between 10 and 14.

Of all the above organic compounds, those containing at least one hydroxyl group in a molecule, or namely, alcohols, are not especially limited as long as they are water soluble. Examples of the alcohols include:

monohydroxy alcohols such as glycolic acid and methoxypolyethylene glycol;
polyhydroxy alcohols, such as ethylene glycol, propylene glycol, glycerin, polyglycerin, pentaerythritol, sorbitol, diethyleneglycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,4-pentanediol, 1,6-hexanediol, 2,5-hexanediol, trimethylolpropane, diethanolamine, triethanolamine, polyethylene glycol, polyvinyl alcohol, a block copolymer of oxyethylene-oxypropylene, a random copolymer of oxyethylene-oxypropylene, water-soluble polysaccharides represented by water-soluble starch, glucose, fructose, and saccharose;
aminoalcohols, such as monoethanolamine; etc.

Of all these examples, polyhydroxy alcohols and aminoalcohols are preferred, and particularly, polyhydroxy alcohols are preferred. Using at least one alcohol selected from a group consisting of polyhydroxy alcohols and aminoalcohols makes it possible to improve urine resistance of the absorbent products using the resulting absorbing agent composition, such as paper diapers.

Among the polyhydroxy alcohols, those having at least three hydroxy groups, such as glycerin, sorbitol, and saccharose, may be modified by etherifying or esterifying a part of hydroxyl groups of these polyhydroxy alcohols, provided

that one molecular contains a plurality of hydroxyl groups and these polyhydroxy alcohols remain water soluble after the modification. Examples of such modified polyhydroxy alcohols include: glycerol monolatty acid ester, polyoxyethylene fatty acid ester, saccharose fatty acid ester, etc.

These polyhydroxy alcohols or aminoalcohols may be prepared before they are mixed with the absorbent resin, or the precursors of these alcohols, namely, ethyleneoxida, alkylencarbonate or the like, may be converted to the polyhydroxy alcohols or aminoalcohols after they are mixed with the absorbent resin. When the absorbent resin is made into agglomerated particles or a sheet, the polyhydroxy alcohols may be used as a plasticizer or binder. The polyhydroxy alcohols exhibit the resulting absorbing agent composition some functions, such as plasticity and adhesive properties to a substrate made of hydrophilic fibers (which will be explained below) or the like. Moreover, besides being able to ensure high safety, the polyhydroxy alcohols can improve the mixing properties of the absorbing agent composition and hydrophilic fibers or the like in the absorbent material without causing coloring.

Of all the above organic compounds, those containing at least one carboxyl group in one molecule, namely, carboxylic acid, is not especially limited as long as they are water soluble. Preferred carboxylic acids are carboxylic acid and a salt thereof, and examples of which include:

aniseate, bezonate, formate, valerate, glyoxylate, glycolate, glycerol phosphate, glutarate acid, chloroacetate, chloropropionate, cinnamate, succinate, acetate, tartrate, lactate, pyruvate, fumarate, propionate, 3-hydroxypropionate, maleate, malonate, butyrate, iso-butyrate, imidinoacetate, malate, citraconate, adipate, itaconate, crotonate, salicylate, gluconate, gallate, sorbate, p-oxybezionate, etc. Of all these salts of carboxylic acid, salts of polycarboxylic acid are preferred, and salts of dicarboxylic acid are more preferred, among which maleate and malonate are particularly preferred.

Of all these organic compounds, the examples of water-soluble compounds containing at least one amide group in one molecule include urea. When the absorbent resin is made into agglomerated particles or a sheet, the urea may be used as a binder.

The inorganic compound is not especially limited as long as it is water soluble. Examples of the inorganic compound include: ammonia, phosphate, diphosphate, tripolyphosphate, sulfate, hydrochloric acid, carbonate, hydrogen carbonate, alkali metal hydroxide, sodium carbonate, sodium hydrogencarbonate, sodium hydroxide, potassium hydroxide, etc. Of all these examples, ammonia, phosphate, carbonate, hydrogen carbonate, and alkali metal hydroxide are preferred, and carbonate and hydrogen carbonate are particularly preferred. Using carbonate or hydrogen carbonate makes it possible to improve urine resistance of the absorbent product using the resulting absorbing agent composition, such as paper diaper.

An amount of use of the non-volatile water-soluble compound varies depending on the use of the resulting absorbing agent composition; however, a preferred range is between 1 percent by weight and 50 percent by weight, more preferably between 2 percent by weight and 45 percent by weight, and most preferably between 5 percent by weight and 40 percent by weight based on the weight of the absorbent resin. Using the non-volatile water-soluble compound within the above ranges makes it possible to improve urine resistance of the absorbent product using the resulting absorbing agent composition, such as paper diaper, while reducing an amount of wet back of an aqueous liquid. Using less than 1 weight percent non-volatile water-soluble compound may make it impossible to improve the urine resistance and to reduce an amount of wet back of the aqueous liquid. Whereas using more than 50 weight percent non-volatile water-soluble compound reduces the liquid permeability or liquid diffusion, thereby making it impossible to obtain an absorbing agent composition exhibiting desired absorbing properties.

One member or a mixture of two or more members selected from these non-volatile water-soluble compounds can be used effectively. The non-volatile water-soluble compounds are either organic or inorganic compounds, or a mixture thereof. The most preferable non-volatile water-soluble compound is polyhydroxy alcohols.

When the absorbent resin and non-volatile water-soluble compound are mixed, water and/or any of the aforementioned hydrophilic organic solvents may be used optionally as a solvent. An amount of use of the solvent varies depending on the kinds and particle diameter of the absorbent resin; however, a preferred range with respect to 100 parts by weight of the absorbent resin is up to 20 parts by weight, and more preferably between 0.1 part by weight and 10 parts by weight. When the absorbent resin and non-volatile water-soluble compound are mixed using the solvent, the resulting absorbing agent composition may be dried optionally by heating or the like. A preferable heating temperature is in a range between 40°C and 300°C, and more preferably between 50°C and 200°C.

The absorbent resin and non-volatile water-soluble compound are mixed by any of the aforementioned mixing devices b. The mixing speed can be either high or slow. When using a solid non-volatile water-soluble compound, it is preferable to use the aforementioned solvents.

The reason why the absorbing agent composition containing the non-volatile water-soluble compound of the present invention exhibits good urine resistance is not clear. However, compounds, such as a decomposing enzyme, that play a role of a catalyst in urine-induced deterioration, are assumed to be made less active because the surface of the absorbent resin is crosslinked more uniformly and the crosslinking density is increased and the specific non-volatile water-soluble compound is added.

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The reason why the absorbing agent composition containing the non-volatile water-soluble compound of the present invention can reduce an amount of wet back of an aqueous liquid even when the liquid permeability is increased is not clear either. However, the non-volatile water-soluble compound is presumed to suppress the wet back of a liquid existing in interstitial spaces among the hydrophilic fibers and among swelled gel (swelled absorbent resin).

Besides the above effect, when the non-volatile water-soluble compound is added to an absorbent resin having diffusing absorbency under pressure of 25g/g or higher with respect to 0.9 weight percent sodium chloride solution under a load of 20g/cm² after 60 minutes since the absorption started, not only the urine resistance of the absorbent product using the resulting absorbing agent composition, such as paper diapers, can be increased, but also an amount of wet back of the aqueous liquid can be reduced.

The absorbing agent composition obtained by any of the above methods has diffusing absorbency index under pressure of 1.5g/g-min or higher with respect to a 0.9 weight percent sodium chloride solution under a load of 20g/cm², thereby exhibiting excellent absorbing properties explained above.

The absorbent material of the present invention includes at least one of the aforementioned absorbing agent compositions in an amount of 40 percent by weight or higher, more preferably 50 percent by weight or higher, further preferably 60 percent by weight or higher, and most preferably 70 percent by weight or higher.

An absorbent material containing an absorbing agent composition having a diffusing absorbency index under pressure of 1.5g/g-min or higher can readily absorb an aqueous liquid supplied in bulk, thereby making increasing an overall absorbing capacity of the absorbent material. In contrast, an absorbent material containing an absorbing agent composition having diffusing absorbency index under pressure below 1.5g/g-min can not readily absorb an aqueous liquid supplied in bulk. In other words, the absorbent material containing such an absorbing agent composition has a low diffusing absorbency index under pressure, and therefore exhibits poor liquid diffusion. For this reason, the above absorbent material can neither readily absorb an aqueous liquid supplied in bulk nor diffuse the same inside. As a result, it takes quite a long time for the absorbent material to absorb the supplied aqueous liquid, thereby reducing an overall absorbing capacity of the absorbent material. Further, an absorbent product using the above absorbent material may cause inconveniences, such as leakage, when an aqueous liquid is supplied in bulk for the reason specified above. Such inconveniences become apparent when the aqueous liquid is repetitively supplied in bulk to the same spot of the absorbent product.

The absorbent material of the present invention may optionally contain hydrophilic fibers besides the absorbing agent composition. An absorbent material made of the absorbing agent composition and hydrophilic fibers is arranged to have the following structures in which:

- the absorbing agent composition and hydrophilic fibers are mixed homogeneously;
- the absorbing agent composition is sandwiched by layers of the hydrophilic fibers;
- the absorbing agent composition and hydrophilic fibers are mixed homogeneously and made into a layer, and after which a layer of the hydrophilic fibers is formed thereon;
- after the absorbing agent composition and hydrophilic fibers are mixed homogeneously and made into a layer to sandwich the absorbing agent composition with another layer of the hydrophilic fibers; etc.

Further, the absorbent material may be the absorbing agent composition made into a sheet with a predetermined amount of water. These structures further improve the absorbing properties of the resulting absorbent material.

Among of all these structures, the preferred is the structure in which the absorbing agent composition and hydrophilic fibers are mixed homogeneously in such a manner that the absorbent material include the absorbing agent composition in an amount (ratio) of 40 percent by weight or more. The more preferred is the structure in which the absorbing agent composition and hydrophilic fibers are mixed homogeneously in such a manner that the absorbent material include at least 50 weight percent, more preferably at least 60 weight percent, and most preferably at least 70 weight percent, absorbing agent composition based on the combined weight of the absorbing agent composition and hydrophilic fibers. In the present invention, the higher the resin concentration the absorbent material has, the more significant the absorption properties appear. Note that the structure of the absorbent material is not limited to the above examples.

Examples of the hydrophilic fibers include, but are not limited to:

- cellulose fibers obtained out of woods, such as mechanical pulp, chemical pulp, semi-chemical pulp, and dissolving pulp;
- artificial cellulose fibers, such as rayon and acetate; etc.

Of all these fibers, cellulose fibers are preferable. The hydrophilic fibers may include synthetic fibers, such as polyamide, polyester, and polyolefin.

When the absorbent material contains the hydrophilic fibers in a relatively small ratio, the absorbent material,

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namely, the hydrophilic fibers, may be adhered to each other using an adhesive binder. By so doing, the resulting absorbent material exhibits better strength and anti-deformation properties before or during the use.

Examples of the adhesive binder include: polyolefin fibers of thermal-fused fibers, such as polyethylene, polypropylene, a copolymer of ethylene-propylene, and a copolymer of 1-butene-ethylene; adhesive emulsion; etc. One member or a mixture of two or more members selected from those binders can be used. A preferable weight ratio of the hydrophilic fibers/adhesive binder(s) is in a range between 50/50 and 99/1, more preferably between 70/30 and 95/5, and most preferably 80/20 and 95/5.

The absorbent material thus obtained exhibits excellent absorbing properties as mentioned above.

The absorbent material of the present invention, when used in sanitary goods, such as paper diapers, sanitary napkins, and incontinence pads, can exhibit excellent properties (absorbing properties), such as high liquid diffusion and absorbency under pressure and a constant absorbing capacity over a long period, even when an amount of the absorbent resin is increased or the resin concentration is high.

The absorbent product of the present invention comprises a liquid permeable sheet and a liquid impermeable sheet sandwiching an absorbent layer containing the above absorbent material. The structure and producing method of the absorbent layer are not especially limited. The method of producing the absorbent product is not especially limited, either.

The liquid permeable sheet is made of a material capable of transmit an aqueous liquid. Examples of such a material include: non-woven fabric, woven fabric; a porous synthetic resin film made of polyethylene, polypropylene, polyester, polyamide; etc. On the other hand, the liquid impermeable sheet is made of a material incapable of transmitting an aqueous liquid. Examples of such a material include: a synthetic resin film made of polyethylene, polypropylene, ethylene vinylacetate, polyvinyl chloride; a film made of the above synthetic resins and non-woven fabric; a film made of the above synthetic resins and woven fabric; etc. Note that the liquid impermeable sheet may transmit steam.

The above-structured absorbent product exhibits the excellent absorbing properties explained above. The absorbent product includes, but is not limited to, sanitary goods, such as paper diapers, sanitary napkins, and incontinence pads. Since the absorbent product of the present invention exhibits excellent absorbing properties, the same can prevent the leakage of urine while securing a feeling of dryness, when used as a paper diaper.

The above absorbing agent composition, absorbent material, and absorbent product may optionally include deodorant, anti-bacterial agent, perfume, foaming agent, pigment, dye, hydrophilic short fiber, fertilizer, oxidizing agent, reducing agent, water, etc. to provide additional functions.

The present invention will be described in detail by way of examples and comparative examples. However, the present invention is not limited to the disclosure below. The properties (physical properties) of the absorbing agent composition, absorbent material, and absorbent product are measured in the following manner.

(a) Absorbency

Here, 0.2g of the absorbing agent composition is uniformly placed into a bag (60mm×60mm) made of non-woven fabric, and allowed to remain immersed in a 0.9 weight percent sodium chloride solution (physiological saline solution) at room temperature for 60 minutes. Then, the bag is taken out, and subject to hydro-extraction for 3 minutes at 250G using a centrifugal separator, and the weight W_1 (g) of the bag is measured. Further, the same processes are carried out with an empty bag, and the weight W_0 (g) of the empty bag is measured. The absorbency (g/g) is calculated using the weights W_1 and W_0 on the basis of the following equation:

$$\text{Absorbency (g/g) Composition(g)} = \frac{(\text{Weight } W_1 \text{ (g)} - \text{Weight } W_0 \text{ (g)})}{\text{Weight of Absorbing Agent}}$$

When the absorbing agent composition includes additives other than the absorbent resin (for example, non-volatile water-soluble compound, water-insoluble inorganic powders, polyamine compound, etc.) in the combined amount of 5 percent by weight or more, the absorbency (g/g) is calculated on the basis of the following equation:

$$\text{Absorbency (g/g)} = \frac{(\text{Weight } W_1 \text{ (g)} - \text{Weight } W_0 \text{ (g)})}{\text{Weight of Absorbent Resin (g)}}$$

where "Weight of Absorbent Resin" is a weight of the absorbent resin contained in 0.2g of the absorbing agent composition.

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(b) Diffusing Absorbency under Pressure

To begin with, a device measuring the diffusing absorbency under pressure of the absorbing agent composition will be briefly explained below with reference to Figures 1 and 2.

As shown in Figure 1, the measuring device includes a balance 1, a container 2 of a predetermined capacity placed on the balance 1, an air-intake pipe 3, a conduit 4, a glass filter 6, and a measuring section 5 placed on the glass filter 6. The container 2 has an opening 2a on the top and an opening 2b on the side, and the air-intake pipe 3 is inserted through the opening 2a while the conduit 4 is fixed to the opening 2b. Further, a predetermined amount of physiological saline solution 12 is poured in the container 2. The lower end portion of the air-intake pipe 3 is dipped into the physiological saline solution 12. The glass filter 6 has a diameter of 70mm. The container 2 and the glass filter 6 communicate with each other through the conduit 4. The glass filter 6 is fixed in such a manner that the upper surface of the same is positioned slightly above the lower end of the air-intake pipe 3.

As shown in Figure 2, the measuring section 5 is provided with a paper filter 7, a sheet 8, a supporting cylinder 9, a metal gauze 10 affixed to the bottom of the supporting cylinder 9, and a weight 11. In the measuring section 5, the paper filter 7, sheet 8, and supporting cylinder 9 (that is, the metal gauze 10) are sequentially placed on the glass filter 6 in this order, and the weight 11 is placed on the metal gauze 10 inside the supporting cylinder 9. The sheet 8 is a 0.1mm-thick toroidal made of polyethylene terephthalate (PET) having an 18-mm-dia opening at the center. The supporting cylinder 9 has an inner diameter of 60mm. The metal gauze 10 is made of stainless steel to have a 400-mesh (the size of each mesh: 38μm) according to the JIS standard. A predetermined amount of the absorbing agent composition is uniformly scattered on the metal gauze 10. The weight 11 is adjusted in such a manner to apply a load of 20g/cm² evenly to the metal gauze 10, that is, the absorbing agent composition.

The diffusing absorbency under pressure of the absorbing agent composition is measured by using the above-arranged measuring device in the manner described below.

To begin with, preparatory operations are carried out, that is predetermined amount of physiological saline solution 12 is poured into the container 2, and the air-intake pipe 3 is inserted into the container 2. Then, the paper filter 7 is placed onto the glass filter 6, and the sheet 8 is placed atop of the paper filter 7 in such a manner that its opening is superimposed on the center of the glass filter 6. At the same time, 1.5g of the absorbing agent composition is uniformly scattered on the metal gauze 10 inside the supporting cylinder 9, and the weight 11 is placed on the absorbing agent composition.

Subsequently, the metal gauze 10, that is, the supporting cylinder 9 having the absorbing agent composition and the weight 11 inside, is placed on the sheet 8 in such a manner that the center of the supporting cylinder 9 is superimposed on the center of the glass filter 6.

Then, the weight W₂(g) of the physiological saline solution 12, which has been absorbed by the absorbing agent composition for 60 minutes since the supporting cylinder 9 was placed on the sheet 8, is measured by the balance 1. As shown in Figures 2 and 3, after passing through the opening of the sheet 8, the physiological saline solution 12 is absorbed by the absorbing agent composition while being diffused almost uniformly in the lateral direction (indicated by an arrow).

The diffusing absorbency under pressure (g/g) of the absorbing agent composition after 60 minutes since the absorption started is calculated on the basis of the following equation:

$$\text{Diffusing Absorbency under Pressure (g/g)} = \frac{\text{Weight } W_2 \text{ (g)}}{\text{Weight of Absorbing Agent Composition (g)}}$$

When the absorbing agent composition includes additives other than the absorbent resin (for example, non-volatile water-soluble compound, water-insoluble inorganic powders, polyamine compound, etc.) in the combined amount of 5 percent by weight or more, the diffusing absorbency under pressure (g/g) is calculated on the basis with the following equation:

$$\text{Diffusing Absorbency under Pressure (g/g)} = \frac{\text{Weight } W_2 \text{ (g)}}{\text{Weight of Absorbent Resin (g)}}$$

where "Weight of Absorbent Resin" is a weight of the absorbent resin contained in 1.5g of the absorbing agent composition.

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(c) Diffusing Absorbency Index under Pressure

The diffusing absorbency index under pressure is measured using the same device used for measuring the diffusing absorbency under pressure. To be more specific, the weight of the physiological saline solution 12 absorbed by the absorbing agent composition after 60 minutes since the supporting cylinder 9 was placed on the sheet 8 is measured in time series using the balance 1. That is to say, the weight of the absorbed physiological saline solution 12 is measured per minute, preferably per second, using the balance 1. Then, the maximum absorbing capacity per unit time is calculated using the result of the above measurement, and defined as the diffusing absorbency index under pressure (g/g·min).

(d) Urine Resistance and Water-Soluble Content

To begin with, sampling urine of the same amount is collected from 10 males in a healthy condition. Then, 2g of the absorbing agent composition is placed in a lidded glass bottle of 100ml and the sampling urine is poured to let the absorbing agent composition swell by 25 times. Subsequently, the glass bottle containing the swelled gel is let stand for 16 hours at 37°C in atmosphere of relative humidity of 90%.

Then, the fluidity of the swelled gel is observed visually and evaluated in four stages: "no fluidity", "no substantial fluidity", "slight fluidity", and "fair fluidity".

Further, the water-soluble content in the swelled gel is measured in the following manner. Some of the swelled gel having solid content (solid content of the absorbent resin) of 0.5g is taken out, and dispersed in an ion exchange water of 1l and the resulting dispersion liquid is subject to stirring for 1 hour to let the gel fully swell. The dispersion liquid is filtered through a paper filter, and the filtrate is subject to titration in a predetermined manner. An amount of a compound dissolved in the filtrate produced as a result of deterioration by urine, namely, water-soluble polyacrylate and/or polyacrylic acid, is calculated based on the titre or the like, and defined as the water-soluble content (percent by weight). It is understood herein that the more the water-soluble content, the more the absorbing agent composition has been deteriorated by urine.

(e) Amount of Wet Back

Five pieces of 90-mm-dia filters (Advantech Toyo Kabushiki Kaisha, Model No. 2) are layered. Then, the supporting cylinder 9 containing the absorbing agent composition swelled by the physiological saline solution, together with the weight 11, is removed from the measuring device used in measuring the diffusing absorbency under pressure, and the same are placed on the 5-fold filters. A weight is added to apply a load of 100g/cm² to the absorbing agent composition uniformly. Then, an amount of physiological saline solution oozed to the 5-fold filter after 1 minute since the load of 100g/cm² was applied is measured, and defined as an amount (g) of wet back.

(f) Diffusing absorbency under Pressure of Absorbent Material

To begin with, a device for measuring the diffusing absorbency of the absorbent material will be described with reference to Figures 4 and 5. Hereinafter, like components are labeled with like reference numerals with respect to the counterpart used in measuring the diffusing absorbency under pressure of the absorbing agent composition, and the description of these components is not repeated for the explanation's convenience.

As shown in Figure 4, the measuring device includes a balance 1, a container 2, an air-intake pipe 3, a conduit 4, a 120-mm-dia glass filter 6, and a measuring section 15 placed on the glass filter 6. As shown in Figure 5, the measuring section 15 is provided with a paper filter 7, a sheet 8, a supporting rectangular tube 19, and a weight 11. Note that the measuring section 15 does not include the metal gauze.

In the measuring section 15, the paper filter 7, the sheet 8, and the supporting rectangular tube 19 are sequentially placed on the glass filter 6 in this order, and the weight 11 is placed inside the supporting rectangular tube 19. The sheet 8 is a 0.1mm-thick rectangle made of polyethylene terephthalate (PET) having a 12.5mm×100mm opening at the center. The supporting rectangular tube 19 has an inner dimension of 100mm×100mm, so that an absorbent material of a predetermined size is placed inside. The rest is identical with the structure of the counterpart used to measure the diffusing absorbency under pressure of the absorbing agent composition.

The diffusing absorbency under pressure of the absorbent material is measured using the above-structured measuring device in the manner described below. To begin with, 50 parts by weight of the absorbing agent composition and 50 parts by weight of comminuted wood pulp serving as the hydrophilic fibers are mixed using a mixer through dry blending. The resulting mixture is made into a 100mm×100mm web, and the web is pressed under a load of 2kg/cm² for 1 minute. As a result, an absorbent material having a basis weight of approximately 0.047g/cm² is obtained.

Prior to the measuring, the measuring device is prepared in a predetermined manner. Then, the filter 7 is placed

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on the glass filter 6, and the sheet 8 is placed on the filter 7 in such a manner that the opening of the same is superimposed on the center of the glass filter 6. Then, the supporting rectangular tube 19 is placed on the sheet 8 in such a manner that the center of the same is superimposed on the center of the glass filter 6.

5 Subsequently, the absorbent material is placed on the sheet 8 inside the supporting rectangular tube 19, upon which the weight 11 is placed. The absorbent material and weight 11 are placed swiftly.

Then, a weight W_3 (g) of the physiological saline solution 12 absorbed in the absorbent material for 60 minutes since the absorbent material was placed on the sheet 8 is measured using the balance 1. Note that, as shown in Figures 5 and 6, the physiological saline solution 12 having passed through the opening of the sheet 8 is absorbed by the absorbent material while being diffused almost uniformly in the lateral direction (indicated by an arrow).

10 Then, the diffusing absorbency under pressure (g/g) of the absorbent material after 60 minutes since the absorption started is calculated using the weight W_3 on the basis with the following equation:

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$$\text{Diffusing Absorbency under Pressure (g/g) of Absorbent Material} = \frac{\text{Weight } W_3 \text{ (g)}}{\text{Weight of Absorbent Material (g)}}$$

(g) Absorbing Rate under Pressure of Absorbent Material (Core Acquisition)

20 The absorbent material subject to measurement is produced in the following manner. To begin with, 8.8g of the absorbing agent composition and 8.8g of comminuted wood pulp are mixed using a mixer through dry blending. Then, the resulting mixture is made into a 260mmx150mm web, or the absorbent material.

On the other hand, synthetic urine is prepared by producing a water solution containing 1.9 weight percent urea, 0.8 weight percent NaCl, 0.1 weight percent CaCl_2 , 0.1 weight percent MgSO_4 .

25 Then, a load of 18g/cm^2 is applied on the entire absorbent material uniformly, and a 30mm-dia cylinder of 120mm high is pressed against the absorbent material around the center to place the cylinder perpendicular to the absorbent material. Then, 50g of the synthetic urine kept at 25°C is poured into the cylinder quickly (at one time). Then, the time since the synthetic urine is poured until the same is absorbed into the absorbent material completely is measured as the first absorbing rate under pressure (sec.) The same process is repeated twice using the same absorbent material with 50-minute interval to measure the second and third absorbing rates under pressure (sec). It is understood herein 30 that the larger the absorbency under pressure, the better the liquid diffusion of the absorbent material.

(h) Properties of Absorbent Product (Using Kewpie Doll®)

35 The absorbent product subject to measurement is produced in the following manner. To begin with, 50 parts by weight of the absorbing agent composition and 50 parts by weight of comminuted wood pulp are mixed using a mixer through dry blending. Then, the resulting mixture is made into a 120mmx400mm web on a wire screen of 400-mesh (the size of each mesh: $38\mu\text{m}$) by a batch-type pneumatic molding device by pneumatic molding. Further, the web is pressed for 5 seconds under a load of 2kg/cm^2 , and as a result, an absorbent material having a basis weight of approximately 0.047g/cm^2 is obtained.

40 Subsequently, a back sheet (liquid impermeable sheet) having a leg gather made of impermeable polypropylene, the above absorbent material, a top sheet (liquid permeable sheet) made of permeable polypropylene are laminated to each other in this order using a both-sided tape. Then, two tape fasteners are attached to the resulting lamination to obtain an absorbent product (i.e., paper diaper).

45 The above absorbent product is put on a Kewpie Doll® (55cm tall and 5kg in weight), and laid with its face downward. Then, a tube is inserted between the absorbent product and doll in such a manner that a physiological saline solution will be supplied around the same spot where a baby would discharge urine. Here, 50ml of the physiological saline solution is repetitively supplied every 20 minutes until the absorbent product can no longer absorb the physiological saline solution and the excessive physiological saline solution starts to leak, and an amount of the physiological saline solution supplied up to this point is measured.

50 The above test is repeated four times and an average amount is calculated, which is defined as an absorbing capacity (g). It is understood herein that the larger the absorbed capacity, the better the properties of the absorbent product.

(Example 1)

55 A reactant solution is prepared by dissolving 3.59g of trimethylolpropane triacrylate serving as an internal crosslinking agent into 5.500g of a water solution of 39 weight percent sodium acrylic acid (hydrophilic unsaturated monomer) neutralized by 75 percent by mole. Then, the reactant solution is subject to deaeration for 30 minutes in nitrogen gas

atmosphere. Then, the reactant solution is poured into a reactor, which is a stainless lidded two-arm type kneader of 10l. with two sigma blades and a jacket. Then, the reactant system is displaced by introducing nitrogen gas while keeping the reactant solution at 30°C.

Next, 2.4g of ammonium persulfate and 0.12g of L-ascorbic acid serving as a polymerization initiator are added to the reactant solution with stirring. Then, the polymerization starts 1 minute later. The polymerization is proceeded at 30°C-80°C until 60 minutes have passed since the polymerization started, and the resulting hydrous gel of polymer is taken out.

The hydrous gel of polymer is finely divided and each particle has a diameter of approximately 5mm. The finely divided hydrous gel of polymer is spread across the 50-mesh metal gauze and subject to hot air drying for 90 minutes at 150°C. Then, the dried gel is pulverized by a vibrating mill, and sieved to a particular diameter size using a 20-mesh metal gauze. As a result, an absorbent resin precursor of an undefined shape having an average particle diameter of 400µm and containing 5 weight percent particles having a diameter smaller than 106µm is obtained.

Then, a surface crosslinking agent solution, made of 0.5 part by weight of ethylene glycol (SP value: $\sigma=14.6(\text{cal}/\text{cm}^3)^{1/2}$) serving as the first surface crosslinking agent, 0.1 part by weight of glycerol polyglycidyl ether (SP value: $\sigma=10.8(\text{cal}/\text{cm}^3)^{1/2}$) serving as the second surface crosslinking agent, 3 parts by weight of water, and 1 part by weight of ethyl alcohol, is mixed with 100 parts by weight of the above absorbent resin precursor. The resulting mixture is subject to heat treatment for 40 minutes at 195°C to obtain an absorbent resin. The average particle diameter of the resulting absorbent resin is 400µm and it contains 3 weight percent particles having a diameter smaller than 106µm.

Finally, the absorbing agent composition of the present invention is obtained by adding 0.5g of microscopic powders of hydrophilic silicon dioxide (Aerosil 200 of the Nippon Aerosil Co., Ltd.) serving as water-insoluble inorganic powders to 100g of the above absorbent resin and mixing the same.

The properties of the absorbing agent composition and the absorbent material and absorbent product using the absorbing agent composition are measured in the manner explained above. Then, the absorbing agent composition has absorbency of 30g/g, diffusing absorbency under pressure of 26.9g/g, and diffusing absorbency index under pressure of 2.87g/g·min. The absorbent material has diffusing absorbency under pressure of 18.9g/g and the first through third absorbing rate under pressure of 34 sec., 69 sec., and 77 sec., respectively. The absorbent product has an absorbing capacity of 275g. These values indicate that each element exhibits excellent properties. The result of the measurement is set forth in TABLE 1 below.

(Example 2)

Herein, 5g of a water solution of 30 weight percent polyethyleneimine having a weight average molecular weight of 70,000 (Epomine P-1000 of Nippon Shokubai Co., Ltd.) serving as the polyamine compound is added to 100g of the absorbent resin obtained in Example 1 and mixed. The resulting mixture is placed in a hot air dryer kept at 90°C for 20 minutes to be set. The resulting set material is sieved to a particular diameter size using a mesh metal gauze (the size of each mesh: 840µm), and 0.3g of microscopic powders of hydrophilic silicon dioxide (Carplex 22S of Shionogi & Co., Ltd.) serving as water-insoluble inorganic powders is added to the set material having passed through the metal gauze and mixed. As a result, the absorbing agent composition of the present invention is obtained.

The properties of the absorbing agent composition, and the absorbent material and absorbent product using the absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

(Example 3)

A reactant solution is prepared by dissolving 2.35g of N,N'-methylenebisacrylamide serving as the internal crosslinking agent into 5,500g of 20 weight percent acrylic acid water solution. Then, the reactant solution is subject to deaeration for 30 minutes in nitrogen gas atmosphere. Then, the reactant solution is poured into a reactor identical with the one used in Example 1, and the reactant system is displaced by introducing nitrogen gas while keeping the reactant solution at 30°C.

Next, 1.5g of ammonium persulfate and 0.07g of L-ascorbic acid are added to the reactant solution with stirring. Then, the polymerization starts about 1 minute later. The polymerization is proceeded at 30°C-80°C and 606.7g of sodium carbonate serving as a neutralizer is added with stirring after 60 minutes since the polymerization started, and after which the polymerization is stopped and the resulting hydrous gel of polymer is taken out.

The hydrous gel of polymer is neutralized 75 percent by mole and finely divided so that each particle has a diameter of approximately 5mm. The finely divided hydrous gel of polymer is spread across the 50-mesh metal gauze and subject to hot air drying for 90 minutes at 150°C. Then, the dried gel is pulverized by a vibrating mill, and sieved to a particular diameter size using a 20-mesh metal gauze. As a result, an absorbent resin precursor of an undefined shape having an average particle diameter of 390µm and containing 4 weight percent particles having a diameter smaller than 106µm

is obtained.

Then, a surface crosslinking agent solution, made of 0.75 part by weight of propylene glycol (SP value: $\sigma=12.6$ (cal/cm^3)^{1/2}) serving as the first surface crosslinking agent, 0.05 part by weight of propylene glycol diglycidyl ether (SP value: $\sigma=10.1$ (cal/cm^3)^{1/2}) serving as the second surface crosslinking agent, 3 parts by weight of water, and 0.75 part by weight of ethylalcohol, is mixed with 100 parts by weight of the above absorbent resin precursor. The resulting mixture is heated for 40 minutes at 195°C to obtain an absorbent resin. The average particle diameter of the resulting absorbent resin is 390 μm and it contains 3 weight percent particles having a diameter smaller than 106 μm .

Finally, the absorbing agent composition of the present invention is obtained by adding 0.3g of microscopic powders of hydrophilic silicon dioxide (Leorosil QS-20 of Tokuyama Kabushiki Kaisha formerly known as Tokuyamasoda Kaishiki Kaisha) serving as the water-insoluble inorganic powders to 100g of the above absorbent resin and mixing the same.

The properties of the absorbing agent composition, and the absorbent material and absorbent product using the absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

(Example 4)

Herein, 5g of a water solution of 30 weight percent polyethyleneimine having a weight average molecular weight of 70,000 (Epomine P-1000 of Nippon Shokubai Co., Ltd.) is added to 100g of the absorbent resin obtained in Example 1 and mixed. Then, the resulting mixture is placed in a hot air dryer kept at 90°C for 20 minutes to be set. The resulting set material is sieved to a particular diameter size using a metal gauze (the size of each mesh: 840 μm), and those having passed through the metal gauze are obtained as the absorbing agent composition of the present invention.

The properties of the absorbing agent composition, and the absorbent material and absorbent product using the absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

(Example 5)

A reactant solution is prepared by dissolving 18.49g of polyethylene glycol diacrylate (whose polyethylene glycol portion is made of an adduct of ethyleneoxide of 8 moles in average) serving as the internal crosslinking agent into 5.500g of a water solution of 30 weight percent sodium acrylic acid neutralized 65 percent by mole. The resulting reactant solution is subject to deaeration for 30 minutes in nitrogen gas atmosphere. Then, the reactant solution is poured into a reactor identical with the one used in Example 1, and the reactant system is displaced by introducing nitrogen gas while keeping the reactant solution at 30°C.

Next, 2.3g of ammonium persulfate and 0.12g of L-ascorbic acid are added to the reactant solution with stirring. Then, the polymerization starts about 1 minute later. The polymerization is proceeded at 30°C-80°C until 60 minutes have passed since the polymerization started, and the resulting hydrous gel of polymer is taken out.

The hydrous gel of polymer is finely divided and each particle has a diameter of approximately 5mm. The finely divided hydrous gel of polymer is spread across the 50-mesh metal gauze and subject to hot air drying for 90 minutes at 150°C. Then, the dried gel is pulverized by a vibrating mill, and sieved to a particular diameter size using a 20-mesh metal gauze. As a result, an absorbent resin precursor of an undefined shape having an average particle diameter of 360 μm and containing 5 weight percent particles having a diameter smaller than 106 μm is obtained.

Then, a surface crosslinking agent solution, made of 0.5 part by weight of glycerin (SP value: $\sigma=16.5$ (cal/cm^3)^{1/2}) serving as the first surface crosslinking agent, 0.05 part by weight of ethylene glycol diglycidyl ether (SP value: $\sigma=10.2$ (cal/cm^3)^{1/2}) serving as the second surface crosslinking agent, 3 parts by weight of water, and 1 part by weight of ethylalcohol, is mixed with 100 parts by weight of the above absorbent resin precursor. The resulting mixture is subject to heat treatment for 30 minutes at 195°C to obtain an absorbent resin. The average particle diameter of the resulting absorbent resin is 360 μm and it contains 5 weight percent particles having a diameter smaller than 106 μm .

Finally, a surface crosslinking agent solution made of 0.5 part by weight of glycerin serving as the first crosslinking agent, 0.05 part by weight of ethylene glycol diglycidyl ether serving as the second surface crosslinking agent, 3 parts by weight of water, and 1 part by weight of ethyl alcohol is mixed with 100 parts by weight of the above absorbent resin. The resulting mixture is subject to heat treatment for 30 minutes at 195°C. As a result, an absorbent resin having undergone the surface crosslinking twice is obtained.

The resulting absorbent resin is used as the absorbing agent composition of the present invention and the properties of the same, and the absorbent material and absorbent product using the absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

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(Example 6)

Herein, 100mg (5 percent by weight based on the weight of the absorbent resin) of glycerin serving as the non-volatile water-soluble compound and 10mg (0.5 percent by weight based on the weight of the absorbent resin) of microscopic powders of hydrophilic silicon dioxide (Aerosil 200 of the Nippon Aerosil Co., Ltd.) are added to 2g of the absorbent resin obtained in Example 3 and mixed. As a result, the absorbing agent composition of the present invention is obtained.

The properties of the absorbing agent composition, and the absorbent material and absorbent product using the absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below. Note that the absorbency and diffusing absorbency under pressure of the absorbing agent composition are calculated based on the weight of the absorbent resin contained in the absorbing agent composition.

Also, the urine resistance of the absorbing agent composition is evaluated as "no fluidity", and the water-soluble content and an amount of wet back of the same are 20.1 percent by weight and 2.3g, respectively

(Comparative Example 1)

The absorbent resin obtained in Example 1 is used as a comparative absorbing agent composition herein. The properties of the comparative absorbing agent composition, and the comparative absorbent material and absorbent product using the comparative absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

(Comparative Example 2)

The absorbent resin obtained in Example 3 is used as a comparative absorbing agent composition herein. The properties of the comparative absorbing agent composition, and the comparative absorbent material and absorbent product using the comparative absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

Also, the urine resistance of the comparative absorbing agent composition is evaluated as "slight fluidity", and the water-soluble content and an amount of wet back of the same are 24.5 percent by weight and 2.8g, respectively.

(Comparative Example 3)

A reactant solution is prepared by dissolving 7.18g of trimethylolpropane triacrylate into 5,500g of a water solution of 39 weight percent sodium acrylic acid neutralized 75 percent by mole. The resulting reactant solution is subject to deaeration for 30 minutes in nitrogen gas atmosphere. Then, the reactant solution is poured into a reactor identical with the one used in Example 1, and the reactant system is displaced by introducing nitrogen gas while keeping the reactant solution at 30°C.

Next, 5.0g of sodium persulfate and 0.25g of L-ascorbic acid are added to the reactant solution with stirring. Then, the polymerization starts about 1 minute later. The polymerization is proceeded at 30°C-80°C until 60 minutes have passed since the polymerization started, and the resulting hydrous gel of polymer is taken out.

The hydrous gel of polymer is finely divided and each particle has a diameter of approximately 5mm. The finely divided hydrous gel of polymer is spread across the 50-mesh metal gauze and subject to hot air drying for 90 minutes at 150°C. Then, the dried gel is pulverized by a vibrating mill, and sieved to a particular diameter size using a 20-mesh metal gauze. As a result, an absorbent resin of an undefined shape having an average particle diameter of 360µm and containing 5 weight percent particles having a diameter smaller than 106µm is obtained.

The resulting absorbent resin is used as a comparative absorbing agent composition herein. The properties of the comparative absorbing agent composition, and the comparative absorbent material and absorbent product using the comparative absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

(Comparative Example 4)

A reactant solution is prepared by dissolving 3.59g of trimethylolpropane triacrylate into 5,500g of a water solution of 39 weight percent sodium acrylic acid neutralized 75 percent by mole. The resulting reactant solution is subject to deaeration for 30 minutes in nitrogen gas atmosphere. Then, the reactant solution is poured into a reactor identical with the one used in Example 1, and the reactant system is displaced by introducing nitrogen gas while keeping the reactant solution at 30°C.

Next, 2.4g of ammonium persulfate and 0.12g of L-ascorbic acid are added to the reactant solution with stirring.

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Then, the polymerization starts about 1 minute later. The polymerization is proceeded at 30°C-80°C until 60 minutes have passed since the polymerization started, and the resulting hydrous gel of polymer is taken out.

5 The hydrous gel of polymer is finely divided and each particle has a diameter of approximately 5mm. The finely divided hydrous gel of polymer is spread across the 50-mesh metal gauze and subject to hot air drying for 90 minutes at 150°C. Then, the dried gel is pulverized by a vibrating mill, and sieved to a particular diameter size using a 20-mesh metal gauze. As a result, an absorbent resin precursor of an undefined shape having an average particle diameter of 400µm and containing 5 weight percent particles having a diameter smaller than 106µm is obtained.

10 Then, a surface crosslinking agent solution, made of 0.5 part by weight of ethylene glycol, 3 parts by weight of water, and 1 part by weight of ethyl alcohol, is mixed with 100 parts by weight of the above absorbent resin precursor. The resulting mixture is subject to heat treatment for 20 minutes at 195°C to obtain an absorbent resin. The average particle diameter of the resulting absorbent resin is 400µm and it contains 3 weight percent particles having a diameter smaller than 106µm.

15 The resulting absorbent resin is used as a comparative absorbing agent composition herein. The properties of the comparative absorbing agent composition, and the comparative absorbent material and absorbent product using the comparative absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

(Comparative Example 5)

20 Herein, 0.3g of microscopic powders of hydrophilic silicon dioxide (Aerosil 200 of Nippon Aerosil Co., Ltd.) are added to 100g of the absorbent resin obtained in Comparative Example 3 and mixed to obtain a comparative absorbing agent composition.

25 The properties of the comparative absorbing agent composition, and the comparative absorbent material and absorbent product using the comparative absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

(Comparative Example 6)

30 Herein 0.5g of microscopic powders of hydrophilic silicon dioxide (Aerosil QS-20 of Tokuyamasoda Kabushiki Kaisha) are added to 100g of the absorbent resin obtained in Comparative Example 4 and mixed to obtain a comparative absorbing agent composition.

35 The properties of the comparative absorbing agent composition, and the comparative absorbent material and absorbent product using the comparative absorbing agent composition are measured in the manner explained above, and the result of which is set forth in TABLE 1 below.

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55 50 45 40 35 30 25 20 15 10 5

EXAMPLE/ COMPARATIVE EXAMPLE	ABSORBING AGENT Composition			ABSORBENT MATERIAL				ABSORBENT PRODUCT
	ABSORBENCY (g/g)	DIFFUSING ABSORBENCY UNDER PRESSURE (g/g)	DIFFUSING ABSORBENCY INDEX UNDER PRESSURE (g/g·min)	DIFFUSING ABSORBENCY UNDER PRESSURE (g/g)	ABSORBING RATE UNDER PRESSURE (Sec.)			ABSORBING CAPACITY (g)
					1ST	2ND	3RD	
1	30	26.9	2.87	18.9	34	69	77	275
2	29	27.0	3.33	18.9	35	52	62	300
3	37	27.0	1.67	18.9	35	72	85	275
4	29	27.6	1.93	19.1	35	70	83	275
5	29	24.4	4.00	18.4	34	48	60	300
6	36	28.2	2.83	18.8	35	66	78	275
1	30	30.1	1.20	19.7	39	102	153	250
2	38	33.9	0.90	20.6	38	114	158	250
3	31	11.7	0.20	15.1	38	133	173	225
4	31	14.7	0.87	15.9	37	98	150	225
5	31	13.4	0.20	15.5	39	121	162	225
6	31	22.0	1.27	17.7	39	103	114	250

TABLE 1

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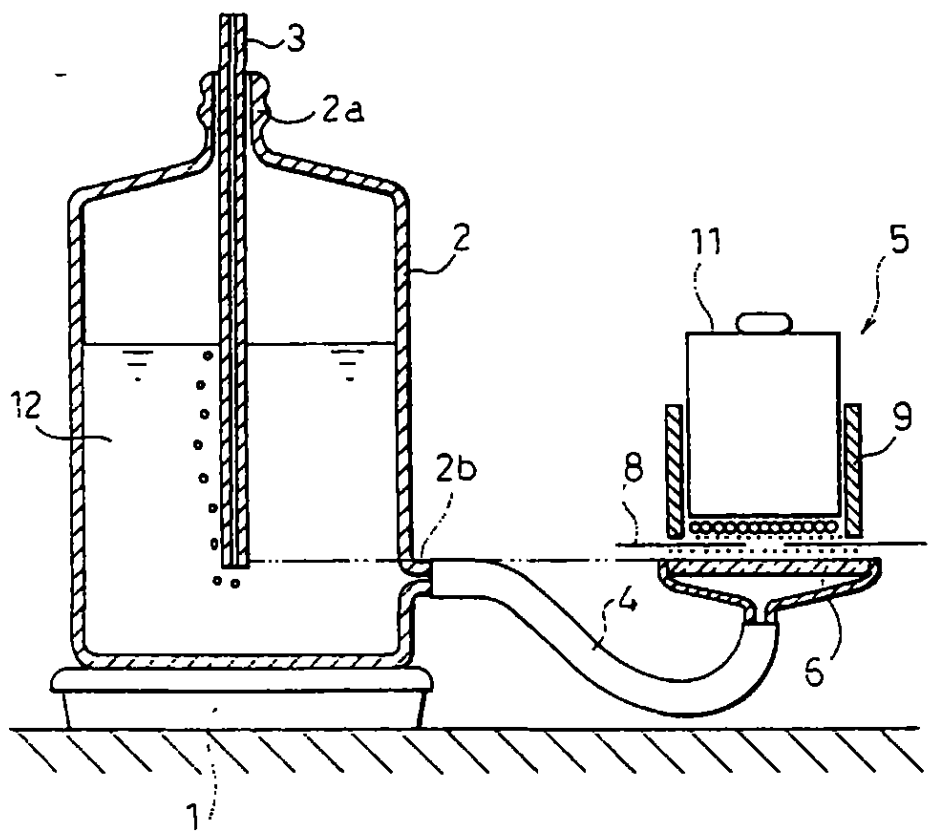
TABLE 1 reveals that the absorbing agent compositions of the present invention excel those of the comparative examples in diffusing absorbency index under pressure. Also, the absorbent materials of the present invention excel those of the comparative examples in absorbing rate under pressure and liquid diffusion. Further, the absorbent products of the present invention excel those of the comparative examples in absorbing capacity. Thus, the absorbing agent composition, absorbent material, and absorbent product of the present invention can readily absorb an aqueous liquid supplied in bulk, while exhibiting excellent properties (absorbing properties), such as capabilities of maintaining high liquid diffusion and a constant absorbing capacity per unit weight.

Claims

1. An absorbing agent composition having a diffusing absorbency index under pressure of 1.5g/g-min or higher with respect to a 0.9 weight percent sodium chloride solution under a load of 20g/cm².
2. An absorbing agent composition according to claim 1, having a diffusing absorbency index under pressure of 3.0g/g-min or higher.
3. An absorbing agent composition according to claim 1 or claim 2, having a diffusing absorbency under pressure of 25g/g or higher with respect to a 0.9 weight percent sodium chloride solution under a load of 20g/cm² after 60 minutes since the onset of absorption.
4. An absorbing agent composition according to any one of claims 1 to 3, comprising a
 - a surface-crosslinked absorbent resin or
 - a mixture of an absorbent resin and a water-insoluble inorganic powder and/or a polyamine compound having a weight average molecular weight of 5,000 or more.
5. An absorbing agent composition according to claim 4, wherein the absorbent resin is an absorbent crosslinked polymer containing carboxyl groups.
6. An absorbing agent composition according to claim 4, wherein the absorbent resin is
 - a partially neutralized crosslinked polymer of acrylic acid;
 - a partially neutralized crosslinked graft polymer of starch-acrylonitrile;
 - a copolymer of isobutylene-maleic acid;
 - a saponified copolymer of vinyl acetate-acrylic acid; or
 - a hydrolyzed polymer of acrylonitrile.
7. An absorbing agent composition according to any one of claims 4 to 6, which also contains a non-volatile water-soluble compound.
8. An absorbent material containing an absorbing agent composition according to any one of claims 1 to 7 and hydrophilic fibers.
9. An absorbent material according to claim 8, containing at least 40 percent by weight of the absorbing agent composition.
10. An absorbent product comprising an absorbent layer containing an absorbent material according to claim 8 or claim 9, sandwiched between
 - a liquid permeable sheet and
 - a liquid impermeable sheet.

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FIG.1



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FIG.2

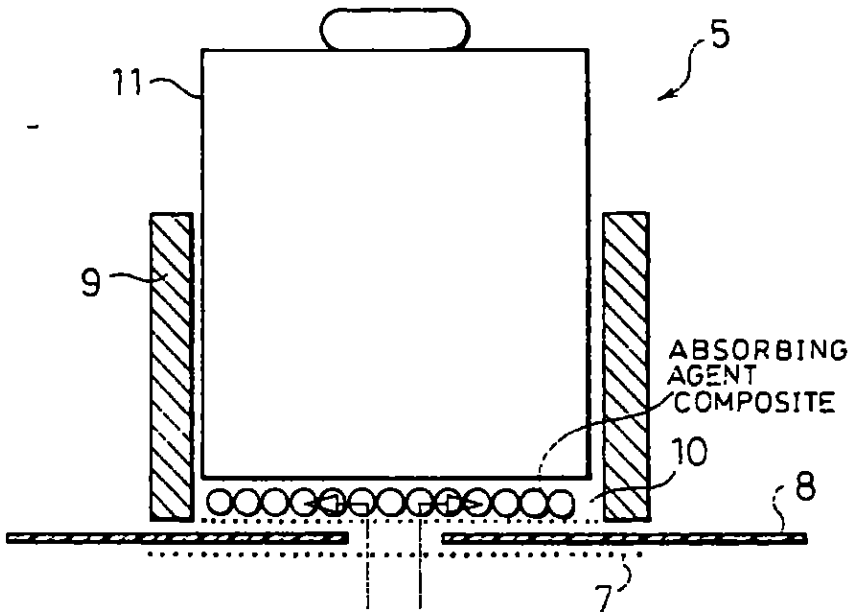


FIG.3

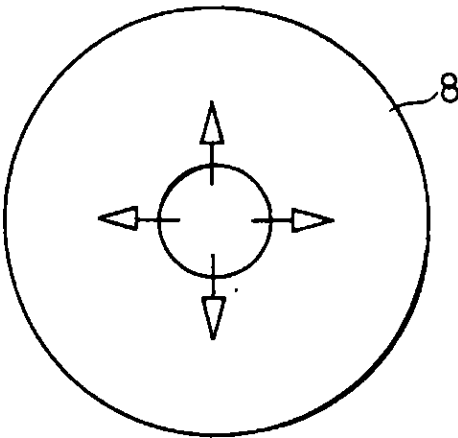


FIG. 4

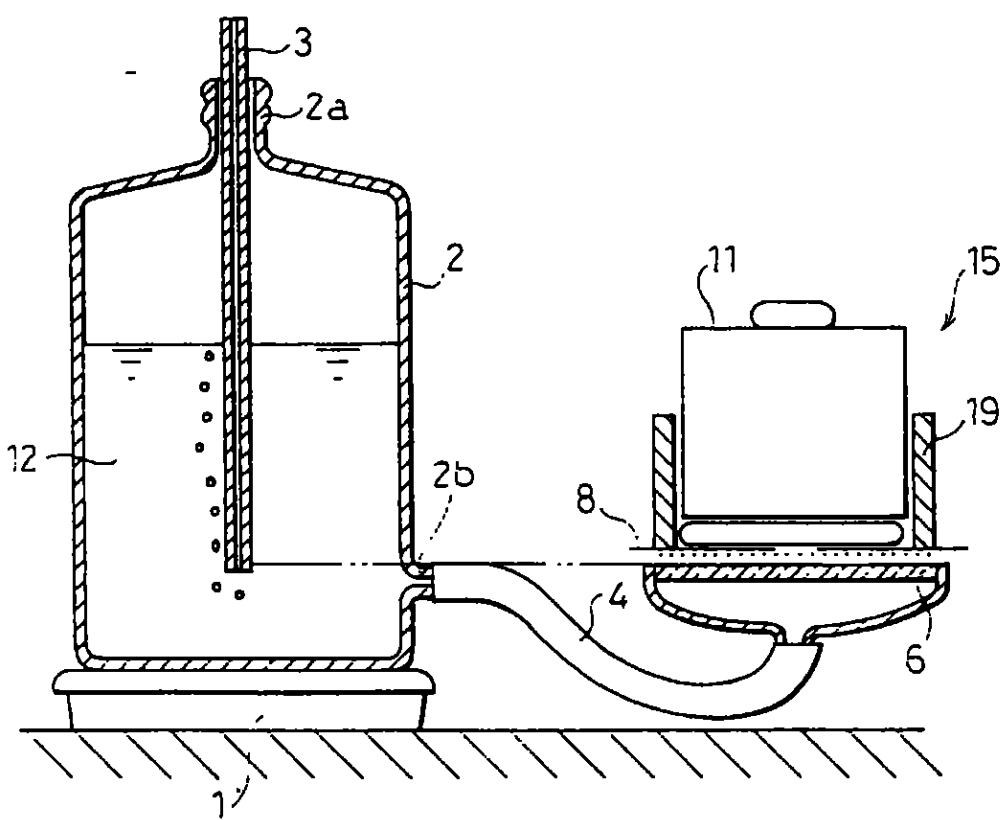


FIG.5

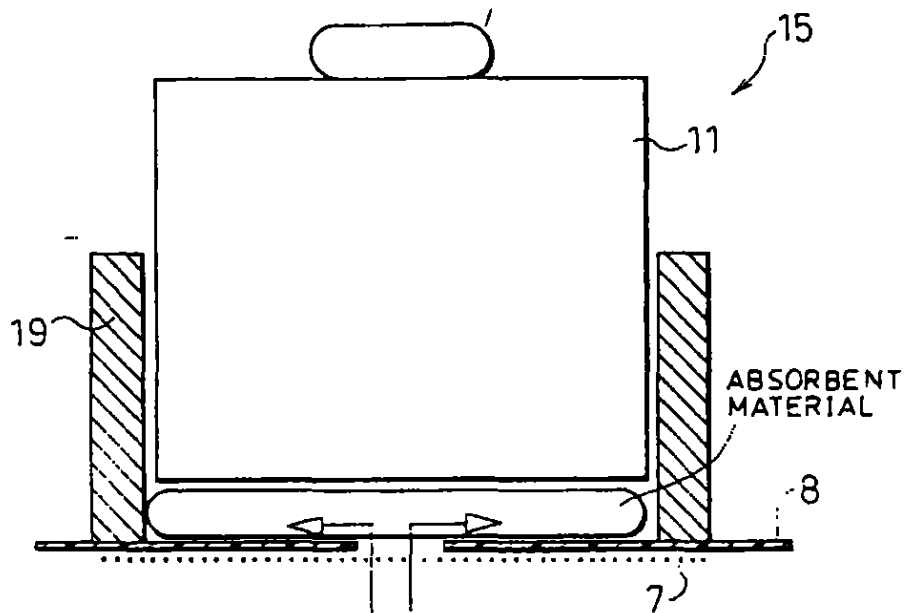
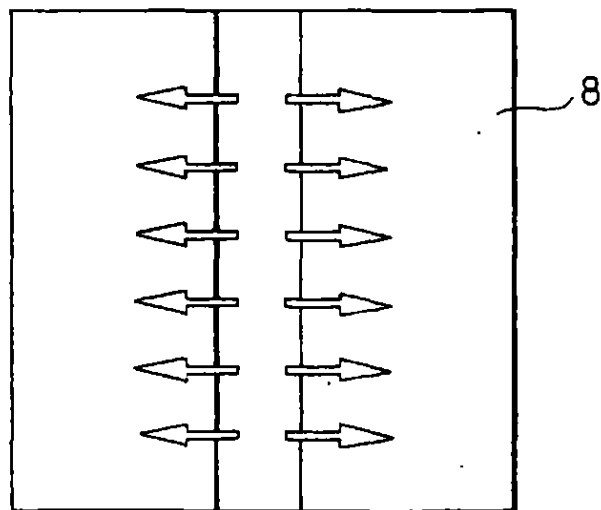


FIG.6



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(21) International Application Number: PCT/US95/00443 (22) International Filing Date: 11 January 1995 (11.01.95) (30) Priority Data: 08/181,494 12 January 1994 (12.01.94) US (71) Applicant: WEYERHAEUSER COMPANY [US/US]; Tacoma, WA 98477 (US). (72) Inventors: HANSEN, Micheal, R.; Apartment A, 2214 N.E. 197th Place, Seattle, WA 98155 (US). HALABISKY, Donald, D.; 1822 Copalis Street, Tacoma, WA 98422 (US). (74) Agents: CRAWFORD, John, M. et al.; Weyerhaeuser Com- pany, CH2J29, Tacoma, WA 98477 (US).		(81) Designated States: AU, BR, CA, JP, KR, NZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: METHOD AND COMPOSITIONS FOR ENHANCING BLOOD ABSORBENCE BY ABSORBENT MATERIALS			
(57) Abstract			
The blood absorbence properties, e.g., free swell blood absorbence capacity and after load blood absorbence capacity of superabsorbent materials is enhanced by combining the superabsorbent materials with enhancing agents which serve to enhance the blood absorbent properties thereof. The enhancing agents can be applied to the superabsorbent materials or they can be provided on a fibrous material to be combined with the superabsorbent materials. The enhancing agents are selected from materials that include functionalities that allow them to hydrogen bond to the superabsorbent material when the enhancing agent is applied directly thereto or combined with materials to which the enhancing agents have been applied.			

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for enhancing the blood absorbence properties of a superabsorbent material having a hydrogen bond functionality comprising the steps:

selecting an enhancing agent from the group consisting of polymeric enhancing agents and combinations thereof nonreactive with each other, the enhancing agents comprising enhancing agent molecules, the enhancing agent molecules having at least one functional group capable of forming a hydrogen bond with the superabsorbent material; and

exposing the superabsorbent material to sufficient amounts of the enhancing agent in liquid or solution form to enhance the blood absorbence properties of the superabsorbent material.

2. The method of Claim 1, wherein the enhancing agent is at least partially bonded to in the superabsorbent material.

3. The method of Claim 1, wherein the enhancing agent is present in an amount ranging from about 0.01 to about 10 percent of the weight of the superabsorbent material.

4. The method of Claim 1, wherein the enhancing agent is present in an amount ranging from about 0.01 to about 3 percent of the weight of the superabsorbent material.

5. The method of Claim 1, wherein the polymeric enhancing agent is polyglycol.

6. The method of Claim 5, wherein the polymeric enhancing agent is polyethylene glycol.

7. The method of Claim 1, wherein the enhancing agent is present in an amount ranging from about 0.01 to about 1 percent of the weight of the superabsorbent material.

8. The method of Claim 1, wherein the free swell blood absorbent capacity for the enhanced superabsorbent material is at least about 1.15 times the free swell blood absorbent capacity for untreated superabsorbent material.

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9. The method of Claim 1, wherein the after load blood absorbent capacity for the enhanced superabsorbent material is at least about 1.15 times the after load blood absorbent capacity for untreated superabsorbent material.

10. The method of Claim 1, wherein the free swell blood absorbent capacity for the enhanced superabsorbent material is at least 1.5 times the free swell blood absorbent capacity for untreated superabsorbent material.

11. The method of Claim 1, wherein the after load blood absorbent capacity for the enhanced superabsorbent material is at least about 1.5 times the after load blood absorbent capacity for untreated superabsorbent material.

12. The method of Claim 1, wherein the superabsorbent material is selected from the group consisting of fibers, particles and combinations thereof.

13. The method of Claim 1, further comprising the step of combining the superabsorbent material with a fibrous material.

14. The method of Claim 13, wherein the step of exposing the superabsorbent material to the enhancing agent comprises the step of exposing the superabsorbent material to the enhancing agent as the superabsorbent materials are being combined with the fibrous material.

15. The method of Claim 13, wherein the step of exposing the superabsorbent materials to the enhancing agent comprises providing the enhancing agent on the superabsorbent material in the absence of the fibrous material, then combining the enhanced superabsorbent material with the fibrous material.

16. The method of Claim 13, further comprising the steps of:
providing the fibrous material in the form of individualized cellulose fibers that have hydrogen bonding functional sites, wherein the individualized fibers are cured in the presence of a crosslinking material to produce high bulk fibers with intrafiber covalent crosslinks, and the fibers are fiberized to reduce interfiber bonding between the cured fibers; and

wherein the step of combining the enhanced superabsorbent material with the fibrous material comprises the step of adding the enhanced superabsorbent material to the fibers before, during or after the fibers are cured.

17. The method of Claim 16, wherein the curing step comprises using any crosslinking material and curing the crosslinking material before combining the enhanced superabsorbent material and the cured fibrous material.

18. The method of Claim 1, wherein the polymeric enhancing agent is selected from the group consisting of a polycarboxylic acid, a polycarboxylate, a poly(lactone) polyol, a polyamide, a polyamine, a polysulfonic acid, a polysulfonate, and combinations thereof.

19. A method for enhancing the blood absorbence properties of superabsorbent material having a hydrogen bond forming functionality comprising the steps:

selecting an enhancing agent from the group consisting of non-polymeric organic enhancing agents and combinations thereof nonreactive with each other, the enhancing agents comprising enhancing agent molecules, the enhancing agent molecules having at least one functional group capable of forming a hydrogen bond with the superabsorbent material; and

exposing the superabsorbent material to sufficient amounts of the enhancing agent in liquid or solution form to enhance the blood absorbence properties of the superabsorbent material.

20. The method of Claim 19, wherein the enhancing agent is at least partially bonded to the superabsorbent material.

21. The method of Claim 19, wherein the nonpolymeric organic enhancing agent has a volatility less than water.

22. The method of Claim 19, wherein the non-polymeric organic enhancing agent is present in an amount ranging from about 0.01 to about 10 percent of the weight of the superabsorbent material.

23. The method of Claim 19, wherein the non-polymeric organic enhancing agent is present in an amount ranging from about 0.01 to about 3 percent of the weight of the superabsorbent material.

24. The method of Claim 19, wherein the non-polymeric organic enhancing agent is present in an amount ranging from about 0.01 to about 1 percent of the weight of the superabsorbent material.

25. The method of Claim 19, wherein the free swell blood absorbent capacity for the enhanced superabsorbent material is at least about 1.2 times the free swell blood absorbent capacity for untreated superabsorbent material.

26. The method of Claim 19, wherein the after load blood absorbent capacity for the enhanced superabsorbent material is at least about 1.2 times the after load blood absorbent capacity for untreated superabsorbent material.

27. The method of Claim 19, wherein the free swell blood absorbent capacity for the enhanced superabsorbent material is at least about double the free swell blood absorbent capacity for untreated superabsorbent material.

28. The method of Claim 19, wherein the after load blood absorbent capacity for the enhanced superabsorbent material is at least about double the after load blood absorbent capacity for untreated superabsorbent material.

29. The method of Claim 19, wherein the nonpolymeric organic enhancing agent has functional groups selected from the group consisting of a carboxyl, a carboxylate, a carbonyl, a sulfonic acid, a sulfonate, a sulfonamide, a hydroxyl, a phosphoric acid, a phosphoramidate, a phosphate, an amide, an amine, and combinations thereof.

30. The method of Claim 29, wherein the non-polymeric organic enhancing agent is selected from the group consisting of glycerin, a glycerin monoester, a glycerin diester, ascorbic acid, urea, glycine, ammonium citrate, taurine, dipropylene glycol, aminosalicic acid, sorbitol, lactic acid, and combinations thereof.

31. The method of Claim 30, wherein the non-polymeric organic enhancing agent is selected from the group consisting of glycerin, glycerin monoester, a glycerin diester, and combinations thereof.

32. The method of Claim 31, wherein the non-polymeric organic enhancing agent is present in an amount ranging from about 0.05 to about 0.1 percent of the weight of the superabsorbent material.

33. The method of Claim 19, wherein the superabsorbent material is selected from the group consisting of fibers, particles, and combinations thereof.

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34. The method of Claim 19, further comprising the step of combining the superabsorbent material with a fibrous material.

35. The method of Claim 34, wherein the step of exposing the superabsorbent particles to the non-polymeric organic enhancing agent comprises the step of exposing the superabsorbent material to the enhancing agent as the superabsorbent material is combined with the fibrous material.

36. The method of Claim 34, wherein the step of exposing the superabsorbent materials to the non-polymeric organic enhancing agent comprises providing the enhancing agent on the superabsorbent material in the absence of the fibrous material, then combining the enhanced superabsorbent material with the fibrous material.

37. The method of Claim 34, further comprising the steps of:
providing the fibrous material in the form of individualized cellulose fibers that have hydrogen bonding functional sites, wherein the individualized fibers are cured in the presence of a crosslinking material to produce high bulk fibers with intrafiber covalent crosslinks, and the fibers are fiberized to reduce interfiber bonding between the cured fibers; and

wherein the step of combining the enhanced superabsorbent material with the fibrous material comprises the step of adding the enhanced superabsorbent material to the fibers before, during or after the fibers are cured.

38. The method of Claim 37, wherein the curing step comprises using any crosslinking material and curing the crosslinking material before combining the enhanced superabsorbent material and the cured cellulose fibers.

39. A modified superabsorbent material for absorbing blood comprising:

a superabsorbent material; and

an enhancing agent for increasing the blood absorbence properties of the superabsorbent material, the enhancing agent selected from the group consisting of polymeric enhancing agents and combinations thereof nonreactive with each other, the enhancing agents comprising enhancing agent molecules, the enhancing agent molecules having at least one functional group capable of forming a hydrogen bond with the superabsorbent material, the enhancing agent being at least partially bonded to

the superabsorbent material in an amount effective to enhance the blood absorbence properties of the superabsorbent material.

40. The modified superabsorbent material of Claim 39, wherein the polymeric enhancing agent is present in an amount ranging between about 0.01 to about 3.0% of the weight of the superabsorbent material.

41. The modified superabsorbent material of Claim 40, wherein the polymeric enhancing agent is polyglycol.

42. The modified superabsorbent material of Claim 41, wherein the polymeric enhancing agent is polyethylene glycol.

43. The modified superabsorbent material of Claim 39, wherein the polymeric enhancing agent is present in an amount ranging between about 0.01 to about 1.0 percent of the weight of the superabsorbent material.

44. The modified superabsorbent material of Claim 39, wherein the free swell blood absorbent capacity for the enhanced superabsorbent material is at least about 1.15 times the free swell blood absorbent capacity for untreated superabsorbent material.

45. The modified superabsorbent material of Claim 39, wherein the after load blood absorbent capacity for the enhanced superabsorbent material is at least about 1.15 times the after load blood absorbent capacity for untreated superabsorbent material.

46. The modified superabsorbent material of Claim 39, wherein the free swell blood absorbent capacity for the enhanced superabsorbent material is at least about 1.5 times the free swell blood absorbent capacity for untreated superabsorbent material.

47. The modified superabsorbent material of Claim 39, wherein the after load blood absorbent capacity for the enhanced superabsorbent material is at least about 1.5 times the after load blood absorbent capacity for untreated superabsorbent material.

48. The modified superabsorbent material of Claim 39, wherein the polymeric enhancing agent is selected from the group consisting of a polycarboxylic

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acid, a polycarboxylate, a poly(lactone) polyol, a polyamide, a polyamine, a polysulfonic acid, a polysulfonate, and combinations thereof.

49. The modified superabsorbent material of Claim 39, wherein the superabsorbent material is selected from the group consisting of fibers, particles, and combinations thereof.

50. The modified superabsorbent material of Claim 39, further comprising a fibrous material including individualized cellulose fibers that have hydrogen bonding functional sites, wherein the individualized fibers are cured in the presence of a crosslinking material to produce high bulk fibers with intrafiber covalent crosslinks.

51. A modified superabsorbent material for absorbing blood comprising:

a superabsorbent material; and

an enhancing agent for increasing the blood absorbence properties of the superabsorbent material, the enhancing agent selected from the group consisting of non-polymeric organic enhancing agents and combinations thereof nonreactive with each other, the enhancing agents comprising enhancing agent molecules, the enhancing agent molecules having at least one functional group capable of forming a hydrogen bond with the superabsorbent material, the enhancing agent being at least partially bonded to the superabsorbent material in an amount effective to enhance the blood absorbence properties of the superabsorbent material.

52. The modified superabsorbent material of Claim 51, wherein the non-polymeric organic enhancing agent is present in an amount ranging between about 0.01 to about 3.0 percent of the weight of the superabsorbent material.

53. The modified superabsorbent material of Claim 51, wherein the non-polymeric organic enhancing agent is present in an amount ranging between about 0.01 to about 1.0 percent of the weight of the superabsorbent material.

54. The modified superabsorbent material of Claim 51, wherein the free swell blood absorbent capacity for the enhanced superabsorbent material is at least 1.2 times the free swell blood absorbent capacity for untreated superabsorbent material.

55. The modified superabsorbent material of Claim 51, wherein the after load blood absorbent capacity for the enhanced superabsorbent material is at least 1.2 times the after load blood absorbent capacity for untreated superabsorbent material.

56. The modified superabsorbent material of Claim 51, wherein the free swell blood absorbent capacity for the enhanced superabsorbent material is at least double the free swell blood absorbent capacity for untreated superabsorbent material.

57. The modified superabsorbent material of Claim 51, wherein the after load blood absorbent capacity for the enhanced superabsorbent material is at least double the after load blood absorbent capacity for untreated superabsorbent material.

58. The modified superabsorbent material of Claim 51, wherein the nonpolymeric organic enhancing agent has functional groups selected from the group consisting of a carboxyl, a carboxylate, a carbonyl, a sulfonic acid, a sulfonamide, a sulfonate, a hydroxyl, a phosphoric acid, a phosphoramidate, a phosphate, an amide, an amine, and combinations thereof.

59. The modified superabsorbent material of Claim 51, wherein the non-polymeric organic enhancing agent is selected from the group consisting of glycerin, a glycerin monoester, a glycerin diester, urea, ascorbic acid, glycine, dipropylene glycol, ammonium citrate, taurine, aminosalicic acid, sorbitol, lactic acid, and combinations thereof.

60. The modified superabsorbent material of Claim 51, wherein the superabsorbent material is selected from the group consisting of fibers, particles, and combinations thereof.

61. The modified superabsorbent material of Claim 51, wherein the nonpolymeric organic enhancing agent is selected from the group consisting of glycerin, glycerin monoester, a glycerin diester, and combinations thereof.

62. The modified superabsorbent material of Claim 61, wherein the non-polymeric organic enhancing agent is present in an amount ranging from about 0.01 to about 0.1 percent of the weight of the superabsorbent material.

63. The modified superabsorbent material of Claim 51, further comprising a fibrous material including individualized cellulose fibers that have

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hydrogen bonding functional sites, wherein the individual fibers are cured in the presence of a crosslinking material to produce high bulk fibers with intrafiber covalent crosslinks.

64. A method for enhancing the blood absorbence properties of a superabsorbent material having hydrogen bond forming functionality comprising the steps:

providing a fibrous material;

selecting an enhancing agent from the group consisting of polymeric enhancing agents, non-polymeric organic enhancing agents, and combinations thereof nonreactive with each other, the enhancing agent comprising enhancing molecules, the enhancing molecules having at least one functional group capable of forming a hydrogen bond with the superabsorbent material; and

exposing the fibrous material to an amount of enhancing agent in liquid or solution form sufficient to enhance the blood absorbence properties of the superabsorbent material;

combining the exposed fibrous material with the superabsorbent material, so that the blood absorbence properties of the superabsorbent materials are enhanced.

65. The method of Claim 64, wherein the nonpolymeric organic enhancing agent has a volatility less than water.

66. The method of Claim 64, wherein the non-polymeric organic enhancing agent has functional groups that are selected from the group consisting of a carboxyl, a carboxylate, a carbonyl, a sulfonic acid, a sulfonamide, a sulfonate, a hydroxyl, a phosphoric acid, a phosphoramidate, a phosphate, an amide, an amine, and combinations thereof.

67. The method of Claim 64, wherein the non-polymeric organic enhancing agent is selected from the group consisting of glycerin, a glycerin monoester, a glycerin diester, ascorbic acid, urea, glycine, ammonium citrate, taurine, dipropylene glycol, aminosalicyclic acid, sorbitol, lactic acid, and combinations thereof.

68. The method of Claim 64, wherein the non-polymeric organic enhancing agent is selected from the group consisting of glycerin, a glycerin monoester, a glycerin diester, and combinations thereof.

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69. The method of Claim 64, wherein the superabsorbent material is selected from the group consisting of fibers, particles, and combinations thereof.

70. The method of Claim 64, wherein the enhancing agent is present in an amount ranging from about 2 to about 30 percent of the weight of the fibrous material and enhancing agent, and the superabsorbent material is present in an amount ranging from about 0.05 to about 80 percent of the weight of the fibrous material and the superabsorbent material.

71. The method of Claim 70, wherein the enhancing agent is present in an amount ranging from about 2 to about 15 weight percent of the weight of the fibrous material and the enhancing agent.

72. The method of Claim 64, wherein the after load blood absorbent capacity of the combined exposed fibrous material and superabsorbent material is at least about 1.3 times the after load blood absorbent capacity for unexposed fibrous material and the superabsorbent material.

73. The method of Claim 64, wherein the step of exposing the fibrous material to the enhancing agent comprises providing the enhancing agent on the fibrous material in the absence of the superabsorbent material, then combining the exposed fibrous material with the superabsorbent material.

74. The method of Claim 64, wherein the polymeric enhancing agent is selected from the group consisting of a polycarboxylic acid, a polycarboxylate, a poly(lactone) polyol, a polyamide, a polyamine, a polysulfonic acid, a polysulfonate, and combinations thereof.

75. The method of Claim 64, wherein the polymeric enhancing agent is a polyglycol.

76. The method of Claim 75, wherein the polymeric enhancing agent is polyethylene glycol.

77. A method for enhancing the blood absorbence properties of a superabsorbent material having hydrogen bond forming functionality comprising the steps:

providing a fibrous material in the form of individualized cellulose fibers that have hydrogen bonding functional sites, wherein the individualized fibers are cured

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in the presence of a crosslinking material to produce high bulk fibers with intrafiber covalent crosslinks while leaving hydrogen bonding functional sites available on the cured fibers for hydrogen bonding, and the fibers are fiberized to reduce interfiber bonding between curing fibers, wherein in the curing step further comprises:

(a) using any crosslinking material and curing the crosslinking material before applying the enhancing agent;

(b) curing the crosslinking material in the presence of the enhancing agent, wherein the enhancing agent is not a crosslinking material; or

(c) curing the crosslinking material in the presence of the enhancing agent, wherein the enhancing agent is also a crosslinking material, and the fibers contain sufficient water when the curing step begins to retard curing so that adequate enhancing agent functional groups will remain to enhance the blood absorbence properties of the superabsorbent material;

adding the superabsorbent material to the fibers before, during, or after the fibers are cured; and

applying the enhancing agent to the fibers before, during, or after the fibers are cured or fiberized.

78. A blood absorbent composition of fibrous material and superabsorbent material comprising:

fibrous material;

a superabsorbent material; and

an enhancing agent selected from the group consisting of polymeric enhancing agents, non-polymeric organic enhancing agents; and combinations thereof nonreactive with each other, applied to the fibrous material in an amount effective to enhance the blood absorbence properties of the superabsorbent material when combined with the enhanced fibrous material, the enhancing agents comprising enhancing agent molecules, the enhancing agent molecules having at least one functional group capable of forming at least one hydrogen bond with the superabsorbent material.

79. The blood absorbent composition of Claim 78, wherein the nonpolymeric organic enhancing agent has a volatility less than water.

80. The blood absorbent composition of Claim 78, wherein the non-polymeric organic enhancing agent has functional groups that are selected from the group consisting of a carboxyl, a carboxylate, a carbonyl, a sulfonic acid, a

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sulfonamide, a sulfonate, a hydroxyl, a phosphoric acid, a phosphoramidate, a phosphate, an amide, an amine, and combinations thereof.

81. The blood absorbent composition of Claim 78, wherein the non-polymeric organic enhancing agent is selected from the group consisting of glycerin, a glycerin monoester, a glycerin diester, ascorbic acid, urea, glycine, ammonium citrate, taurine, tartaric acid, dipropylene glycol, aminosalicilic acid, sorbitol, lactic acid, and combinations thereof.

82. The blood absorbent composition of Claim 78, wherein the nonpolymeric organic enhancing agent is selected from the group consisting of glycerin, a glycerin monoester, a glycerin diester, and combinations thereof.

83. The blood absorbent composition of Claim 78, wherein the polymeric enhancing agent is selected from the group consisting of a polyglycol, a polycarboxylic acid, a polycarboxylate, a poly(lactone) polyol, a polyamide, a polyamine, a polysulfonic acid, a polysulfonate, and combinations thereof.

84. The blood absorbent composition of Claim 83, wherein the polymeric enhancing agent is polyethylene glycol.

85. The blood absorbent composition of Claim 78, wherein the fibrous material comprises individualized, high bulk fibers having intrafiber covalent bonds wherein the fibers have hydrogen bonding functionalities and the superabsorbent material is selected from the group consisting of particles, fibers, and combinations thereof.

86. An superabsorbent article produced by the method of Claim 12, 13, 16, 19, 33, 34, 37, 64, 69, or 77.

87. An superabsorbent article comprised of the modified superabsorbent material of Claim 39, 42, 49, 50, 59, or 60.

88. An article comprised of the blood absorbent composition of Claim 78, 82, 84, or 85.

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(54) FIBERS WHICH CAN BE DENSIFIED AND METHOD FOR THEIR PRODUCTION
FASERN DIE VERDICHET WERDEN KÖNNEN UND VERFAHREN ZU IHRER HERSTELLUNG
FIBRES DENSIFIABLES ET PROCEDE DE PRODUCTION

(84) Designated Contracting States: AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL PT SE (30) Priority: 16.02.1994 US 197483 (43) Date of publication of application: 04.12.1996 Bulletin 1996/49 (73) Proprietor: WEYERHAEUSER COMPANY Tacoma, WA 98477-0001 (US) (72) Inventors: HANSEN, Michael, R. Seattle, WA 98155 (US)	• YOUNG, Richard, H., Sr. Maple Valley, WA 98038 (US) (74) Representative: Spall, Christopher John Barker Brettell, 138 Hagley Road Edgbaston, Birmingham B16 9PW (GB) (56) References cited: WO-A-94/04351WO-A-94/04352 US-A- 4 103 062US-A- 4 186 165
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Description

Field of the Invention

5 [0001] This invention concerns the use of polymeric and non-polymeric organic densifying agents for fibers in a method for producing fibers that can be densified. The fibers treated with such agents may be easily densified by external application of pressure. The densifying agents may be applied to fibers on a wet-laid fiber sheet manufacturing line, and subsequently fiberized for processing using air lay equipment. In particular embodiments, the invention concerns a mass of fibers treated with the densifying agents which may be then be used, for example, to make absorbent
10 fibers that are densified and incorporated into absorbent products and articles.

Background of the Invention

15 [0002] Densification of fibers used in products designed to absorb fluids, for example body fluids is known and is used to overcome problems of low cohesive strength, poor shape and stability, low capillarity, low fluid retention and low absorption capacity under conditions of use.
[0003] US-A-4 186 165 discloses the formation of a densified bonded layer in an air laid panel of wood pulp fiber containing particulate hydrocolloid material. The densified bonded layer is formed by subjecting both sides of the panel to a predetermined pressure at a predetermined temperature differential.
20 [0004] Although ways to achieve a densified region of fibers are known there remains the need to improve the actual densification properties of the fibers.

Summary of Invention

25 [0005] The forgoing and other problems have been overcome by providing fibers with hydrogen bonding functional sites and densifying agents that have volatility less than water. The densifying agents, when applied to the fibers, improve the densification properties of the fibers such that fibers carrying densifying agent can be densified to a given density utilizing less pressure and lower temperatures compared to the pressures and temperatures needed to densify untreated fibers to a similar density. The densifying agents that are useful in accordance with the present invention
30 include materials described as binders below.
Accordingly, the claimed invention provides a method for producing fibers, which can be densified as set out in claim 1.
[0006] The claimed invention further provides a mass of fibers, which can be densified in accordance with claim 13, and absorbent articles made using the fibers.
[0007] The claimed invention is further illustrated by section XIII of the specification; although the remaining sections
35 are not or only to a certain extent illustrative of the invention they serve to clarify it, inter alia by describing aspects relating to binders that may function as densifying agents.

Brief description of the Drawings

40 [0008]
FIG. 1 is a schematic illustration of a wet laid sheet manufacturing line in accordance with the present invention.
FIG. 2 is schematic depiction of the components of an apparatus of the present invention that produces high bulk fibers.
45 FIG. 3 is a top plan view of a structure into which fibers of the present invention are incorporated, the fibers being in the form of an illustrated absorbent pad.
FIG. 4 represents a partial sectional view of the pad of FIG. 3
FIG. 5 illustrates a plan of a bandage incorporating fibers of the present invention.
FIG. 6 is a sectional view of the bandage of FIG 5, taken along the line 7-7 of FIG. 5.
50 FIG. 7 is a plan view of a disposable diaper including a core of fibers of the present invention.
FIG. 8 is a vertical sectional view along line 9-9 of the diaper of FIG. 7.

DETAILED DESCRIPTION OF THE SEVERAL PREFERRED EMBODIMENTS OF THE INVENTION

55 I. Processing of Fibers

[0009] FIG. 1 illustrates a wet laid sheet manufacturing line such as a pulp sheet manufacturing line 10. In this manufacturing line, a pulp slurry 12 is delivered from a headbox 14 through a slice 16 and onto a Fourdrinier wire 18.

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The pulp slurry 12 typically includes cellulose fibers such as wood pulp fibers and may also include synthetic or other non-cellulose fibers as part of the slurry. Water is drawn from the pulp deposited on wire 18 by a conventional vacuum system, not shown, leaving a deposited pulp sheet 20 which is carried through a dewatering station 22, illustrated in this case as two sets of calendar rolls 24, 26 each defining a respective nip through which the pulp sheet or mat 20 passes. From the dewatering station, the pulp sheet 20 enters a drying section 30 of the pulp manufacturing line. In a conventional pulp sheet manufacturing line, drying section 30 may include multiple canister dryers with the pulp mat 20 following a serpentine path around the respective canister dryers and emerging as a dried sheet or mat 32 from the outlet of the drying section 30. Other alternate drying mechanisms, alone or in addition to canister dryers, may be included in the drying stage 30. The dried pulp sheet 32 has a maximum moisture content pursuant to the manufacturer's specifications. Typically, the maximum moisture content is no more than 10% by weight of the fibers and most preferably no more than about 6% to 8% by weight. Otherwise, the fibers tend to be too damp. Unless overly damp fibers are immediately used, these fibers are subject to degradation by, for example, mold or the like. The dried sheet 32 is taken up on a roll 40 for transportation to a remote location, that is, one separate from the pulp sheet manufacturing line, such as at a user's plant for use in manufacturing products. Alternatively, the dried sheet 32 is collected in a baling apparatus 42 from which bales of the pulp 44 are obtained for transport to a remote location.

[0010] A binder of the type explained in detail below is applied to the pulp sheet from one or more binder applying devices, one of which is indicated at 50 in FIG. 1. Any binder applying device may be used, such as sprayers, roll coaters, immersion applicators or the like. Sprayers are typically easier to utilize and incorporate into a pulp sheet manufacturing line. As indicated by the arrows 52, 54 and 56, the binder may be applied at various locations or at multiple locations on the pulp sheet manufacturing line, such as ahead of the drying stage 30 (indicated by line 52), intermediate the drying stage 30 (as indicated by line 54), or downstream from the drying stage 30 (as indicated by the line 56). Water-based binders, such as non-polymeric urea, are typically applied at a location where sufficient drying can still take place in the drying stage to produce a dried binder containing fiber sheet with no more than the maximum desired moisture content. Consequently, to take advantage of the drying stage 30, water-based binders are typically applied at locations 52 or 54. At location 52, the water remaining in the sheet or mat 20 at this stage tends to interfere with the penetration of the binder into the sheet. Consequently, application of the binder after some drying has taken place, for example at location 54, is preferable. If water-based binders are applied at location 56 in an amount which would cause the moisture content of the sheet to exceed the desired maximum level, an additional drying stage (not shown) may be included in the pulp manufacturing line to bring the moisture content down to the desired level.

[0011] A non-aqueous based binder, such as glycerin, is most preferably added downstream from the drying stage at location 56 or during the drying stage as indicated by location 54. However, liquid non-aqueous binders may also be added at a location, such as location 52, upstream of the drying stage. At this latter location, the water in the wet web at this point may tend to attract these binders into the mat or sheet as the binders tend to be hygroscopic. Since non-aqueous binders typically do not enhance the degradation of the product due to the addition of moisture to the sheet, they can be applied downstream from the drying stage without bringing the moisture content of the sheet above the desired maximum level.

II. Fiber Characteristics

[0012] The present invention includes a method of producing fibers that can be densified and the product, including absorbent end-products, that are produced by such method. In particularly preferred embodiments, the product is a cellulose or synthetic fiber treated with a densifying agent (or binder that may function as a densifying agent). Suitable fibers include wood pulp fibers, which can be obtained from well known chemical processes such as the Kraft and sulfite processes. The invention also includes a combination of wood pulp and certain binders, which for the purpose of this combination are bulk fibers in roll form having a basis weight of at least 350 grams per square meter (g/m²) or bale form. The bulk fibers can have a density of at least about 400 kg/m³. Preferred bulk fibers are wood pulp fibers or softwood pulp fibers. The pulp fibers may be chemical or thermomechanical or chemithermomechanical or combinations thereof. The preferred pulp fiber is chemical. In these processes, the best starting material is prepared from long fiber coniferous wood species, such as pine, douglas fir, spruce and hemlock. Wood pulp fibers can also be obtained from mechanical processes, such as ground wood, mechanical, thermomechanical, chemimechanical and chemithermomechanical pulp processes. The fibers are preferably elongated, for example having a length to width ratio of about 10:1 to 5:1.

[0013] The fibers of the present invention also include fibers that are pretreated prior to the application of a binder to the fibers. This pretreatment may include physical treatment, such as subjecting the fibers to steam or chemical treatment, such as cross-linking the fibers. Although not to be constructed as a limitation, examples of pretreating fibers include the application of the fire retardants to the fibers, such as by spraying the fibers with fire retardant chemicals. Specific fire-retardant chemicals include, by way of example, sodium borate/boric acid, urea, urea/phosphates, etc. In addition the fibers may be pretreated with surfactants or other liquids, such as water or solvents, which modify the

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surface of the fibers. Other pretreatments include exposure to antimicrobials or pigments.

[0014] The fibers also may be pretreated in a way which increases their wettability. The fibers also may be pretreated with conventional cross-linking materials and may be twisted or crimped, as desired. Pretreating cellulose fibers with chemicals which result in lignin or cellulose rich fiber surfaces also may be performed in a conventional manner.

[0015] Bleaching processes, such as chlorine or ozone/oxygen bleaching may also be used in pretreating the fibers. In addition, the fibers may be pretreated, as by slurring the fibers in baths containing various solutions. For example, antimicrobial solutions (such as solutions of antimicrobial particles as set forth below), as well as solutions of fertilizers and pesticides, and/or fragrances and flavors, for release over time during the life of the fibers. Fibers pretreated with other chemicals, such as thermoplastic and thermoset resins also may be used. Combinations of pretreatments also maybe employed with the resulting pretreated fibers then being subjected to the application of the binder coating as explained below.

[0016] Ground fibers, recycled or secondary wood pulp fibers, and bleached and unbleached wood-pulp fibers can be used. Details of the production of wood fibers are well known to those skilled in the art. These fibers are commercially available from a number of companies including Weyerhaeuser Company, the assignee of the present invention.

[0017] The fibers also can be any of a variety of other natural or synthetic fibers; however, all of the fibers to which particles are attached include a hydrogen-bonding functionality. This does not preclude the blending of such fibers with fibers lacking this characteristic. However, the fibers lacking a hydrogen bonding functionality will not have particles bonded thereto with the strength and manner of the bonds that would be present if the fibers had a hydrogen-bonding functionality.

[0018] A hydrogen bond is an intermolecular force that occurs between hydrogen atoms that are covalently bonded to small, strongly electronegative elements (such as nitrogen and oxygen) and nonbonding electron pairs on other such electronegative elements. A hydrogen bonding functionality is a functional group that contains an oxygen or nitrogen atom, for example hydroxyls, carboxyl's, sulfonic acids, sulfonamides, ethers, esters, epoxides, carbonyls, amines, urethanes and others, that is capable of forming a hydrogen bond. The orbitals of the nonbonding electron pairs on the oxygen or nitrogen overlap with the relatively empty 1s orbital of the hydrogen covalently bonded to another nitrogen or oxygen atom. The 1s orbital of the hydrogen is relatively empty due to the unequal sharing of the electrons in the covalent bond between it and the small electronegative atom (oxygen or nitrogen) to which it is bound.

[0019] Specific examples of natural fibers that contain a hydrogen bonding functionality include chopped silk fibers, wood pulp fibers, bagasse, hemp, jute, rice, wheat, bamboo, corn, sisal, cotton, flax, kenaf, peat moss, and mixtures thereof. Suitable synthetic fibers with hydrogen bonding functionalities include acrylic, polyester, carboxylated polyolefins, rayon and nylon. The hydrogen-bonding functionality is an ester in acrylic fibers and a carboxylic acid in carboxylated polyolefin fibers, an ester in polyester, an amide in nylon, and a hydroxyl in rayon. Polyethylene and polypropylene would be unsuitable fibers for use in particle to fiber bonding because they include only carbons and hydrogens without any other atoms, such as oxygens or nitrogens, that can participate in hydrogen bonds.

[0020] For purposes of convenience, and not to be constructed as a limitation, the following description proceeds with reference to the treatment of individual chemical wood-pulp fibers. The fibers are individualized, for example by defiberization in a hammermill. Such individualized fibers are conventionally formed into a mat, and are commercially available, for example as NB 416 fibers from the Weyerhaeuser Company. Another suitable cellulosic mat would include Rayfloc JLD from ITT Rayonier. The cellulose fibers may be in the form of a cellulosic web or loose cellulose fibers.

III Polymeric Binder Characteristics

[0021] The densifying agents may comprise polymeric binders, which maybe water soluble, selected from predetermined group of polymeric binders. The polymeric binders comprise binder molecules, wherein the binder molecules have at least one hydrogen bonding functionality or coordinate covalent bond forming functionality. The polymeric binder may comprise repeating units, wherein each repeating unit of polymer preferably, but not necessarily, includes at least one hydrogen bonding functionality or coordinate covalent bond forming functionality. In accordance with the present invention, the predetermined groups of polymeric binders include the group of binders consisting of polyglycols (especially poly(propyleneglycol)), a polycarboxylic acid, a polycarboxylate, a poly(lactone) polyol, such as diols, a polyamide, a polyamine, a polysulfonic acid, a polysulfonate, and combinations thereof. Specific examples of some of these binders, without limitation, are as follows: polyglycols may include polypropylene glycol (PPG); poly(lactone) diols include poly(caprolactone) diol; polycarboxylic acid include polyacrylic acid (PPA); polyamides include polyacrylamide or polypeptides; polyamines include polyethylenimine and polyvinylpyridine; polysulfonic acids or polysulfonates include poly(sodium-4-styrenesulfonate) or poly(2-acrylamido-methyl-1-propanesulfonic acid; and copolymers thereof (for example a polypropylene glycol/polyethylene glycol copolymer). The polymeric binder typically has repeating units. The repeating unit may be the backbone of a compound, such as with a polypeptide, wherein the repeating polyamides occur in the peptide chain. The repeating unit also may refer to units other than backbones, for instance repeating acrylic-acid units. In such a case, the repeating units may be the same or different. The binder molecule has

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a functional group capable of forming a hydrogen bond or a coordinate covalent bond with particles, and a functional group capable of forming a hydrogen bond with the fibers.

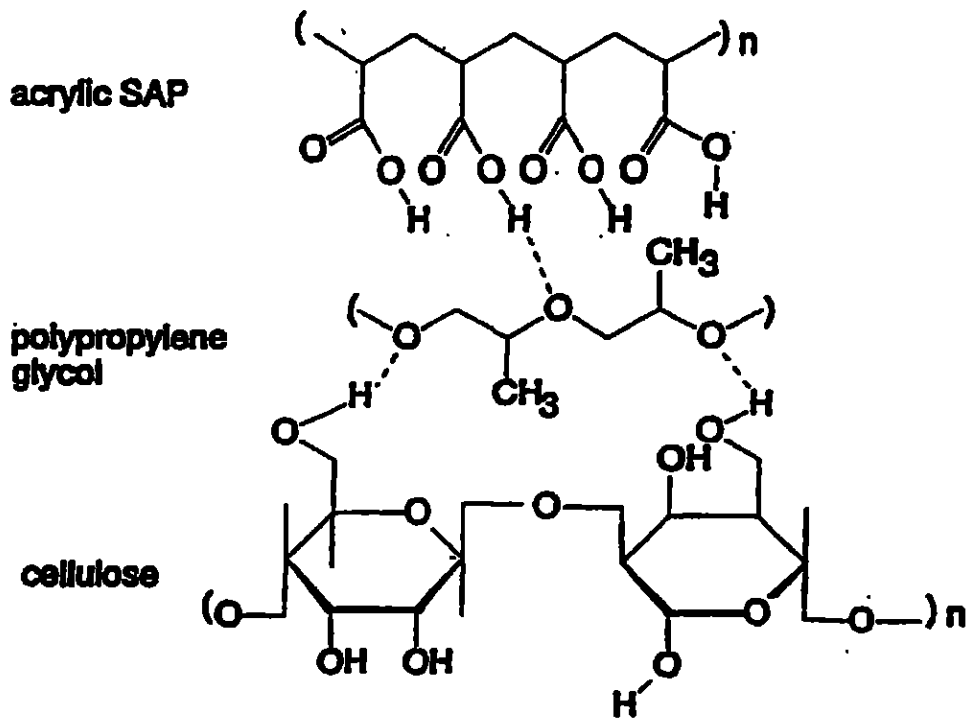
[0022] As used herein, a polymer is a macromolecule formed by chemical union of 5 or more identical or different combining units (monomers). A polyamine is a polymer that contains amine functional groups and a polyamide is a polymer that contains amide functional groups. Each of the binders has a hydrogen bonding or a coordinate covalent bonding functionality. The functionality may be a hydroxyl, a carboxyl, a carboxylate, a sulfonic acid, a sulfonate, an amide, an ether, an amine or combinations thereof. These binders are capable of forming hydrogen bonds because they have a functional group that contains an electronegative element, such as oxygen or a nitrogen.

[0023] The polyglycol has repeating ether units with hydroxyl groups at the terminal ends of the molecule. The polycarboxylic acid, such as polyacrylic acid, has a repeating carboxyl group in which a hydrogen is bound to an electronegative oxygen, creating a dipole that leaves the hydrogen partially positively charged. The polyamide (such as a polypeptide) or polyamine has a repeating NR group in which a hydrogen may be bound to an electronegative nitrogen that also leaves the hydrogen partially positively charged. The hydrogen in both cases can then interact with an electronegative atom, particularly oxygen or nitrogen, on the particle or fiber to form a hydrogen bond that adheres the binder to the particle and fiber. The electronegative oxygen or nitrogen of the binder also can form a hydrogen bond with hydrogen atoms in the particle or fiber that have positive dipoles induced by electronegative atoms, such as oxygens or nitrogens, to which the hydrogen is attached. The polyamide also has a carbonyl group with an electronegative oxygen that can interact with hydrogen atoms in the particles or fibers. Thus, the polymeric binders can enhance the hydrogen bonding (a) between the fibers and binder; and (b) in the case of particles with hydrogen bonding functionalities, between the binder and the particles.

[0024] Alternatively, the polymeric binder may form a coordinate covalent bond with the particles and a hydrogen bond to the fibers. For example, the oxygen or nitrogen on the binder has an unbound pair of electrons that can be donated to an empty orbital in the particle to form a coordinate covalent bond. For example, one free pair of electrons on the oxygen or nitrogen can be donated to the empty *p* orbital of a boron-containing particle to form a coordinate covalent bond that adheres the particle to the binder. The fibers themselves contain functional groups that can form hydrogen bonds with the binder, and allow the binder to adhere to the fiber. Cellulosic and synthetic fibers, for example, may contain hydroxyl, carboxyl, carbonyl, amine, amide, ether and ester groups that will hydrogen bond with the hydroxyl, carboxylic acid, amide or amine groups of the binder. Hence, the polymeric binder will adhere the particle with a coordinate covalent bond and the fiber will adhere with a hydrogen bond.

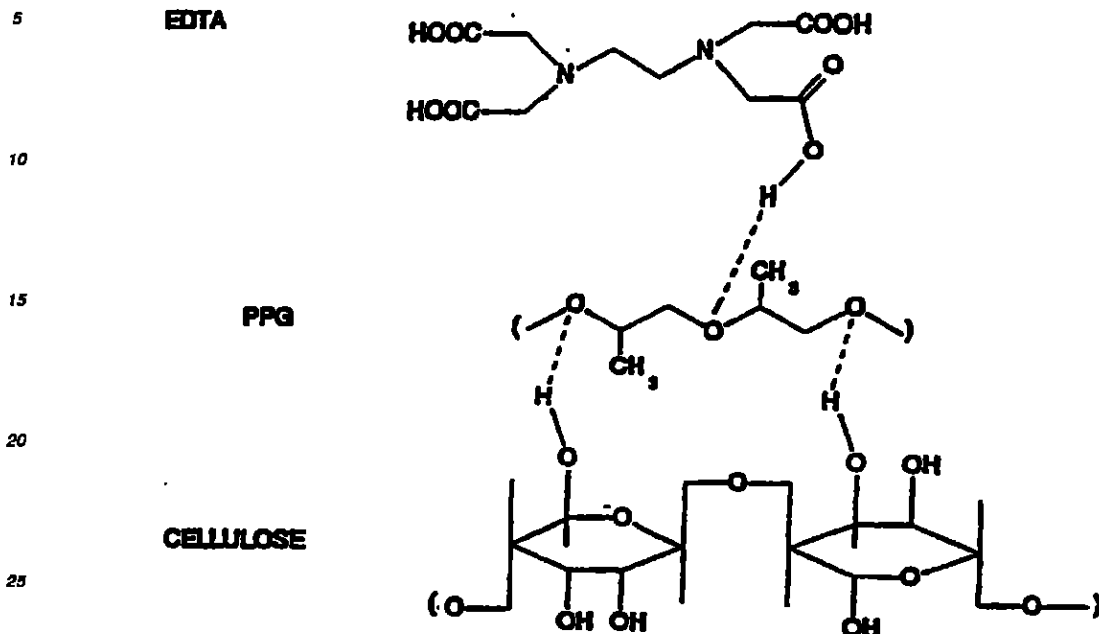
[0025] In some preferred embodiments, the polymeric binder is bound to both the fibers and the particle by hydrogen bonds. A polypropylene glycol binder, for example, can be used to bind water-insoluble polyacrylate hydrogel particles to cellulosic fibers. The hydroxyl and ether groups on the glycol binder participate in hydrogen-bonding interactions with the hydroxyl groups on the cellulose fibers and the carboxyl groups on the polyacrylate hydrogel, as shown below:

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Alternatively, a polypropylene glycol (PPG) binder, for example, can be used to bind a water-soluble particle to cellulosic fibers. The hydroxyl and ether groups on the glycol binder participate in hydrogen bonding interactions with the hydroxyl groups on the cellulose fibers and appropriate functionalities on the water-soluble particle, as shown below:

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30 Hence, the binder will adhere both the particle and fiber with hydrogen bonds. The presence of a hydrogen-bonding functionality on each repeating unit of the polymeric binder has been found to increase the number of hydrogen bonding interactions per-unit-mass of polymer, which provides superior binding efficiency and diminishes separation of particles from the fibers. The repeating ether functionality on the glycol binder provides this efficiency in the examples diagrammed above. A repeating carboxyl group is the repeating functionality on polyacrylic acid, while repeating carbonyls and NR groups (wherein R is either an H or alkyl, preferably lower alkyl i.e., less than five carbon atoms, in a normal or iso configuration) of the amide linkages are the repeating functionalities on polyamides such as polypeptides. A repeating amine group is present on polyamines.

35 [0026] The polymeric organic binders of the present invention have been found to increase in binding efficiency as the length of the polymer increases, at least within the ranges of molecular weights that are reported in the examples below. This increase in binding efficiency is attributable to the increased number of hydrogen bonding or coordinate covalent bonding groups on the polymer with increasing molecular length. Each of the polymeric binders has a hydrogen bonding or coordinate covalent bonding functionality. If each repeating unit of the polymer has repeating functionalities, longer polymers provide more hydrogen bonding groups or coordinate covalent bonding groups that can participate in hydrogen bonding interactions or in coordinate covalent bonds.

40 [0027] Although the invention is not limited to polymeric binders of particular molecular weights, polymeric binders having a molecular weight greater than 500 grams/mole are preferred because they provide attractive physical properties, and the solid is less volatile as compared to low-molecular-weight polymeric binders. Polymeric binders with molecular weights greater than 4000 grams/mole are especially preferred because they have minimal volatility and are less likely to evaporate from the fibers. Low-molecular weight materials typically are more mobile than are the higher-molecular weight materials. Low-molecular weight materials can more easily move to the fiber-particle interface, and are more easily absorbed by the fiber where they are less available to bond the particles to the fibers. The higher molecular weight materials are less apt to be absorbed by the fibers, and are less volatile than the low-molecular weight materials. As a result, higher molecular weight polymeric binders, to a greater extent, remain on the surface of the particles where they are more available to bond particles to fibers. In some particular embodiments, polymers with molecular weights between 4,000 and 8000 grams/mole have been used. Polymers with molecular weights above 8000 may be used, but such exceedingly high molecular weight polymers may decrease binding efficiency because of processing difficulties.

55 [0028] Certain polymeric binders have greater binding efficiency because their repeating functionality is a more ef-

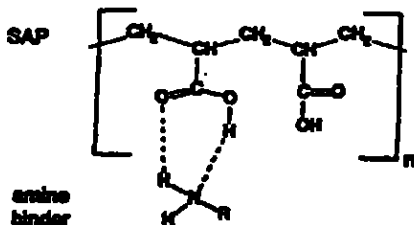
ficient hydrogen bonding group. It has been found that repeating amide groups are more efficient than repeating carboxyl functionalities, which are more efficient than repeating hydroxyl functionalities, which in turn are more efficient than amine or other functionalities. Hence, polymeric binders may be preferred that have repeating amine or other functionalities, more preferably repeating hydroxyl functionalities, and even more preferably repeating carbonyl or carboxyl functionalities, and most preferably repeating amide functionalities. Binding may occur at any pH, but is suitably performed at a neutral pH of 5-8, preferably 6-8, to diminish acid hydrolysis of the resulting fibrous product. Suitable binders may be selected from the group consisting of polyglycols such as polyethylene glycol or polypropylene glycol, polycarboxylic acids such as polyacrylic acid, polyamides, polyamines, poly(lactone) diols, such as poly(caprolactone) diol and combinations or copolymers thereof.

[0029] The group consisting of polycarboxylic acids (such as acrylic acid), polyamides and polyamines has been found to have a especially good binding efficiency. Among polyamides, polypeptides are especially preferred.

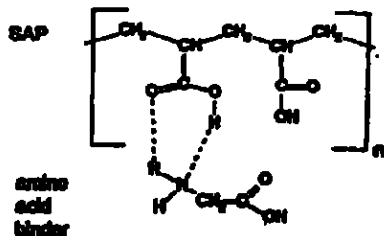
IV. Non-Polymeric Binder Characteristics

[0030] The densifying agent may comprise nonpolymeric organic binders selected from a predetermined group of binders that each have a volatility less than water. The vapor pressure of the binder may, for example, be less than 10 mm Hg at 25°C, and more preferably less than 1 mm Hg at 25°C. The non-polymeric binders comprise non-polymeric binder molecules wherein the molecules have at least one functional group that forms hydrogen bonds or coordinate covalent bonds with the particles. In accordance with the present invention, the predetermined group of non-polymeric binders may include a functional group selected from the group consisting of a carboxyl, a carboxylate, a carbonyl, a sulfonic acid, a sulfonate, a phosphate, a phosphoric acid, a hydroxyl, an amide, an amine, and combinations thereof (such as an amino acid or hydroxy acid) wherein each binder includes at least two such functionalities, and the two functionalities are the same or different. A requirement for the non-polymeric binder is that it have a plurality of functional groups that are capable of hydrogen bonding, or at least one group that can hydrogen bond and at least one group that can form coordinate covalent bonds. As used herein, the term "non-polymeric" refers to a monomer, dimer, trimer, tetramer, and oligomers, although some particular non-polymeric binders are monomeric and dimeric, preferably monomeric.

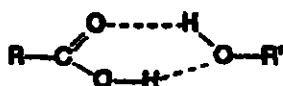
[0031] Particularly preferred non-polymeric organic binders are capable of forming five or six membered rings with a functional group on the surface of the particle. An example of such a binder is an amine or amino acid (for example, a primary amine or an amino acid such as glycine) which forms six-membered rings by forming hydrogen bonds:



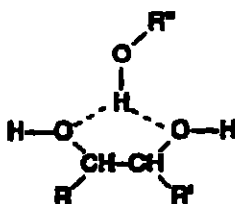
or



[0032] A six-membered ring also is formed by the hydroxyl groups of carboxylic acids, alcohols, and amino acids. for example:



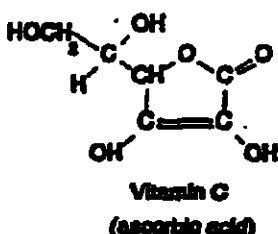
A five membered ring can be formed by the binder and the functionality on the surface of the particle, for example:



wherein the particle is a water-insoluble particle such as SAP and the binder is an alcohol, such as a polyol with hydroxyl groups on adjacent carbons, for example 2,3-butanediol. A binder that forms a five-membered ring can also be used with a water soluble particle, for example wherein the particle is EDTA and the binder is an alcohol, such as a polyol with hydroxyl groups on adjacent carbons, for example 2,3-butanediol.

[0033] Other alcohols that do not form a five-membered ring also can be used, for example alcohols that do not have hydroxyl groups on adjacent carbons. Examples of suitable alcohols include primary, secondary or tertiary alcohols.

[0034] Amino alcohol binders are alcohols that contain an amino group ($-\text{NR}_2$), and include binders such as ethanolamine (2-aminoethanol), and diglycolamine (2-(2-aminoethoxy) ethanol)). Non-polymeric polycarboxylic acids contain more than one carboxylic acid functional group, and include such binders as citric acid, propane tricarboxylic acid, maleic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid, benzene tetracarboxylic acid and tartaric acid. A polyol is an alcohol that contains a plurality of hydroxyl groups, and includes diols such as the glycols (dihydric alcohols), ethylene glycol, propylene glycol and trimethylene glycol; triols such as glycerin (1,2,3-propanetriol). Esters of hydroxyl-containing binders also may be used with mono- and diesters of glycerin, such as monoglycerides and diglycerides, being especially preferred. In the case of the diglycerides, at least one of the esterifying acid moieties must also include a functional group that is capable of forming at least one hydrogen bond with the fibers, or at least one functional group capable of forming a hydrogen bond or a coordinate covalent bond with the particles. Examples of polyhydroxy or polycarboxylic acid compounds include tartaric acid or ascorbic acid (vitamin C):



[0035] Hydroxy acid binders are acids that contain a hydroxyl group, and include hydroxyacetic acid (CH_2OHCOOH) and lactic, tartaric, ascorbic, citric, and salicylic acid. Amino acid binders include any amino acid, such as glycine, alanine, valine, serine, threonine, cysteine, glutamic acid, lysine, or β alanine.

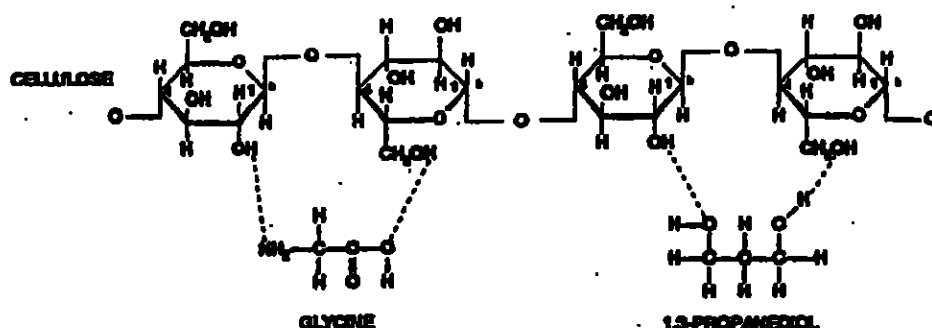
[0036] Sulfonic acid binders and sulfonates are compounds that contain a sulfonic acid group ($-\text{SO}_3\text{H}$) or a sulfonate ($-\text{SO}_3^-$). Amino-sulfonic acids also can be used. One example of an amino-sulfonic acid binder suitable for the present invention is taurine, which is 2-aminoethanesulfonic acid. Non-polymeric polyamide binders are small molecules (for example, monomers or dimers) that have more than one amide group, such as oxamide, urea and biuret. Similarly, a non-polymeric polyamine binder is a non-polymeric molecule that has more than one amine group, such as ethylene

diamine, EDTA or the amino acids asparagine and glutamine.

[0037] Although other non-polymeric organic binders are suitable in accordance with the discussion above, the non-polymeric organic binder is preferably selected from the group consisting of glycerin, a glycerin monoester, a glycerin diester, glyoxal, ascorbic acid, urea, glycine, pentacrythritol, a monosaccharide, a disaccharide, citric acid, taurine, tartaric acid, dipropylene glycol, urea derivatives, phosphate, phosphoric acid, a hydroxy acid, and combinations thereof. The non-polymeric binder also is most preferably selected from the group consisting of glycerin, a glycerin monoester, a glycerin diester, polyglycerin oligomers, urea and combinations thereof. The non-polymeric binders also preferably include functionalities selected from the group consisting of a carboxyl, a carboxylate, a carbonyl, a sulfonic acid, a sulfonate, a phosphate, a phosphoric acid, a hydroxyl, an amine, an amide, and combinations thereof (such as an amino acid or hydroxy acid). The non-polymeric binders must have at least two functionalities from such group, and the groups may be the same or different.

[0038] Each of the non-polymeric binders disclosed above is capable of forming hydrogen bonds because it has a functional group that contains electronegative atoms, particularly oxygens or nitrogens, or has electronegative groups, particularly groups containing oxygens or nitrogens, and that also include a hydrogen. The amino alcohol, amino acid, carboxylic acid, alcohol and hydroxy acid all have a hydroxyl group in which a hydrogen is bound to an electronegative oxygen, creating a dipole that leaves the hydrogen partially positively charged. The amino alcohol, amino acid, amide and amine all have an NR group in which a hydrogen may be bound to an electronegative nitrogen that also leaves the hydrogen partially positively charged. The partially positively charged hydrogen in both cases then can interact with an electronegative element, such as oxygen or nitrogen, on the particle or fiber to help adhere the binder to the particle and fiber. The polycarboxylic acid, hydroxy acid, amino acid and amide also have a carboxyl group with an electronegative oxygen that can interact with hydrogen atoms in the particles and fibers, or in intermediate molecules between the binder and particles or fibers. Similarly, electronegative atoms (such as oxygen or nitrogen) on the fiber or particle can interact with hydrogen atoms on the binder that have positive dipoles, and partially positive hydrogen atoms on the fiber or particle can interact with electronegative atoms on the binder.

[0039] Several proposed hydrogen bonding interactions of two of the binders (glycine and 1,3-propanediol) with cellulose are shown below:



[0040] The hydrogen bonding interactions are shown as dotted lines. One such interaction is shown between the nitrogen of glycine and a hydrogen of an -OH on cellulose. A hydrogen bond with glycine is also shown between an oxygen of the -OH on glycine and the hydroxy hydrogen of an alcohol sidechain on cellulose. Hydrogen bonding interactions of the 1,3-propanediol are shown in dotted lines between an oxygen on an -OH group of the binder and a hydrogen of an -OH group on the cellulose molecule. Another hydrogen bond is also shown between a hydrogen on an -OH group of the glycol binder and an oxygen in an alcohol sidechain of the cellulose.

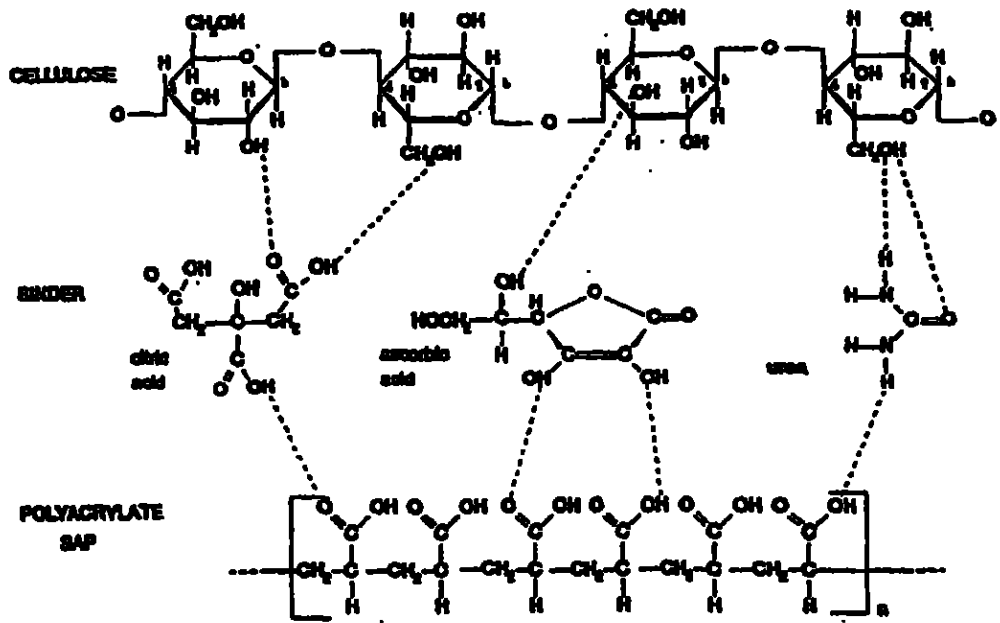
[0041] It also is possible for water or other hydrogen bonding molecules to be interposed between the fiber and binder, such that the fiber and binder are both hydrogen bonded to the water molecule.

[0042] Alternatively, an atom on the binder may have an unbound pair of electrons, such as a lone pair of electrons from an oxygen or nitrogen atom, that can be donated to an empty orbital of an acceptor atom in the particle to form a coordinate covalent bond. The free pair of electrons on the oxygen or nitrogen can be donated to the empty *p*, *d* or *f* orbital of a particle (for example a boron-containing particle) to form a coordinate covalent bond that adheres the particle to the binder. The fibers themselves do not normally contain functional groups that can act as electron acceptors in the formation of coordinate covalent bonds with the binders, but hydrogen bonding interactions allow the binder to adhere to the fiber. Cellulosic and synthetic fibers, for example, contain hydroxyl, carboxyl and ester groups that will hydrogen bond with the hydroxyl, carboxylic acid, amide, amine or other groups of the binder. Non-cellulosic or non-

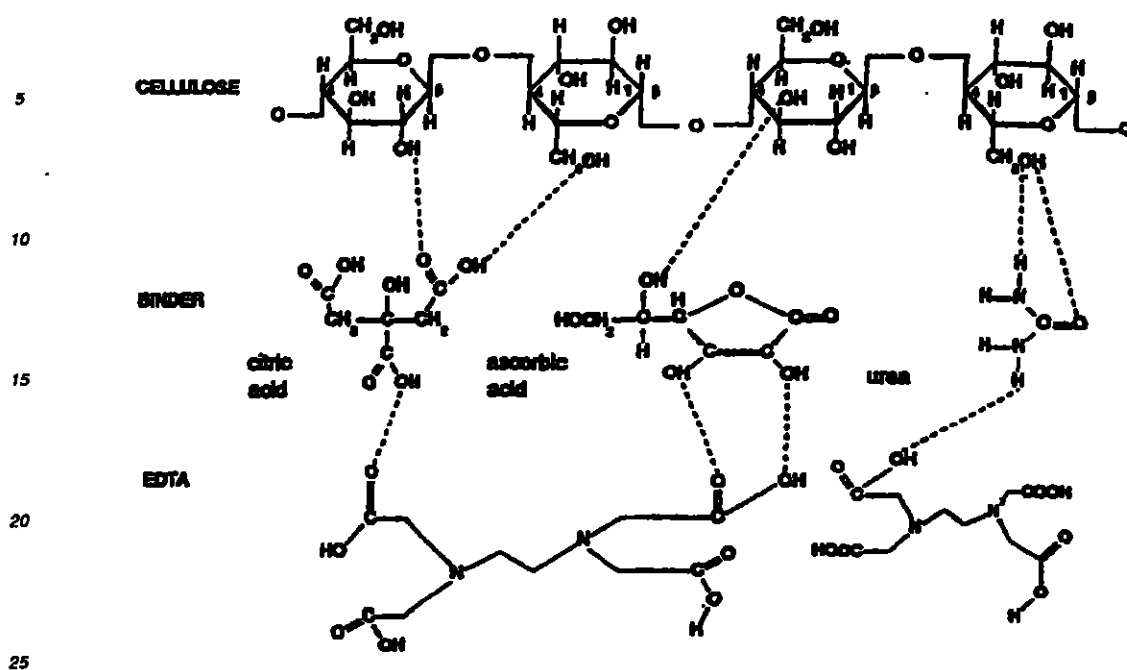
synthetic fibers that have these functionalities also can be used, for example silk, which has an amide linkage. Hence the binder will adhere the particle with a coordinate covalent bond and the fiber with a hydrogen bond.

[0043] In some preferred embodiments, the binder is bound to both the fibers and the particle by hydrogen bonds. A polyol binder, for example, can be used to bind polyacrylate hydrogel particles to cellulosic fibers. The hydroxyl groups on the polyol binder participate in hydrogen-bonding interactions with the hydroxyl groups on the cellulose fibers and the carboxyl groups on the polyacrylate hydrogel. Hence, the binder will adhere to both the particle and fiber with hydrogen bonds. These hydrogen bonds provide excellent binding efficiency and diminish separation of bound particles from the fibers.

[0044] A structural drawing is shown below in which citric acid, vitamin C and urea adhere water-insoluble SAP particles to cellulose with hydrogen bonds, or water-soluble EDTA particles. Some of the possible hydrogen bonding interactions are shown as dashed lines. It is possible that other molecules (such as water molecules) also may participate in some of these bonds, for example, as an intermediary between the binder and particle or fiber.



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[0045] Particularly efficient hydrogen bonding binders include those with carboxyl groups, such as ascorbic acid, or amide groups, such as urea. Hydroxyl groups are also very efficient binders. Amine and ether functionalities are less efficient binders.

[0046] Binders have functional groups that may be selected independently or in combination from the group consisting of a carboxyl, a carboxylate, a carbonyl, a hydroxyl, a sulfonic acid, a sulfonate, a phosphoric acid, a phosphate, an amide, an amine, and combinations thereof. These functional groups might be provided by the following exemplary chemical compounds: a carboxyl group could be provided by carboxylic acids, such as ascorbic acid; a carboxylate, which is an ionized carboxylic acid, could be provided by a material such as ascorbate; a carbonyl group can be provided by an aldehyde, such as ketone; a hydroxyl, such as an alcohol or a polyol, such as glycerol, or a mono- or diglyceride, which are esters of glycerol; an amide, such as a peptide; and an amine, which may be provided by an alkyl amine, such as ethylenimine wherein the binder has at least two of these functional groups, and each of the functional groups can be the same (for example, a polyol, polyaldehyde, polycarboxylic acid, polyamine or polyamide) or different (for example, an amino alcohol, hydroxyamide, carboxyamide, or amino acid). Functional groups also may be selected independently or in combination from the group consisting of carboxyl, an alcohol, an amide and an amine. An aldehyde may optionally be a member of each of these groups, particularly if it is oxidized to a carboxylic acid.

[0047] Combinations of the polymeric and non-polymeric binders, as well as with other binders, also may be used, providing that they are non-reactive. That is, providing that the binders do not react in a manner which prevents the binders from possessing the functional groups required to be present for binding in accordance with the present invention.

V. Process Advantages

[0048] The densifying agents of the present invention also provide numerous process advantages. Binding of particles to the fibers can occur, for example, without external application of heat. Hence, if desired, particle binding may occur at ambient temperature. The present invention therefore is distinct from prior-art crosslinking processes in which elevated temperatures are required to covalently crosslink cellulose groups to one another. Moreover, the densifying agents of the present invention have the advantage of being activatable by addition of a fluid, such as a liquid solvent (sometimes referred to herein as a activation liquid, one example of which is water). Hence, a liquid binder (which would include a solution of a solid or liquid binder, or a binder that has a melting point or softening point below room temperature) can be applied to a cellulose mat in the absence of the particles to be bound and the binder allowed to dry, for example until the fiber product reaches an equilibrium moisture content with the moisture in the ambient air. The binders then may be activated to bind the particles in place. Some of the binders (especially the liquid binders)

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diffuse throughout the fibers to reach an equilibrium distribution of the binder. Alternatively, the binder can be applied as a solid, for example as particles or a powder. At a later stage of processing, water or another activating fluid or liquid may be added to those portions of the mat where particulate binding is desired. The particles then may be added to the mat and adhered to those portions of the mat that have been moistened. Alternatively, the particles may be added to the mat prior to or simultaneously with activation of the binder.

[0049] The binders may be liquids at room temperature (such as glycerin), or liquid solutions of binders that are solids at room temperature (for example, an aqueous solution of glycine), or liquid hot melts of solid binders. Solid binders can be applied to the fibers as a supersaturated solution or the solid binder may be heated above its melting point and applied to the fibers. Upon solidifying the binder is deactivated. Solid binders may be added to fibers in particulate form, for example, by sprinkling binder particles on the fibers, provided they are fixed by the subsequent application of heat or liquid.

[0050] The binding reaction of the present invention can occur across a broad range of pH without requiring a catalyst. A suitable pH range without a catalyst is 1-14, but preferred ranges are 5-8 or 8-8 because such neutral pH ranges will produce fibrous products (such as cellulose products) that are less prone to damage by acid hydrolysis. A non-acidic pH (7 or greater) will provide an environment that inhibits formation of ester bonds, and promotes formation of the hydrogen bonds or coordinate covalent bonds that adhere the particles of the present invention to the fibers with the binder.

[0051] When water-insoluble particles are used, the moisture content of the fibers during the binding reaction is 0.5-50%, suitably 5-40%, or preferably 5-20% water by weight of the fibers, binder and particle. A moisture content greater than 20%, preferably 30%, or in the range 20-50%, or 30-50%, can be used even though such high moisture contents interfere with intermediate anhydride formation and inhibits formation of covalent bonds in the production of high-bulk crosslinked fibers. When water-soluble particles are used, the moisture content of the fibers during the binding reaction is 0.5-30%, suitably 5-25%, preferably 12-20%. Particles may be added to the fibers with the particles distributed throughout a fibrous product without being confined to a surface of the product. The particles can be distributed throughout the depth of a fiber product such as a mat or web.

[0052] The binder suitably is present in the treated product in an amount of at least 1 percent, and no more than 80 percent, by weight of the fibrous material ("percent by weight"). In especially preferred embodiments, the binder is present in an amount of 1 - 80, or more preferably, 1 to 40 or 1 to 25 percent by weight of the fibrous material. Below about 1 percent, when placed on the fiber, an insufficient amount of binder is present to achieve adequate binding. Using excessive amounts of binder can introduce unnecessary expense into the binding process. High percentages of binder can also cause processing problems because the binder material transfers to equipment surfaces. Therefore, it is often preferred to use no more binder than is required to bind the particles and fibers.

[0053] Thermoplastic binders also may be used to help bind fibers to each other and particles to fibers. The binder that has the hydrogen bonding or coordinate covalent bonding functionalities itself may be thermoplastic. The polymeric binders and some non-polymeric binders of the present invention have the advantage of being thermoplastic solids. Hence, fibers treated in accordance with the present invention can be thermobonded by elevating the fiber temperature above the softening temperature of the binder to soften the thermoplastic binder and thermoplastically bind the fibers to each other and the fibers to the particles. Alternatively, an auxiliary or second binder can be applied to the fibers as a solid at room temperature, and the temperature of the second binder elevated above its softening point to thermobond the fibers and particles. The auxiliary binder may be applied to the fibers either before or after the primary binder is applied, but before thermobonding.

[0054] The densifying agents of the present invention may be used with fibers that have substantial intrafiber covalent crosslinks (such as HBA available from Weyerhaeuser) or fibers which are substantially free of intrafiber covalent crosslinking. Examples of individualized intrafiber crosslinked fibers are seen in EP-A-440 472 A1 and 427 317 A2, which produce products that those publications describe as being substantially free of interfiber bonds. The fibers of the present invention do not need to be processed as in those European applications to eliminate interfiber bonds. The present invention can therefore be used with natural fibers that have substantial interfiber bonding, which are defined as fibers that have not been processed as in EP-A-0 440 472 A1 and 427 317 A2 to substantially eliminate interfiber bonds. Cellulose fibers that have not been so processed are substantially free of intrafiber bonds.

[0055] The fibrous product of the present method (with or without intrafiber crosslinking) may further be densified by external application of pressure. The densified product is compact and easily transported. And, when the particles are superabsorbent particles, the resulting fibrous product has superior properties as compared to nondensified products. The inventors have found that the binders of the present invention produce a product that can be easily densified. Easy densification is associated with the hydrogen bonds and coordinate covalent bonds formed between the binder and the particles and fibers. The fibers are particularly easily densified when at least 5% by weight of the fibers, particles and binder, more preferably 10%, are SAP particles adhered to the fibers.

[0056] In accordance with this invention, the densifying agents may be applied to fibers before, subsequent, or simultaneously with addition of the particles. Simultaneous addition can be accomplished by two separate streams of

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particles and binder that are simultaneously directed at a fibrous substrate, or alternatively merged immediately or some time prior to impacting against the substrate. Without limiting the invention, it appears that the addition of small amounts of moisture to the particles may help bind superabsorbent particles and perhaps other types of particles to the fibers. For example, exposing the particles to air at 65 percent humidity as they are delivered to binder containing fibers has been found to enhance the particle bonding.

[0057] Binding may be performed under conditions that favor formation of hydrogen bonds or coordinate covalent bonds, and discourage formation of covalent bonds. Conditions that favor covalent bonds are those disclosed in US-A-4,412,036 and US-A-4,467,012 wherein particle and binder would be laminated between tissue layers under high temperature and pressure to form laminated adherent tissue layers. That patent teaches that minimal adhesion occurs at 35,7 kg/cm (200 pli : pounds per linear inch, as in a calendar press) if no external heat is supplied, but adhesion improves as the reaction temperature increases. Improved adhesion of the tissue layers occurs because of enhanced covalent bonding as the temperature increases.

[0058] Conditions that favor covalent bond formation are also shown in EP-A-440 472 A1; 427 317 A2; 427 316 A2; and 429 112 A2. Those European publications use polycarboxylic acid crosslinkers, and require elevated temperatures (for example above 145°C) and acidic conditions (pH less than 7) to promote formation of intrafiber covalent ester bonds and inhibit reversion of the ester bonds. The present invention, in contrast, can form hydrogen or coordinate covalent bonds below 145°C, below 100°C, and even at room temperature. The densifying agents of the present invention also can bind particles to fibers under neutral or alkaline conditions, i.e., at a pH above 7, but preferably at a pH of 5-8 or 7-8. Fibers that have high bulk from intrafiber covalent crosslinks are prepared by individualizing the fibers (for example, in a fiberizer) and curing them at an elevated temperature (above 150°C). Initial application of the binder on such high-bulk fibers preferably occurs after the curing step, particularly if the binder is capable of functioning as a crosslinking material. The specific types of binders disclosed herein that also can crosslink are polyols, polyaldehydes, polycarboxylic acids, and polyamines (polymeric or nonpolymeric binders with more than one amine group). If such binders are present during curing, the binder will be consumed during the curing step to form covalently crosslinked bonds. When this occurs, the binder is no longer available for hydrogen bonding or coordinate covalent bonding, and particle binding to fibers is ineffective.

[0059] The intrafiber covalent bond forming processes described in the above European publications require formation of an anhydride that then reacts with a hydroxy group on cellulose to form a covalent ester bond. The presence of more than about 20% water by weight in the fibers is believed to interfere with the formation of the anhydride and inhibits covalent bond formation. Hence, in processes that use polycarboxylic acids, polyols and polyamines (which includes both polymeric and nonpolymeric amines having more than one amine group) as binders in the present invention, the fibers should contain at least 20% water (or 20-50% water) by weight if the particles and binder are present in the fibers when curing occurs. The water inhibits covalent bond formation, and prevents all of the binder from being used to form covalent intrafiber crosslinks. Hence, some of the binder remains available to form the non-covalent bonds with the particles and produce ease of densification in fiber products made by the process of the present invention.

VI. Application of Binder

[0060] The binders of the present invention that may function as densifying agents can be added to the fibers in any convenient manner. One such procedure is to spray the binder or binders on a web of the fibers that is conveyed past a sprayer on a conveyor belt. Alternatively, loose fibers may be allowed to fall past a sprayer, or loose fibers may be moved on a conveyor belt past a sprayer. The loose fibers may also be slurried with or immersed in binder. It also is preferable to roll coat the binders on the web, particularly if the binder is viscous. For solid binders, blending of the fiber and binder may be accomplished or the binder may simply be sprinkled onto or otherwise commingled with the fibers, followed by a fixation step such as addition of heat or liquid. The fibers may also be sprayed or immersed in the binder, or binder particles may be applied thereto. These fibers can, while still wet in the case of a liquid binder or following activation of a liquid or solid, be combined with the particles.

[0061] The fibers also can be allowed to dry for later activation with an activation fluid, such as an activation liquid, and combined with the particles at that time. An example of when it may be desirable to apply the binder to the fiber and thereafter activate the binder in the presence of particles is when the particles are added at a remote site. For instance, the binder may be activated from an inactive state at a second location that is remote from a first location where the binder is applied to the fibers. The second location maybe, for example, a location where a manufacturer combines fibers and particles into articles, such as absorbent articles. Particles may be added from conventional volumetric feeders in a hammermill or from injectors on a paper making line.

[0062] One method for uniformly coating the fibers with a binder and adding the particles is shown in US-A-5,064,689. However, the invention is not limited to any specific mechanism for combining the fiber, binder and particles.

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VII. Production of High Bulk Fibers

[0063] Production of high bulk fibers with intrafiber crosslinks is known in the art. Processes for making such fibers are described in EP 440 472 A1; EP 427 317 A2; EP 427 316 A2; and EP 429 112 A2. These high bulk fibers may be used in the present invention, with particles bound to them by the binders disclosed herein. Since methods of making high bulk fibers are known, only a brief description of one such process is given below.

A. Overall System

[0064] The apparatus 110 (FIG. 2) of the present invention comprises a conveying device 112 for transporting a mat 114 of cellulose fibers or other fibers through a fiber treatment zone 116; an applicator 118 for applying a treatment substance such as a crosslinking substance from a source 119 thereof to the mat 114 at the fiber treatment zone 116; a fiberizer 120 for completely separating the individual cellulose fibers comprising the mat 114 to form a fiber output comprised of substantially unbroken cellulose fibers substantially without nits or knots; and a dryer 122 coupled to the fiberizer for flash evaporating residual moisture from the fiber output and for curing the crosslinking substance, thereby forming dried and cured cellulose fibers.

[0065] The mat 114 of cellulose fibers is preferably in an extended sheet form stored in the form of a roll 124 until use. It is normally not necessary that the cellulose fibers comprising the mat 114 be completely dry. Since cellulose is a hydrophilic substance, molecules thereof will typically have a certain level of residual moisture, even after drying. The level of residual moisture is generally 10% wt/wt or less, which is not detectable as "wetness." FIG. 2 also shows that more than one supply, such as multiple rolls 124, of the mat 114 of cellulosic fibers can be simultaneously processed using the present invention.

[0066] At the fiber treatment zone 116, sprayers or other applicators 118 apply chemicals such as crosslinking agents to the mat. Typically chemicals are applied uniformly to both sides of the mat. The wetted mat passes between a pair of rollers 128 which assist in distributing the chemicals uniformly through the mat. Other applicators may also, of course, be used.

[0067] The crosslinking substance is a liquid solution of any of a variety of crosslinking solutes known in the art. If required, the crosslinking substance can include a catalyst to accelerate the bonding reactions between molecules of the crosslinking substance and cellulose molecules. However, many if not most crosslinking substances do not require a catalyst.

[0068] Preferred types of crosslinking substances are selected from a group consisting of urea derivatives such as methylolated urea, methylolated cyclic ureas, methylolated lower alkyl substituted cyclic ureas, methylolated dihydroxy cyclic ureas, and mixtures thereof. A specifically preferred crosslinking substance would be dimethyloldihydroxyethylene urea (DMDHEU). In addition, crosslinking substances can be polycarboxylic acids, such as citric acid. Crosslinking materials are known in the art, such as described in the previously mentioned Chung patent, US-A-4,935,022 to Lash, et al., US-A-4,889,595 to Herron, et al., US-A-3,819,470 to Shaw, et al., US-A-3,658,613 to Steijer, et al., US-A-4,822,453 to Dean, et al., and US-A-4,853,086 to Graef, et al.

[0069] Suitable catalysts include acidic salts which can be useful when urea-based crosslinking substances are used. Such salts include ammonium chloride, ammonium sulfate, aluminum chloride, magnesium chloride, or mixtures of these or other similar compounds. Alkali metal salts of phosphorus-containing acids may also be used.

[0070] In FIG. 2, the crosslinking substance applied to the mat 114 is obtained from a supply 119 thereof, such as a tank or analogous vessel.

[0071] Crosslinked cellulose fibers are individual fibers each comprised of multiple cellulose molecules where at least a portion of the hydroxyl groups on the cellulose molecules have been covalently bonded to hydroxyl groups on neighboring cellulose molecules in the same fiber via crosslinking reactions with extraneously added chemical reagents termed "crosslinking substances" or "crosslinking agents." Suitable crosslinking agents are generally of the bifunctional type which create covalently bonded "bridges" between said neighboring hydroxyl groups.

B. Conveying Device

[0072] Referring further to FIG. 2, each mat 114 of cellulosic fibers is conveyed by a conveying device 112, which carries the mats through the fiber treatment zone 116. FIG. 2 also shows a further portion of one type of conveying device comprised of a first pair of rollers 126 and a second pair of rollers 128 for each mat 114. The first and second pair of rollers 126, 128 are particularly effective for urging the corresponding mat at a substantially constant and controlled rate of speed.

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C. Fiber Treatment Zone

[0073] Each mat 114 is urged by the first and second pair of rollers 126, 128 through the fiber treatment zone 116 where the mat 114 is impregnated with a liquid crosslinking substance. The crosslinking substance is preferably applied to one or both surfaces of the mat using any of a variety of methods known in the art useful for such a purpose, such as spraying, rolling, dipping, or analogous method. Combinations of spray and roller applicators can also be employed. [0074] The crosslinking substance is typically applied in an amount ranging from about 2 kg to about 200 kg chemical per ton of cellulose fiber and preferably about 20 kg to about 100 kg chemical per ton of cellulose fiber.

D. Fiberizer

[0075] The next subsystem following the fiber treatment zone is a fiberizer 120 which serves to comminute one or more mats 130 impregnated with the crosslinking substance into individual substantially unbroken cellulose fibers comprising a fiber output.

[0076] Referring further to FIG. 2, a first conveyor fan 260 of conventional design can be utilized for propelling the fibers from the outlet 162 of the attrition device 132 through a conduit 262.

[0077] An optional component of the fiberizer 120 is a first cyclone 264 or similar apparatus known in the art, utilized in a conventional manner to concentrate the fibers passing out of the outlet 162 of the attrition device 132. The first cyclone 264 receives the fibers through the conduit 262 coupled thereto.

[0078] Excess air can be recovered at the top 266 of the first cyclone 264 and recycled as required through a conduit 268 to a location upstream of the first conveyor fan 260 (if used). Such additional air can be beneficial for easing the transfer of the fibers through the first conveyor fan 260.

[0079] A disk refiner 268 is another optional component of the fiberizer 120 which can be employed to effect additional separation of fibers (removal of knots) if required. The disk refiner 268 is of a type known in the art and comprises a disk refiner inlet 270 and a disk refiner outlet 272. A representative disk refiner 268 is type DM36 manufactured by Sprout-Bauer, Incorporated of Muncie, Pennsylvania. If the disk refiner 268 is used, the inlet 270 thereof is coupled via a conduit 274 to an outlet 276 of the first cyclone 264.

[0080] A second conveyor fan 278 may optionally be utilized to urge propagation of the fibers through a conduit 180 downstream of the disk refiner 268. Excess air can be recovered from the top 286 of the first cyclone 264 and routed via a conduit 281 to a tee 282 just upstream of the second conveyor fan 278.

[0081] Another optional component of the fiberizer 120 is a fluff generator 290 which receives the fibers from the optional second conveyor fan 278 through a conduit 284. The fluff generator is described in detail below

E. Dryer

[0082] Referring further to FIG. 2, a preferred embodiment of the present apparatus 110 includes a dryer 122 which is utilized to perform two sequential functions: remove residual moisture from the fibers and cure the crosslinking agent. Preferably, the dryer 122 comprises a drying zone 373 for receiving fibers, e.g. from fluff generator outlet 304 and for removing residual moisture from the fibers via a "flash drying" method and a second drying zone 360, 362 for curing the crosslinking agent. In FIG. 2, the curing starts in zone 360 and continues through zone 362.

[0083] The FIG. 2 embodiment shows that zone 373 is coupled to the fluff generator outlet by a conduit 372 and to a source 374 of heated air, typically produced by combustion of a supply of natural gas 376 and fresh air 378. The temperature of heated air is regulated to maintain the temperature of the drying zone 373 within a range of about 200°C to about 315°C. As the fiber output passes into the drying zone 373, the wet fibers comprising the fiber output are substantially instantaneously exposed to the high temperature in this zone. Such rapid exposure to high temperature imparts a "flash drying" effect to the fibers, thereby causing rapid and thorough drying and separation of the fibers. The passage time through the drying zone 373 is preferably less than one second.

[0084] The FIG. 2 embodiment shows that the first zone 360 is comprised of a first tower 364 comprised of a body portion 366, an inlet 368, and a first tower outlet 370. The dryer zone 373 is coupled via a conduit 372 to the outlet of the fluff generator 290.

[0085] In FIG. 2, the first tower 364 is shown preferably coupled via a conduit 380 to a down tube 382, which is coupled via a conduit 384 to a third conveyor fan 386 located at an inlet 388 of a second tower 390. The third conveyor fan 386 transports the fibers through the dryer which thereby pass into the second tower 390. As the fibers are lofted through the second tower 390, they are still exposed to a curing temperature within a range of about 140°C to about 180°C, which is sufficient to effect curing of the crosslinking agent without scorching the dry fibers. The lofting keeps the fibers separated until the crosslinking reaction is complete. The curing temperature depends upon the type of crosslinking material used to treat the fibers and also is set at a level so as to not scorch the fibers during curing. It should be noted that single stage dryers may also be used.

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[0086] The dried and cured fibers exiting the dryer outlet of tower 390 have an extremely low level of nits and virtually no knots. Further, they are not discolored from scorching and the like, and have a median fiber length substantially unchanged from the median length of the fibers comprising the mat 14.

[0087] FIG. 2 also shows a second cyclone 400 of conventional design coupled via a conduit 402 to the outlet of tower 390, serving to concentrate the fibers passing therethrough in preparation for collection. The resulting concentrated fibers can be collected using any of a number of collection devices 408 known in the art, such as fiber bagging devices.

EXAMPLE I

[0088] In this example, non-woven fibrous mats were impregnated with a crosslinking agent, fiberized, dried, and cured using the apparatus as diagrammed schematically in FIG. 2.

[0089] Two 1.32m (52-inch) wide mats of southern pine kraft wood pulp fibers (type NB316 from Weyerhaeuser Company) and having a basis weight of 680 g/M² were fed to the apparatus. The mats were impregnated using dimethyldihydroxyethylene urea at a concentration of about 5%, applied over both sides of each mat using a combination of spray nozzles and impregnation rollers. The loading level of crosslinking agent was about 4.5% w/w.

[0090] The treated fiber mats were fed at the rate of 8 meters/min to the attrition device 132. The specific attrition device used in this example was equipped with six mat inlets and a rotor having 16 rows of hammers as described above around the circumference of the rotor. The rotor had a diameter of 76.2cm (30 inches) and was rotated at an angular velocity of 1200 rpm by an electric motor. Other rpm rates have also been tested and have proven satisfactory, including extremely high rpm rates.

[0091] Random samples of fibers were obtained from the output attrition device and observed for nits. These samples were 2.6 grams and were consistently observed to have fewer than three nits on the average with most samples having no nits. The attrition device was flushed with water once every sixteen hours for cleaning purposes.

[0092] A disk refiner 268 was employed downstream of the attrition device. This specific disk refiner was a DM36 refiner as previously mentioned. A fluff generator 290 as described in FIG. 2 was also employed in this downstream of the disk refiner. The temperature at the dryer input in this example was within the range of 200°C to 315°C. The temperature at the second tower outlet was within the range of 140°C to 180°C. Crosslinked fiber at the output of the dryer was produced at a rate of about 6.3x10⁻¹ kg/s (5000 pounds per hour). The particle binders and particles of the present invention can be added before, after, or simultaneously with curing. The term "curing in the presence of the binder" means that the binder is added before or simultaneously with curing. Curing in the presence of the binder is not usually a problem because the binder cannot always participate in the intrafiber crosslinking reaction, and the binder is not affected by the curing step. In certain situations, however, the binder can also form covalent intrafiber crosslinks. Polycarboxylic acids (such as citric acid), polyols (such as dipropylene glycol) and polyamines (such as ethylene diamine) can function as crosslinking agents, and are consumed during the curing step in the formation of covalent crosslinks. Hence in the limited case in which the crosslinking agent is also a binder material, steps should be taken to prevent the binder from being consumed as a crosslinker in the curing step.

[0093] Formation of the intrafiber covalent ester bond requires an anhydride intermediate. Formation of the anhydride intermediate can be inhibited by the presence of water. The present inventors have found that about 20% water (more preferably at least 30% water) by weight in the fibers will sufficiently retard curing so that adequate binder functional groups will remain available in the fibers to bind the particles to the fibers. Hence when curing the crosslinking material in the presence of a binder that is also a crosslinking material, the fibers should contain at least about 20% water by weight of the fibers when curing begins. When curing the crosslinking material in the presence of a binder that is not also a crosslinking material, steps to prevent covalent bond formation are not usually necessary. When the crosslinking material is not cured in the presence of the binder, that is when the binder is applied after curing, no steps need be taken to inhibit covalent bond formation.

VIII. Composite Absorbent Product

[0094] In accordance with the present invention, absorbent structures or articles may be made from the fibers, with binder and optionally adhered particulates. These articles may be composite structures (e.g., made of plural materials). For example, the articles may have a core of plural types of fibers, or fiber layers, with or without covering materials. These products are capable of absorbing significant quantities of water and other fluids, such as urine and other body fluids. Such products include, but are not limited to, disposable diapers, sanitary napkins, incontinent pads, towels and the like.

[0095] FIGS. 3-4 illustrate an absorbent pad structure which may be formed from fibers of the present invention, whether or not they are blended with other fibers. FIGS. 3 and 4 represent an absorbent pad 410 having a heat embossed screen pattern 412. Pads having no pattern may also be used. A pad having a cover sheet 414 and a backing

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sheet 416 may be formed, for example, by placing a square fiber piece cut from the sheet onto a corresponding precut backing sheet. A corresponding precut cover sheet is placed over the top of the fiber 418 on the backing sheet. This assembly may then be adhesively bonded around a continuous margin 420.

[0096] With reference to FIGS. 5-6, an absorbent structure in the form of a bandage is shown. A bandage 430 for application to a wound to absorb blood and other bodily fluids is shown. An absorbent pad 440 is securely mounted to an exterior or pad mounting surface 434 of a backing strip 436. Fibers 441 are contained in pad 440, and particles are attached to the fibers 441. Any suitable mounting or securing means may be used to affix pad 440 to the surface 434 of the strip 436. However, it is preferable for surface 434 to be coated with an adhesive so that the pad 440 may be adhesively mounted in place. An exemplary adhesive is ethylene vinyl acetate adhesive. It is also desirable for the overall surface 438 of backing strip 436 to be coated with a conventional adhesive. Surface 438 is the surface which is affixed to the area of the skin surrounding the wound. Conventional "peel-back" tabs may be used to protect the adhesive coating and pad 440 until the bandage is to be applied. This type of backing strip is well known in the art.

[0097] The backing strip 436 may be of any known flexible material suitable for application to the skin. It is preferable for the strip 416 to be of a material which is impermeable to the passage of liquid so that fluid from a wound is contained by the bandage. However, the strip 436 may be apertured or otherwise breathable to permit air to reach the wound to promote the healing process. A specific example of a suitable backing strip 436 is a polyethylene film.

[0098] As in the other structures described, a variety of combinations of antimicrobials and other particles may be used in the fibers 441 of such a bandage. Again, however, the particles are adhered securely in place when the particles have a hydrogen bonding or a coordinate covalent bonding functionality, the fibers to which these particles are bound have a hydrogen bonding functionality, and wherein the binder is selected from the group consisting of a polypropylene glycol, a polypropylene glycol/polyethylene glycol copolymer, a polycarboxylic acid, such as polyacrylic acid, a poly (lactone) diol, such as poly(caprolactone) diol, a polyamide, a polyamine, a polysulfonic acid, a polysulfonate, polycarboxylate and combinations thereof. The polymeric binder has a hydrogen bonding or a coordinate covalent bond forming functionality. Nonpolymeric binders would include organic binders such as glycerin, monoglycerides, diglycerides, ascorbic acid, urea, glycine, pentaerythritol, a monosaccharide or a disaccharide, citric acid, tartaric acid, taurine, dipropylene glycol, and urea derivatives such as DMDHEU. Suitable saccharides include glucose, sucrose, lactose, ribose, fructose, mannose, arabinose, and erythrose. Two different particles, such as different antimicrobials in particulate form, may be adhered to the same fiber. In the alternative, each different type of antimicrobial particle or other particle may be adhered separately to different fibers. Also, blends of fibers may be included in absorbent structures such as pad 366. For example, these blends may include fibers with adhered antimicrobial (one or more antimicrobials) particles and adhered superabsorbent particles; fibers with one or more antimicrobial particles without superabsorbent particles blended with fibers having adhered superabsorbent particles with or without antimicrobial particles; and combinations of such fibers with untreated fibers and/or binder coated fibers without superabsorbent particles or antimicrobial particles. In addition, other particles, such as anticoagulants or hemostatics may be attached to the fibers.

[0099] The absorbent pad of bandage 430 may also include a cover sheet that is typically made of any suitable material which will readily permit the passage of liquid through the cover sheet to the fibers 441, such as nonwoven fiber webs of fibers such as, for example, rayon, nylon, polyester, propylene and blends thereof. One specifically preferred cover sheet material is a 70 percent rayon/30 percent polyester blend having a basis weight of 18 g/m² from Scott Paper Company.

[0100] FIGS. 7 and 8 illustrate a conventional disposable diaper 550 with a core 552 which is comprised of fibers of the present invention with adhered superabsorbent particulate materials. These particulate materials may be confined to a target zone (for example, the front or crotch portion of a diaper indicated at 558) or of a heavier concentration in the target zone. This can be accomplished by airlaying fibers of the present invention in such a zone. Also, the core may be activated by melting the binder or moistening the target zone with water. The superabsorbent particles may be sprinkled on or otherwise applied to this wetted zone. As the zone dries, the particles are adhered in place.

IX. Densification

[0101] The products such as described above, as well as webs of the fibers of the present invention, can also be densified by external application of pressure to the web. The web could be densified by passing it through a set of calendar rolls set at 10-71 and 16-07 kg/m (60 and 90 pli (pounds per linear inch, as in a calendar press)) respectively to yield sheets with increased densities. Densification may alternatively be provided by compaction rolls or presses. The inventors have found that densification is facilitated in SAP-containing products treated with binders of the present invention, when the densification occurs with the binder in an active state. Products that are treated with these binders require less heat and pressure than untreated fibers to densify to a given density. Densification is preferably performed to produce a product that has a density of about 0.05 to 0.7 g/cc, more preferably 0.1 to 0.3 g/cc.

[0102] An example of densification using some of the binders of the present invention is given below:

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EXAMPLE 2

[0103] The products of the present invention can be formed into 550 gram/square meter sheets 15.24cm (six inches) in diameter, in a laboratory padformer. Those pads are then passed through a set of calendar rolls set at 10.71 and 16.07 kg/m (60 and 90 pli), respectively to yield sheets with densities of 0.3 and 0.5 g/cc.

EXAMPLE 3

[0104] A 50gram amount of polypropylene glycol is diluted with 50 grams deionized water. The resulting solution is sprayed on 321 grams of an intrafiber crosslinked cellulose fluff (HBA pulp from Weyerhaeuser Company of Tacoma, WA) that was air entrained in a blender like mixing device. While the HBA fiber is still damp, 438 grams of IM1000F (supplied by Hoechst-Celanese, of Portsmouth, Virginia) is added to the mixture. The resultant mixture is then vacuumed from the blender and spread on a counter to dry overnight. Then 550 gram/square meter handsheets, 15.24cm (six inches) in diameter, are made in a laboratory padformer. Those pads are then pressed at 1.38×10^7 Pa and 2.07×10^7 Pa (or 10.71 and 16.07 kg/m in a calendar roll) (2000 and 3000 psi (or 60 and 90 pli in a calendar roll)), respectively to yield sheets with densities of 0.3 and 0.5 g/cc. Alternatively, pads of untreated HBA pulp blended with 45% IM1000F would require heating to 100°C and pressures between 5.52×10^7 Pa and 7.58×10^7 Pa (8,000 and 11,000 psi) to produce pads of similar densities.

EXAMPLE 4

[0105] HBA pulp with 40% IM1000F and HBA pulp with 12% glycerin and 40% IM1000F were formed into 15.24cm (six inches) pads in the padformer then pressed at about 4.48×10^7 Pa (6500 psi) for 15 seconds. HBA pulp without glycerin binder reached a density of 0.4 g/cc and HBA pulp with glycerin bound particles reached a density of 0.57 g/cc. This example illustrates that fibers treated with method of the present invention achieve a greater density than untreated fibers at the same compression pressure.

X. Water Addition

[0106] In some embodiments of the invention, a crosslinking material is added to the fibers and cured to form intrafiber covalent bonds that produce high bulk fibers. If the crosslinking material and binder are the same (for example, a polycarboxylic acid), or are both different but capable of intrafiber crosslinking, and the binder is added before curing occurs, substantially all of the crosslinking material/binder will be used in the covalent crosslinking reaction, such that none will be available for subsequent binding of the particles to the fibers with hydrogen bonds and coordinate covalent bonds. In this particular instance (where the crosslinking material and binder are both capable of crosslinking, and are added before curing) water may be added to the fibers before curing to retard initiation of the curing step and ensure that a portion of the binder's functionality is not consumed in the crosslinking reaction. At least 20% water by weight in the fibers sufficiently retards intrafiber covalent bond formation to allow residual polycarboxylic acid on the fibers to bind the particles to the fibers. The following example illustrates this process.

EXAMPLE 5

[0107] A 100 gram pulp sheet was sprayed with 44.5% intrafiber crosslinking material, and the pulp sheet was then delaminated and fed in small bits into a padformer while adding superabsorbent particles to delaminated pulp sheet at the same time. The material was run a second time through the padformer to fluff it up, and the material was then subsequently cured for 20 minutes in an oven at 150°C.

[0108] In a first run, the crosslinking material was a modified ethylene urea and citric acid, while the particulate material was IM1000F. To the 100 g pulp sheet was added 63.4 grams of the ethylene urea, 16.76 grams citric acid, and 70 grams of IM1000F, for a final crosslinker content of 35.2% ethylene urea and 9.3% citric acid, by weight. No water was added in this run.

[0109] In a second run, the 100 gram pulp sheet was crosslinked with 30.83 grams of a polyaldehyde (glyoxal), 5.03 grams of a glycol, 0.2 grams alum, 0.2 grams citric acid, and 15 grams distilled water. Curing was performed after 70 grams of IM1000F SAP was added to the pad.

[0110] Attachment of the particles to the pad was poor in both of these runs.

[0111] Each of these runs was then repeated, except 50 grams of distilled water was added before curing. Hence there was 50 g of water in the first run and 65 g of water in the second run. Particle attachment to the fibers was greatly improved.

[0112] Electron microscopic examination of the fibers from these runs showed that particle bonding did not occur in

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the absence of the 50g water addition. In the presence of 50 grams distilled water, however, electromicroscopic data showed actual bonding of the particles to the fibers.

XI. Fiber Mixtures

[0113] The fibers of the present invention, such as fiber 600, can be mixed with other types of fibers, such as that disclosed in US-A-5,057,166. The latex coated fibers of that patent can be mixed with the fibers of the present invention to produce an absorbent product that has characteristics of both types of fibers.

XII. Additional Binder Characteristics

[0114] US-A-3,903,889 discloses a process for adhering absorbent particles to pulp fibers using syrup, honey, and other polysaccharides such as dextrans. An essential requirement of these adhesive agents is that they must possess the property of being permanently pliable, and not rigidifying into a brittle film. The binders of the present invention, in contrast, are capable of functioning as a binder after solidifying into a rigid crystalline material. Even the binders of the present invention that do not rigidify into a solid (such as glycerin and PPG) are very hygroscopic, and can be present on fibers having a total water content of no more than 15%, or even 12%. This is in contrast to the adhesives such as honey and corn syrup disclosed in US-A-3,903,889 that are not hygroscopic. Polysaccharides (such as corn syrup, honey and dextrans) are excluded as binders from some embodiments of the invention because they remain tacky upon drying. Tacky binders make processing the binder-coated fibers difficult. The polysaccharide polymers are also excluded from non-polymeric embodiments of the binder of the present invention. Moreover, the non-polymeric saccharides such as monosaccharides and disaccharides, lack the high viscosity and tacky adhesive physical properties of polysaccharides such as corn syrup and honey. The non-polymeric saccharides of the present invention may be solids, which avoid the viscosity and handling problems associated with polymers.

[0115] As used in this application, a particle that is soluble in water will completely dissolve at least 10 grams of the particle in 300 ml. water at 25°C. A particle that is sparingly soluble in the binder will completely dissolve no more than about 5 grams of the particle in 300 ml. of the binder at 25°C.

[0116] Some of the binders of the present invention are also water soluble. A binder that is water will completely dissolve at least 10 grams of the binder in 300 ml. water at 25°C.

XIII. Fiber Densification Without Particles

[0117] In accordance with another aspect of this invention, the present inventors have observed that when densifying agents such as those described below are applied to fibers for example those described above which have hydrogen bonding functionality, the fibers density to a greater degree than fibers that have not been treated with a densifying agent. Densifying agents that can be used to improve the densifiability of the fibers generally include, but are not limited to organic and inorganic materials that have a density greater than the dry density of the fibers. Such densifying agents can be applied to the fibers in the same manner that the binders described above are applied to fibers. In addition to the methods for densifying fibers described above, the advantages of this aspect of the present invention also apply to densification of the fibers in a bale former.

[0118] Organic densifying agents that are useful include the organic polymeric and non-polymeric binders described above. When such binders are employed as densifying agents, it is not necessary that the molecules contain functionality to bind particles. Hence, organic molecules containing only one hydrogen bonding functionality may be useful as a densifying agent. Although the densifying agents are not required to bond to the fibers, in preferred embodiments they do bond to the fibers. In addition to the binder functionalities expressly described above, binders that are useful as densifying agents may also include sulfonamide or phosphoramidate functionalities. At this time, preferred non-polymeric organic densifying agents include sorbitol, glycerin, propylene glycol, and mixtures thereof. In accordance with this aspect of the present invention, the organic densifying agents can be applied to the fibers in an amount ranging from about 0.1% to about 30% by weight based on the combined weight of the fibers and densifying agent.

[0119] In addition to improving the densification properties of the fibers, it has also observed that the preferred densifying agents sorbitol and glycerin improve the softness of the fibers and articles containing the fibers before and after densification. The organic acid, lactic acid, while not improving the densifiability of fibers when applied thereto has been observed to soften fibers treated therewith. Softness relates to stiffness of the fibers or articles containing the fibers, the drape or hand of articles including the fibers. Another aspect of softness relates to abrasiveness or lack thereof of a fiber or article containing the fiber. Compressibility is another aspect of softness. Various tests exist to evaluate some of these aspects of softness, including Gurley stiffness, Taber stiffness, measurements of coefficients of friction, handometers, and the like. It should be understood that none of the tests listed above completely quantifies or evaluates softness of fibers or articles containing fibers; therefore subjective testing is also done to assess the

softness of a material.

[0120] In addition to the polymeric and non-polymeric organic densifying agents described above, the present inventors have also observed that some inorganic materials also improve the densifiability of fibers to which the agents are applied. As with the organic densifying agents, the inorganic densifying agents generally include, but are not limited to those characterized by a density greater than the density of the dry fibers. In addition, the inorganic densifying agents when added to the fibers will increase the mass of the fibers without appreciably affecting the volume of the fibers. The inorganic densifying agents may increase the mass without appreciably affecting the volume of the fibers by occupying the preexisting spaces within the fibers, such as the lumen, pores, and the like. Preferably, any increase in volume of the fibers caused by the addition of the densifying agent will be less than the increase in mass of the fibers, such that the density of the fibers is increased.

[0121] Examples of inorganic densifying agents which may have a density greater than the fibers and that will increase the mass of the fibers without appreciably affecting the volume of the fibers include inorganic acid salts in which the cation is monovalent, such as alkali metal, ammonium, or substituted ammonium (such as mono-, di-, tri-, or tetra-alkyl substituted ammonium, with the alkyl groups having from one to six carbon atoms, for example, triethyl or trimethyl ammonium, tetramethyl or tetraethyl ammonium). Suitable densifying agents include alkali metal, ammonium, or substituted ammonium salts of pyrophosphates, hexametaphosphates, tripolyphosphates, hypophosphates, polyphosphoric acid, ethylenediaminetetraacetic acid, hydroxyethylidenediphosphonate; and aminotri-(methylenephosphonate). Specific densifying agents include sodium hypophosphate tetrapotassium pyrophosphate, and tetrasodium pyrophosphate. Tetrasodium pyrophosphate and tetrapotassium pyrophosphate are particularly useful. Other specific densifying agents include sodium hexametaphosphate, sodium salt of ethylenediaminetetraacetic acid, sodium polyphosphate, sodium salt of diethylenetriaminepentaacetic acid, sodium salt of hydroxyethylethylenediaminetriacetic acid, and sodium salt of dihydroxyethylglycine. Still other densifying agents include alkali metal, ammonium or substituted ammonium salts of oxalates, phosphates, and tungstates. Sodium oxalate, dibasic sodium phosphate and sodium tungstate are particularly useful. Mixtures of the foregoing densifying agents are also useful. In accordance with this aspect of the present invention the inorganic densifying agents can be applied in an amount from about 1.0% to about 50% by weight based on the fibers and densifying agent.

[0122] Without intending to limit the scope of the present invention, one possible explanation for the effect the densifying agents have on the densifiability and softness of the fibers can be explained by considering the hydrogen bonding that occurs between cellulose molecules within a cellulose fiber and within a specific cellulose molecule. The densifying agents when applied to the fibers may disrupt or promote the disruption of existing hydrogen bonding between cellulose molecules or within a given cellulose molecule. In other words, the densifying agent may occupy sites on the cellulose molecule that would otherwise form hydrogen bonds within the molecule or with other cellulose molecules.

[0123] With respect to the inorganic densifying agents, such as TKPP, another possible explanation for the effect the inorganic densifying agent has on the densifiability and softness of the fibers or articles containing the fibers relates to TKPP's hygroscopic property wherein it attracts moisture from the surrounding environment into the fibers which have been treated with TKPP. This moisture may disrupt or participate in the disruption of hydrogen bonding between cellulose molecules or within a cellulose molecule as explained above. In addition to increasing the densifiability of fibers, the present inventors have also observed that TKPP softens the fibers when applied thereto. Other inorganic densifying agents that are hygroscopic and may also soften the fibers include many alkali metal, ammonium, or substituted ammonium salts of pyrophosphates, hexametaphosphates, tripolyphosphates, hypophosphates, polyphosphoric acid, ethylenediaminetetraacetic acid, hydroxyethylidenediphosphonate; and aminotri-(methylenephosphonate). Specific hygroscopic densifying agents include sodium hypophosphate, tetrapotassium pyrophosphate, and disodium phosphate. Tetrapotassium pyrophosphate is particularly useful. Other specific, densifying agents that are hygroscopic include sodium hexametaphosphate and potassium salt of ethylenediaminetetraacetic acid. Mixtures of hygroscopic and non-hygroscopic densifying agents are also useful.

[0124] The advantages of this aspect of the present invention extend to products in composition that include fibers treated with a densifying agent as described above where no particulate material, such as super absorbent is present

[0125] The following examples illustrate how the application of a densifying agent to pulp fibers yields a product that is easier to density than the same untreated pulp fibers.

EXAMPLE 6

[0126] A sample of NB 416 pulp sheet (available from Weyerhaeuser Company, Tacoma, Washington) was sprayed with different levels of glycerin, while passing through a slitter/rewind apparatus, to produce several rolls of material that comprise different levels of pulp and glycerin. The pulp sheets were then fed into a commercial sized hammermill connected to a pocket former and an adult incontinent product manufacturing line. During the final stage of manufacture, the products made from these pulps treated with various levels of glycerin were passed through a set of debulking rolls set to a constant pressure for the entire range of materials. The finished products were then opened up and the densities

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of the core material was tested. Results are as follows:

Sample	Basis Weight (g/ m ²)	Density (g/ cm ³)
0% Glycerin	673	0.173
5% Glycerin	730	0.192
6% Glycerin	701	0.162
7% Glycerin	767	0.199
8% Glycerin	673	0.228
9% Glycerin	721	0.237
9% Glycerin (aged)	653	0.282

[0127] The percentages given above are weight percent glycerin based on the dry weight of pulp fibers. The 9% aged glycerin sample had glycerin applied to the pulp sheet approximately three months prior to feeding to the commercial sized hammermill. These results demonstrate that increasing levels of glycerin on pulp fibers yield products with increasing densities for a given set of densifying conditions. Based on the results for the aged sample, it is believed that the additional time allowed for additional hydrogen bond disruption within the cellulose fibers.

EXAMPLE 7

[0128] This example illustrates how adding other densifying agents, along with glycerin produces a product that is easier to density than untreated pulp fibers.

[0129] A sample of NB 416 pulp sheet (available from Weyerhaeuser Company, Tacoma, Washington) was sprayed with a solution of 33% lactose and 66% glycerin so that the resulting product was comprised of 91% O.D. (i.e. oven dried) pulp and 9% additive. A second sample of pulp sheet was sprayed with a solution of 50% glucose and 50% glycerin to obtain a product with similar add-on levels. These products were then, in turn, processed in a manner similar to that described in Example 38. Measurement of the core densities of the products made from these materials yielded the following results:

Sample	Basis Weight (g/ m ²)	Density (g/ cm ³)
0% Glycerin	673	0.173
3% Lactose/6% Glycerin	689	0.263
4.5% Glucose/4.5% Glycerin	751	0.228

[0130] These results demonstrate that densifying agents in addition to glycerin on pulp fibers yield products with increased densities for a given set of densification conditions.

EXAMPLE 8

[0131] This example illustrates how adding other densifying agents, by themselves, also produces a product that is easier to density than an untreated pulp.

[0132] Samples of NB 416 pulp sheet (available from Weyerhaeuser Company, Tacoma, Washington) were treated, by passing through a roll coating device, with solutions of 70% sorbitol; 64% sorbitol and 6.4% lactic acid; and 51.2% sorbitol, 12.8% tetrapotassium pyrophosphate, and 6.4% lactic acid respectively to produce sheets with 8%-9% add-on levels of densifying agent per sample. The sheets were then air dried over night and the treated pulp sheets were then fed into a Fitz hammermill fitted with a 6.45cm² (1 in²) square holed screen, shunted to an air lay machine (an M & J air lay machine from the M & J Company, Horsens, Denmark) and air laid into a web. Similar samples were made from an untreated pulp sheet and one treated with 9% glycerin alone. All three of the sample webs and the two control webs were then passed through a set of debulking rolls set to a pressure of 1.72x10⁵Pa (25 psi) and the densities of the resulting materials was determined with the following results:

Sample	Basis Weight (g/m ²)	Density (g/cm ³)
0% Glycerin	176	0.1270

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(continued)

Sample	Basle Weight (g/m ²)	Density (g/cm ³)
9% Glycerin	168	0.2242
9% Sorbitol	167	0.1904
8% Sorbitol/1% Lactic acid	178	0.1396
6% Sorbitol/2% Potassium Pyrophosphate/ 1% Lactic acid	172	0.1719

[0133] These results clearly demonstrate that other densifying agents on pulp also yield products with increased densities for a given set of processing conditions.

EXAMPLE 9

[0134] This example illustrates how the method of adding glycerin to some crosslinked pulps yields a product that is easier to density than a corresponding untreated crosslinked pulp.

[0135] 300 gram samples of HBA and HBAFF (crosslinked pulps produced by Weyerhaeuser Company, Tacoma, Washington) were each air entrained in a blenderlike mixing device and 33 grams of glycerin dissolved in 50 milliliters of deionized water was sprayed onto the pulp. In each case, the mixer was stopped, the product was vacuumed out and allowed to dry overnight. Ten grain samples of the treated pulps and ten gram samples of the corresponding untreated pulps were air laid into 6 inch diameter pads in a laboratory pad former then pressed at 4.8×10^6 Pa (700 psi) for one minute. The thickness of the resulting pads was determined and densities were calculated with the following results:

Sample	Basle Weight (g/m ²)	Density (g/cm ³)
HBAFF	542	0.206
HBAFF/10% Glycerin	520	0.285
HBA	529	0.128
HBA/10% Glycerin	521	0.0942

[0136] These results show that in the case of HBAFF, addition of the glycerin gives a product that is more easily densified for a given set of densifying conditions.

[0137] The following example demonstrates how the application of certain densifying agents in accordance with the present invention on pulp yeld products with improved softness for a given set of processing conditions.

EXAMPLE 10

[0138] This example illustrates how certain densifying agents affect the stiffness which is one aspect of the softness of an air laid web of fibers treated with a densifying agent.

[0139] A sample of NB 416 pulp sheet (available from Weyerhaeuser Company, Tacoma, Washington) was treated, by passing through a roll coating device to coat the pulp sheet to 5.8% weight (of a mixture of equal amounts of sorbitol and lactic acid) based on the mass of the fibers and added densifying agents. Another sample of NB 416 was sprayed with a solution of 50% TKPP to a level of 5% TKPP based on the mass of the fibers and TKPP. The sheets were then air dried over night and the treated pulp sheets and an untreated control were then fed into a Fitz hammermill fitted with a 6.45cm² (1 in²) square holed screen. while simultaneously adding IM 3900 (a superabsorbent available from Hoochst Celanese, of Portsmouth, VA) at a rate to produce a material that was 60% treated fiber and 40% IM 3900. This mixture was shunted to an air lay machine (an M & J air lay machine from the M & J Company, Horsens, Denmark) and air laid into webs. Samples of each of the webs were placed in a flat press and pressed to obtain an equivalent density. Press conditions were adjusted so that all the samples were densified to approximately equal densities. The Gurley Stiffness test was then performed on each of the pressed samples with the following results:

Sample	Density (g/cm ³)	Gurley Stiffness
NB 416	0.141	131.7
5.8% Sorbitol/Lactic acid	0.145	96.2
5% TKPP	0.138	125.1

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[0140] The results demonstrate how densified air laid webs of pulp fibers treated with certain densifying agents are less stiff than corresponding densified air laid webs of untreated pulp fibers. This stiffness data when evaluated in combination with other qualities of the web such as compressibility, pressure required to achieve the given density, and drape, give some indication that the treated fibers are softer than untreated fibers.

EXAMPLE 11

[0141] This example illustrates how a densifying agent added to pulp fibers produces material with increased mass without an appreciable increase in volume.

[0142] A sample of NB 416 pulp sheet (available from Weyerhaeuser Company, Tacoma, Washington) was treated, by passing through a roll coating device to coat the pulp sheet to 9% glycerin based on the mass of the fibers and glycerin. Another sample of NB 416 was sprayed with a solution of 50% TKPP to a level of 5% TKPP based on the mass of the fibers and TKPP. The sheets were then air dried over night and the treated pulp sheets and an untreated control were then fed into a Fitz hammermill fitted with a 6.45cm² (1 in²) square holed screen, while simultaneously adding IM 3900 (a superabsorbent available from Hoechst Celanese, of Portsmouth, VA) at a rate to produce a material that was 60% treated fiber and 40% IM 3900. This mixture was shunted to an air lay machine (an M & J air lay machine from the M & J Company, Horsens, Denmark) and air laid into webs. Each of the webs had a basis weight of approximately 375 grams/meter². The undensified webs were then calipered and densities were calculated.

Sample	Caliper (mm)	Density (g/cm ³)
0% Glycerin	4.1	0.091
9% Glycerin	3.6	0.104
5% TKPP	2.8	0.134

[0143] The results demonstrate shows how air laid webs made from fibers treated with certain densifying agents exhibit a decreased caliper for the same mass of fibers.

Claims

1. A method for producing fibers which can be densified comprising:

providing fibers that have hydrogen bonding functional sites, said fibers densifying to a first density when compressed under a first set of conditions; and
applying densifying agent to the fibers in an amount effective to provide fibers having the densifying agent applied thereto that densify to a second density when compressed under the first set of conditions with no particulate material present, the second density being greater than the first density;

wherein the densifying agent comprises (a) polymeric materials with repeating units, wherein each repeating unit has a functional group capable of forming a hydrogen bond with a fiber and the polymeric material is selected from the group consisting of polyglycol, a polycarboxylic acid, a polycarboxylate, a poly(lactone) polyol, a polyamide, a polyamine, a polysulfonic acid, a polysulfonate acid and combinations thereof; or (b) non-polymeric organic materials with a functional group capable of forming a hydrogen bond with a fiber and the non-polymeric organic material includes a functionality selected from the group consisting of a carboxyl, a carboxylate, a carbonyl, a sulfonic acid, a sulfonate, a sulfonamide, a hydroxyl, a phosphoric acid, a phosphate, a phosphoramidate, an amide, an amine and combinations thereof.

2. The method of Claim 1, wherein the densifying agent has a volatility less than water.

3. The method of Claim 1 or Claim 2, wherein the densifying agent comprises glycerin, sorbitol, ethylene glycol, butylene glycol, trimethylene glycol, propylene glycol, or combinations thereof.

4. The method of Claim 1 or Claim 2 wherein the densifying agent is a diol.

5. The method of any one of Claims 1-4, wherein the densifying agent is applied in an amount ranging from 0.1% to 30.0% by weight based on the weight of dry fibers and densifying agent.

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6. The method of any preceding claim, further comprising densifying the fibers having the densifying agent applied thereto by applying external pressure on the fibers.
- 5 7. The method of Claim 6, further comprising the step of forming the fibers into a web, sheet (32) or bale (44) before densification such that the web, sheet (32) or bale (44) is densified by applying external pressure on the web, sheet or bale.
- 10 8. The method of Claim 7, wherein the densifying step comprises applying external pressure on the web or sheet (32) by passing the web or sheet (32) through a nip of a calendar roll (24,26).
9. The method of Claim 7, wherein the densifying step comprises applying external pressure on the web or sheet in a press.
- 15 10. The method of Claim 7, wherein the densifying step comprises applying external pressure on the bale (44) in bale form.
11. The method of any preceding claim, wherein the fibers are wood pulp fibers.
- 20 12. The method of any preceding claim, wherein the fibers include intra-fiber crosslinks.
13. A mass of fibers which can be densified comprising:
- 25 fibers having hydrogen bonding functional sites, said fibers densifying to a first density when compressed under a first set of conditions;
densifying agent in an amount effective to provide fibers having the densifying agent applied thereto that density to a second density when compressed under the first set of conditions with no particulate material present, the second density being greater than the first density;
- 30 wherein the densifying agent comprises (a) polymeric materials with repeating units, wherein each repeating unit has a functional group capable of forming a hydrogen bond with a fiber, and the polymeric material is selected from the group consisting of polyglycol, a polycarboxylic acid, a polycarboxylate, a poly(lactone) polyol, a polyamide, a polyamine, a polysulfonic acid, a polysulfonate, and combinations thereof; or (b) non-polymeric organic materials with a functional group capable of forming a hydrogen bond with a fiber and the non-polymeric organic material includes a functionality selected from the group consisting of a carboxyl, a carboxylate, a carbonyl, a sulfonic acid, a sulfonate, a sulfonamide, a hydroxyl, a phosphoric acid, a phosphate, a phosphoramidate, an amide, an amine, and combinations thereof.
- 35 14. The mass of fibers of Claim 13, wherein the densifying agent comprises glycerin, sorbitol, ethylene glycol, butylene glycol, trimethylene glycol, propylene glycol and combinations thereof.
- 40 15. The mass of fibers of Claim 13 wherein the densifying agent is a diol.
16. The mass of fibers of Claim 13, Claim 14 or Claim 15, wherein the densifying agent is applied in an amount ranging from 0.1% to 30.0% by weight based on the weight of the dry fibers and densifying agent.
- 45 17. The mass of fibers of any of claims 13-16, wherein the fibers are wood pulp fibers.
18. The mass of fibers of any of claims 13-17, wherein the fibers include intra-fiber crosslinks.
- 50 19. An article comprising the mass of fibers of Claims 13,14,17 or 18.
20. The article of Claim 19 consisting of diapers (100,550), incontinent devices, bod pads, wipes, feminine hygiene products or bandages(430).
- 55 21. The article of Claim 19, wherein the article (410) is absorbent.

Revendications

1. Procédé de production de fibres qui peuvent être densifiées, comprenant :

5 l'apport de fibres qui possèdent des sites fonctionnels à liaison hydrogène, lesdites fibres se densifiant à une première densité quand elles sont comprimées selon un premier ensemble de conditions : et l'application d'un agent de densification des fibres en une quantité efficace pour fournir des fibres sur lesquelles est appliqué l'agent de densification, qui se densifient à une seconde densité quand elles sont comprimées sous le premier ensemble de conditions sans présence de matière particulaire, la seconde densité étant supérieure à la première densité :

10 dans laquelle l'agent de densification comprend (a) des substances polymères avec des motifs répétés, dans lesquelles chaque motif répété possède un groupe fonctionnel capable de former une liaison hydrogène avec une fibre, et la substance polymère est choisie dans le groupe constitué par le polyglycol, un acide polycarboxylique, un polycarboxylate, un polyol de (poly)lactone, un polyamide, une polyamine, un acide polysulfonique, un acide polysulfonate, et des combinaisons de ceux-ci ; ou (b) des substances organiques non polymères avec un groupe fonctionnel capable de former une liaison hydrogène avec une fibre, et la substance organique non polymère comprend une fonctionnalité choisie dans le groupe constitué par un carboxyle, un carboxylate, un carbonyle, un acide sulfonique, un sulfonate, un sulfonamide, un hydroxyle, un acide phosphorique, un phosphate, un phosphoramide, un amide, une amine et des combinaisons de ceux-ci.

2. Procédé selon la revendication 1, dans lequel l'agent de densification a une volatilité inférieure à l'eau.

3. Procédé selon la revendication 1 ou la revendication 2, dans lequel l'agent de densification comprend la glycérine, le sorbitol, l'éthylèneglycol, le butylèneglycol, le triméthylèneglycol, le propylèneglycol, ou des combinaisons de ceux-ci.

4. Procédé selon la revendication 1 ou la revendication 2, dans lequel l'agent de densification est un diol.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel l'agent de densification est appliqué en une quantité allant de 0,1 à 30,0% en poids, en se basant sur le poids des fibres sèches et de l'agent de densification.

6. Procédé selon l'une quelconque des revendications précédentes, comprenant en outre la densification des fibres sur lesquelles est appliqué l'agent de densification en appliquant une pression externe sur les fibres.

7. Procédé selon la revendication 6, comprenant en outre l'étape de formation des fibres en une toile, une feuille (32) ou une balle (44) avant la densification, de telle manière que la toile, la feuille (32) ou la balle (44) est densifiée par application d'une pression externe sur la toile, la feuille ou la balle.

8. Procédé selon la revendication 7, dans lequel l'étape de densification comprend l'application d'une pression externe sur la toile ou la feuille (32) en passant la toile ou la feuille (32) à travers un espacement d'un rouleau presseur (24, 26).

9. Procédé selon la revendication 7, dans lequel l'étape de densification comprend l'application d'une pression externe sur la toile ou la feuille dans une presse.

10. Procédé selon la revendication 7, dans lequel l'étape de densification comprend l'application d'une pression externe sur la balle (44) sous forme de balle.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel les fibres sont des fibres de pâte de bois.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel les fibres comprennent des réticulations intra-fibres.

13. Masse de fibres qui peuvent être densifiées, comprenant :

des fibres qui possèdent des sites fonctionnels à liaison hydrogène, lesdites fibres se densifiant à une première

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densité quand elles sont comprimées sous un premier ensemble de conditions :
un agent de densification en une quantité efficace pour fournir des fibres sur lesquelles est appliqué l'agent
de densification, qui se densifient à une seconde densité quand elles sont comprimées sous le premier en-
semble de conditions sans présence de matière particulaire, la seconde densité étant supérieure à la première
densité :

dans laquelle l'agent de densification comprend (a) des substances polymères avec des motifs répétés, dans
lesquelles chaque motif répété possède un groupe fonctionnel capable de former une liaison hydrogène avec une
fibre, et la substance polymère est choisie dans le groupe constitué par le polyglycol, un acide polycarboxylique,
un polycarboxylate, un polyol de (poly)lactone, un polyamide, une polyamine, un acide polysulfonique, un poly-
sulfonate et des combinaisons de ceux-ci ; ou (b) des substances organiques non polymères avec un groupe
fonctionnel capable de former une liaison hydrogène avec une fibre, et la substance organique non polymère
comprend une fonctionnalité choisie dans le groupe constitué par un carboxyle, un carboxylate, un carbonyle, un
acide sulfonique, un sulfonate, un sulfonamide, un hydroxyle, un acide phosphorique, un phosphate, un phospho-
ramide, un amide, une amine, et des combinaisons de ceux-ci.

14. Masse de fibres selon la revendication 13, dans laquelle l'agent de densification comprend la glycérine, le sorbitol,
l'éthylèneglycol, le butylèneglycol, le triméthylèneglycol, le propylèneglycol, et des combinaisons de ceux-ci.

15. Masse de fibres selon la revendication 13, dans laquelle l'agent de densification est un diol.

16. Masse de fibres selon la revendication 13, la revendication 14, ou la revendication 15, dans laquelle l'agent de
densification est appliqué en une quantité allant de 0,1 à 30,0% en poids, en se basant sur le poids des fibres
sèches et de l'agent de densification.

17. Masse de fibres selon l'une quelconque des revendications 13 à 16, dans laquelle les fibres sont des fibres de
pâte de bois.

18. Masse de fibres selon l'une quelconque des revendications 13 à 17, dans laquelle les fibres comprennent des
réticulations intra-fibres.

19. Article comprenant la masse de fibres des revendications 13, 14, 17 ou 18.

20. Article selon la revendication 19, comprenant des couches de bébé (100, 550), des dispositifs d'incontinence, des
coussins de lit, des lingettes, des produits hygiéniques féminins, ou des bandages (430).

21. Article selon la revendication 19, dans lequel l'article (410) est absorbant.

Patentansprüche

1. Verfahren für die Herstellung von Fasern, die verdichtet werden können und das folgende Schritte umfasst:

die Bereitstellung von Fasern mit funktionellen Wasserstoff bindenden Stellen, wobei diese Fasern auf einen
ersten Dichtewert verdichtet werden, wenn sie unter ersten Verfahrensbedingungen komprimiert werden; und
Vermischung dieser Fasern mit einem Verdichtungsagens in einer Menge, die ausreicht, um die mit dem Ver-
dichtungsagens vermischten Fasern auf einen zweiten Dichtewert zu verdichten, wenn sie unter den ersten
Verfahrensbedingungen in Abwesenheit von Partikeln komprimiert werden, wobei der zweite Dichtewert höher
ist, als der erste Dichtewert,

dadurch gekennzeichnet, dass

das Verdichtungsagens (a) ein Polymer mit wiederholenden Einheiten aufweist, und jede der wiederholenden
Einheiten eine funktionelle Gruppe aufweist, welche die Bindung von Wasserstoff mit den Fasern bewirken kann,
und das Polymer aus der Gruppe ausgewählt wird, die folgendes umfasst: Polyglycol, eine polyhomocyclische
Säure, ein Polycarboxylat, ein Poly(lacton) Polyol, ein Polyamid, ein Polyamin,, eine Polysulfonsäure, eine Poly-
sulfonatsäure und deren Kombinationen; oder (b) nicht polymerische organische Materialien mit einer funktionellen
Gruppe, die fähig ist, eine Bindung von Wasserstoff mit der Faser herzustellen, und das nicht polymerische Material
eine Funktionalität aufweist, die aus der Gruppe ausgewählt wird, die folgendes umfasst: ein Carboxyl, ein Car-

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boxylat, ein Carbonyl, eine Sulfonsäure, ein Sulfonat,, ein Sulfonamid, ein Hydroxyl, eine Phosphorsäure, ein Phosphat, ein Phosphoramid, ein Amid, ein Amin und deren Kombinationen.

- 5 2. Verfahren nach Anspruch 1,
dadurch gekennzeichnet, dass
das Verdichtungsagens eine Flüchtigkeit hat, die geringer ist, als die Flüchtigkeit von Wasser.
- 10 3. Verfahren nach einem der Ansprüche 1 oder 2,
dadurch gekennzeichnet, dass
das Verdichtungsagens Glycerin, Sorbitol, Ethylenglycol, Butylenglycol, Trimethylenglycol, Propylenglycol oder deren Kombinationen enthält.
- 15 4. Verfahren nach einem der Ansprüche 1 oder 2,
dadurch gekennzeichnet, dass
das Verdichtungsagens ein Diol ist.
- 20 5. Verfahren nach einem der Ansprüche 1 bis 4,
dadurch gekennzeichnet, dass
das Verdichtungsagens in einer Menge zwischen 0,1 Gew.-% und 30,0 Gew.-% bezogen auf das Trockengewicht der Fasern und des Verdichtungsagens beigemischt wird.
- 25 6. Verfahren nach einem der vorausgegangenen Ansprüche,
dadurch gekennzeichnet, dass
die mit dem Verdichtungsagens vermischten Fasern durch die Beaufschlagung eines äußeren Druckes auf die Fasern weiter verdichtet werden.
- 30 7. Verfahren nach Anspruch 6,
dadurch gekennzeichnet, dass
es einen weiteren Schritt enthält, in dem die Fasern vor der Verdichtung in Form eines Gewebes, in Bahnen (32) oder Ballen (44) so geformt werden, dass das Gewebe, die Bahnen (32) oder der Ballen (44) durch Beaufschlagung eines äußeren Druckes auf dieses Gewebe, diese Bahnen oder diesen Ballen verdichtet werden.
- 35 8. Verfahren nach Anspruch 7,
dadurch gekennzeichnet, dass
der Schritt der Verdichtung die Beaufschlagung eines äußeren Druckes auf das Gewebe oder die Bahn (32) dadurch durchgeführt wird, dass das Gewebe oder die Bahn (32) durch die Spannbacke einer Kalandrwalze (24, 26) geleitet wird.
- 40 9. Verfahren nach Anspruch 7,
dadurch gekennzeichnet, dass
der Schritt der Verdichtung die Beaufschlagung eines äußeren Druckes auf das Gewebe oder die Bahn in einer Presse beinhaltet.
- 45 10. Verfahren nach Anspruch 7,
dadurch gekennzeichnet, dass
der Schritt der Verdichtung die Beaufschlagung eines äußeren Druckes auf den Ballen (44) beinhaltet.
- 50 11. Verfahren nach einem der vorausgegangenen Ansprüche,
dadurch gekennzeichnet, dass
die Fasern aus Holzstofffasern bestehen.
- 55 12. Verfahren nach einem der vorausgegangenen Ansprüche,
dadurch gekennzeichnet, dass
die Fasern interne Vernetzungen aufweisen.
13. Fasermasse, die verdichtet werden kann,
dadurch gekennzeichnet, dass
sie folgendes enthält:

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die Bereitstellung von Fasern mit funktionellen Wasserstoff bindenden Stellen, wobei diese Fasern auf einen ersten Dichtewert verdichtet werden, wenn sie unter ersten Verfahrensbedingungen komprimiert werden; Vermischung der Fasern mit einem Verdichtungsagens in einer Menge, die ausreicht, um die mit dem Verdichtungsagens vermischten Fasern auf einen zweiten Dichtewert zu verdichten, wenn sie unter den ersten Verfahrensbedingungen in Abwesenheit von Partikeln komprimiert werden, wobei der zweite Dichtewert höher ist, als der erste Dichtewert;

wobei das Verdichtungsagens (a) ein Polymer mit wiederholenden Einheiten aufweist, und jede dieser wiederholenden Einheiten eine funktionelle Gruppe aufweist, welche die Bindung von Wasserstoff mit den Fasern bewirken kann, und das Polymer aus der Gruppe ausgewählt wird, die folgendes umfasst: ein Polyglycol, eine polyhomozyklische Säure, ein Poly(lacton)Polyol, ein Polyamid, ein Polyamin, eine Polysulfonsäure, ein Polysulfonat und deren Kombinationen; oder (b) nicht polymerische organische Materialien mit einer funktionellen Gruppe, die fähig ist, eine Bindung von Wasserstoff mit der Faser herzustellen, und das nicht polymerische Material eine Funktionalität aufweist, die aus der Gruppe ausgewählt wird, die folgendes umfasst: ein Carboxyl, ein Carboxylat, ein Carbonyl, eine Sulfonsäure, ein Sulfonat, ein Sulfonamid, ein Hydroxyl, eine Phosphorsäure, ein Phosphat, ein Phosphoramid, ein Amid, ein Amin und deren Kombinationen.

14. Fasermasse nach Anspruch 13,

dadurch gekennzeichnet, dass

das Verdichtungsagens Glycerin, Sorbitol, Ethylenglycol, Butylenglycol, Trimethylenglycol, Propylenglycol oder deren Kombinationen enthält.

15. Fasermasse nach Anspruch 13,

dadurch gekennzeichnet, dass

das Verdichtungsagens ein Diol ist.

16. Fasermasse nach einem der Ansprüche 13, 14 oder 15,

dadurch gekennzeichnet, dass

das Verdichtungsagens in einer Menge beigelegt wird, die zwischen 0,1 Gew.-% und 30,0 Gew.-% bezogen auf das Gewicht der trockenen Fasern und des Verdichtungsagens liegt.

17. Fasermasse nach einem der Ansprüche 13 bis 16,

dadurch gekennzeichnet, dass

die Fasern aus Holzfasern bestehen.

18. Fasermasse nach einem der Ansprüche 13 bis 17,

dadurch gekennzeichnet, dass

die Fasern interne Vernetzungen aufweisen.

19. Artikel,

dadurch gekennzeichnet, dass

er die Fasermasse nach einem der Ansprüche 13, 14, 17 oder 18 aufweist.

20. Artikel nach Anspruch 19,

dadurch gekennzeichnet, dass

er aus Windeln (100, 500), Inkontinenzwindeln, Bettelagen, Wischtüchern, Hygieneprodukten für Damen oder Bandagen (430) besteht.

21. Artikel nach Anspruch 19,

dadurch gekennzeichnet, dass

der Artikel (410) aus einem absorbierenden Material besteht.

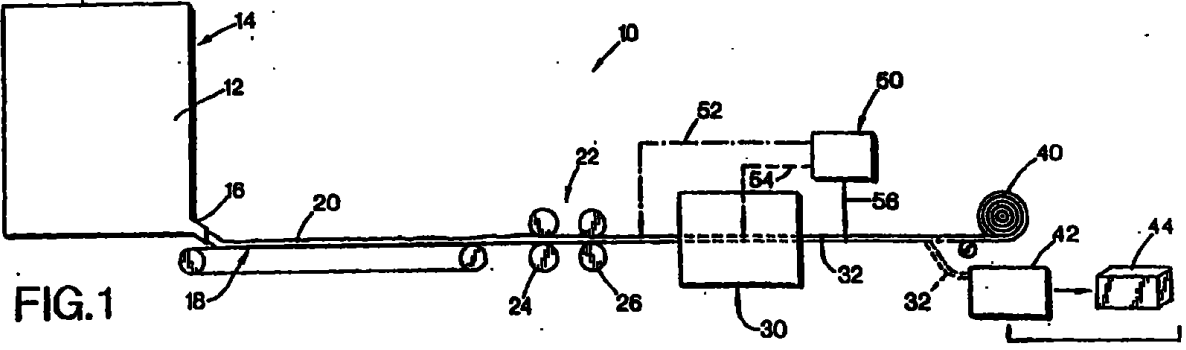
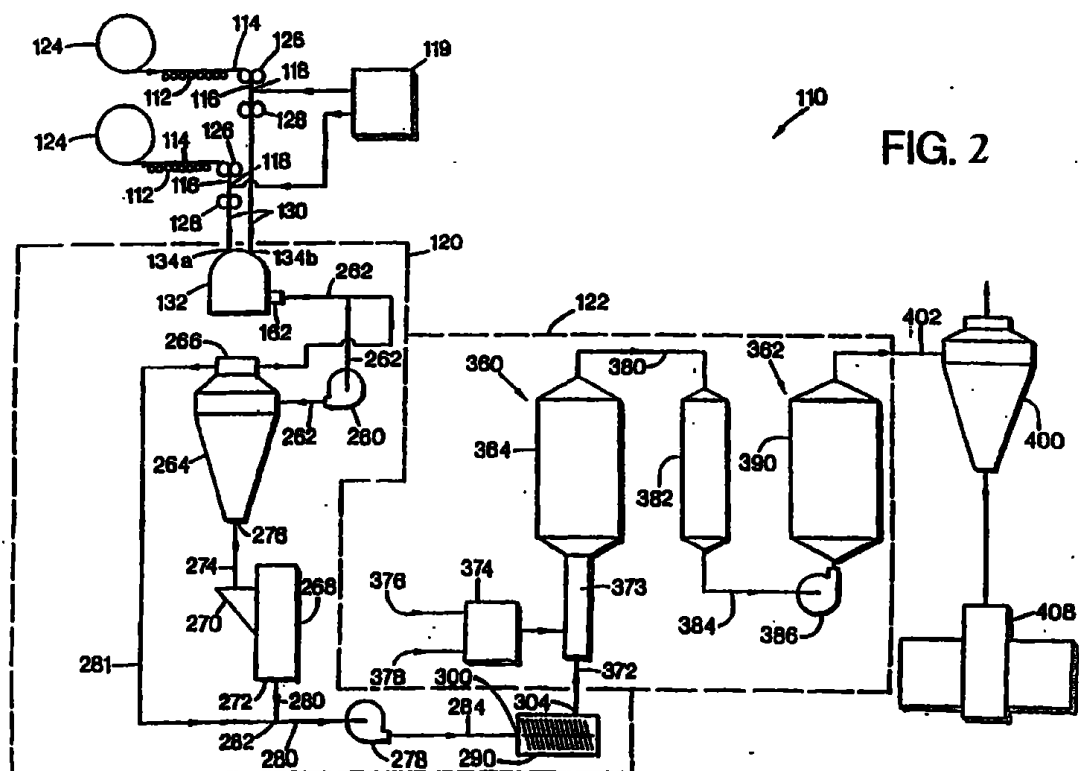


FIG.1

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FIG. 3

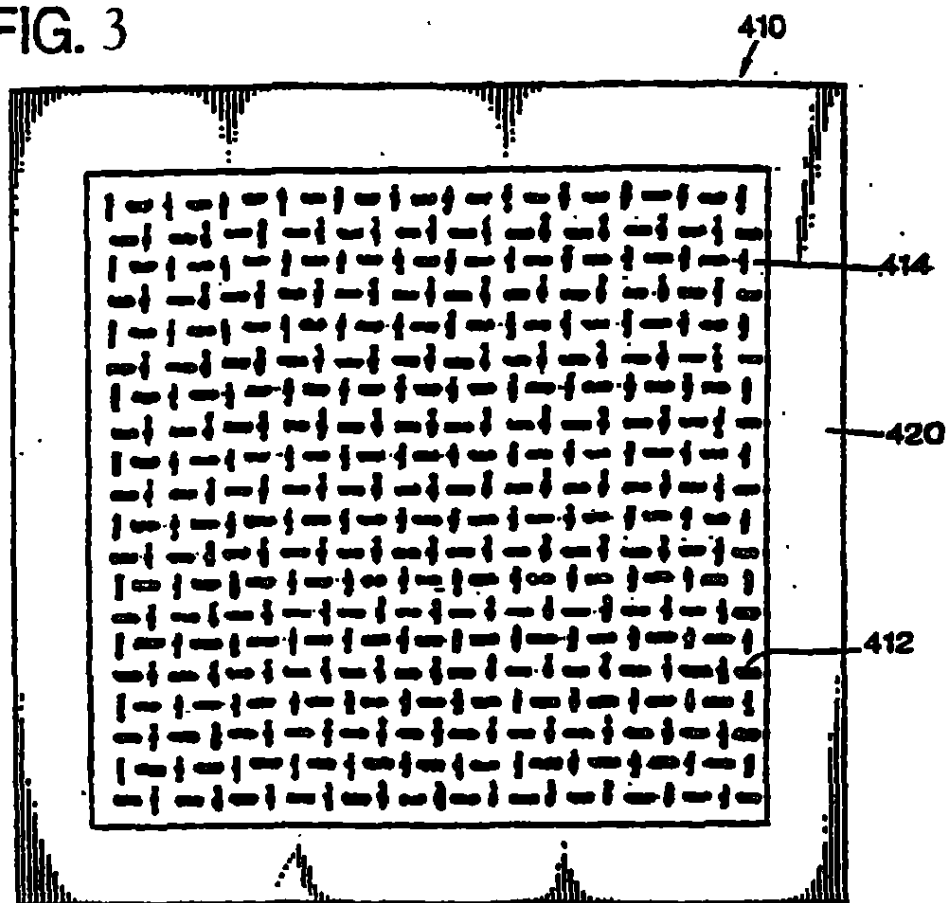
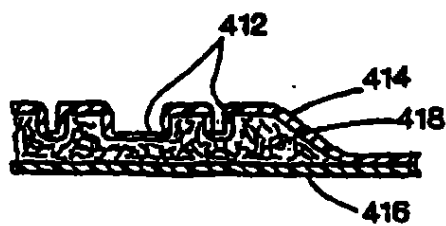


FIG. 4



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FIG. 5

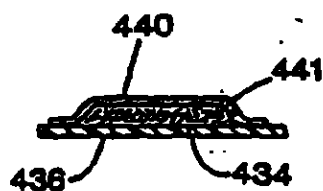
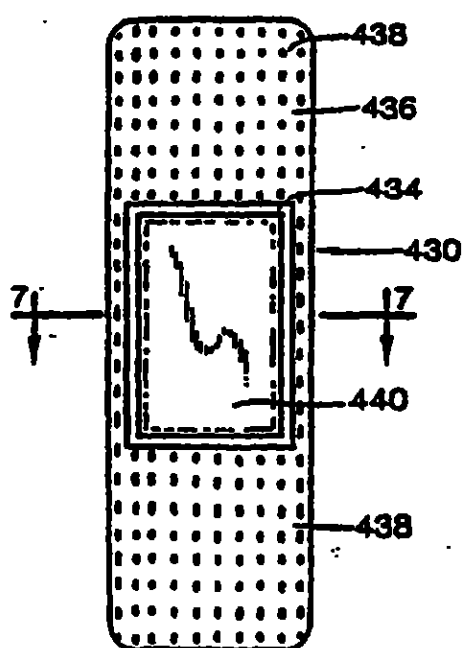


FIG. 6

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FIG. 7

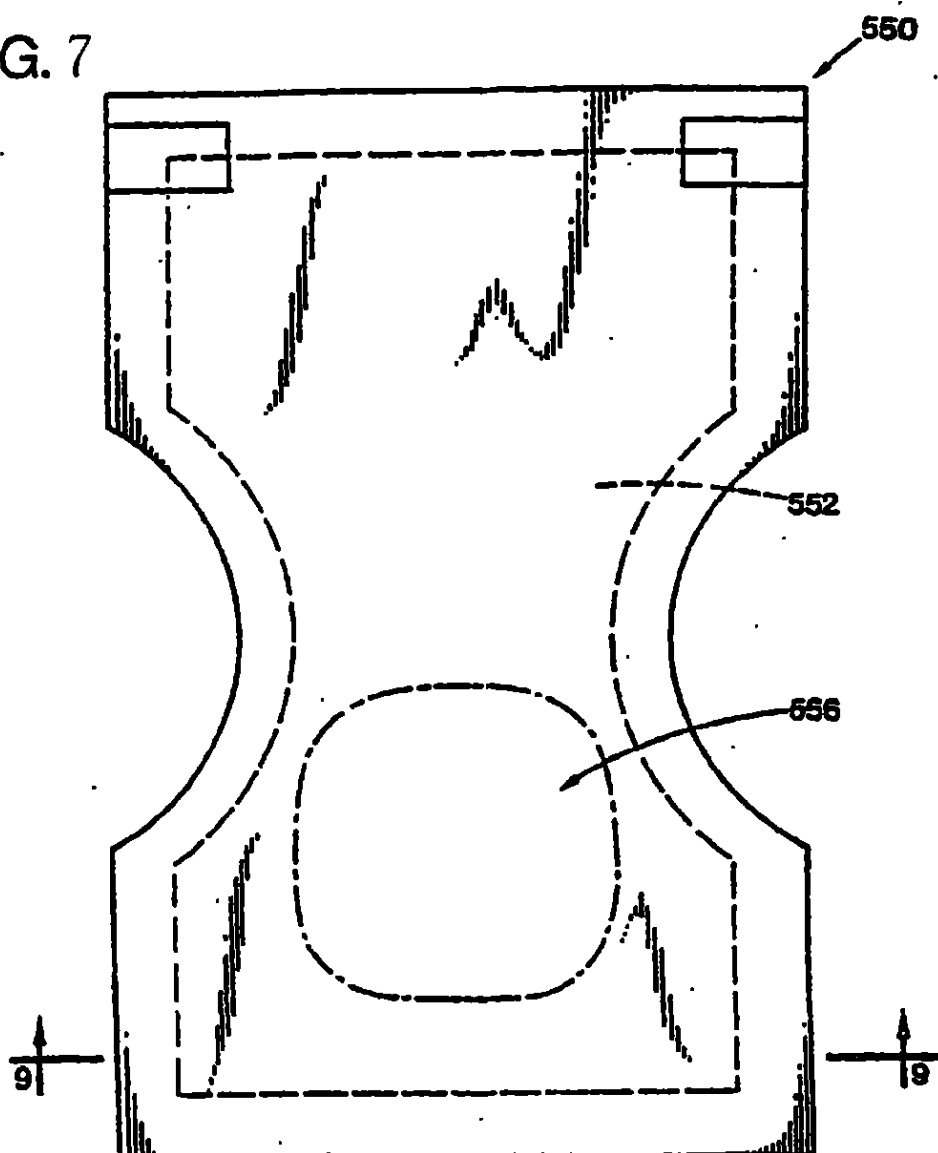


FIG. 8



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Hygienischer Zellstoffartikel.

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Anmerkung: Innerhalb von neun Monaten nach der Bekanntmachung des Hinweises auf die Erteilung des europäischen Patents kann jedermann beim Europäischen Patentamt gegen das erteilte europäische Patent Einspruch einlegen. Der Einspruch ist schriftlich einzureichen und zu begründen. Er gilt erst als eingelegt, wenn die Einspruchsgebühr entrichtet worden ist (Art. 99(1) Europäisches Patentübereinkommen).

Beschreibung

Die Erfindung betrifft einen hygienischen Zellstoffartikel wie beispielsweise eine Windel, eine Krankenunterlage, eine Damenbinde, eine Slipelinlage oder dergl.. Derartige Zellstoffartikel sind bekannt; sie weisen ein oder mehrere Saugkissen auf, welche aus Zellstoff bestehen und in aller Regel Zusätze an Quellstoffen und gegebenenfalls Hilfsmaterialien haben. Die Artikel sind meist mit einer oberen flüssigkeitsdurchlässigen Abdeckung ausgerüstet und sie haben eine untere flüssigkeitsdichte Schicht oder Einlage. Die obere flüssigkeitsdurchlässige Abdeckung kann auch entfallen, wenn zumindest die obere Schicht des Saugkörpers derart verfestigt ist, daß der Saugkörper nicht mehr flusen kann. Eine solche Verfestigung kann durch Zusatz von thermoplastischen Fasern und anschließender zumindest oberflächlicher Wärmebehandlung herbeigeführt werden.

Auch die untere flüssigkeitsdichte Schicht oder Einlage kann notfalls entfallen; sie wird aber in den meisten Fällen vorhanden sein.

Der Zusatz der erwähnten Quellstoffe hat den Zweck, das Flüssigkeitsaufnahmevermögen des Artikels zu vergrößern. Als Quellstoffe werden heute meist synthetisch hergestellte Polymere verwendet, welche in der Lage sind, unter Vergrößerung ihres Volumens, erhebliche Mengen Flüssigkeit aufzunehmen. Es kommen hierzu Stoffe wie Polyacrylate, Pflropfpolymerisate aus Stärke und Acrylsäure oder ähnliche Verbindungen in Betracht, welche in der Literatur eingehend beschrieben sind. Als Fundstellen werden beispielsweise die amerikanischen Patentschriften US-A-4 382 919, US-A 3 964 486 sowie US-A-3 669 103 genannt. Eine weitere Fundstelle ist die europäische Patentanmeldung EP-A-202 167.

Hygienische Zellstoffartikel der hier genannten Art weisen gegebenenfalls auch noch Hilfsmaterialien auf; hierunter sind solche Stoffe zu verstehen, die entweder den als Saugstoff wirkenden Zellstoff ganz oder teilweise ersetzen sollen, wie beispielsweise bestimmte Schaumstoffe, insbesondere hydrophile Polyurethanschäume oder die den Zweck haben, den pH-Wert des Saugkissens, der sich bei Benetzung mit Wasser oder physiologischen Flüssigkeiten einstellt, in den leicht sauren Bereich zu verschieben. Es hat sich dies als vorteilhaft erwiesen, da im sauren Bereich das Wachstum der meisten Mikroorganismen gehemmt oder unterbunden ist, so daß die Windel durch diese Zusätze zumindest für eine begrenzte Zeit gegen den Abbau der in ihnen gespeicherten Körperflüssigkeiten stabilisiert ist. Der Zusatz derartiger saurer Hilfsstoffe ist in der bereits genannten europäischen Patentanmeldung EP-A-202 127 beschrieben, aber auch in der deutschen Offenlegungsschrift DE-A-20 27 809.

Es sind bereits zahlreiche Versuche unternommen worden, hygienische Zellstoffartikel sowohl mit pH-Wert-regulierenden Stoffen, beispielsweise Zitronensäure als auch mit Quellstoffen auszurüsten. Dabei hat sich jedoch gezeigt, daß das Flüssigkeitsaufnahmevermögen der bekannten Quellstoffe stark erniedrigt wird, wenn der pH-Wert der Saugkörper in denjenigen Bereich gerückt wird, der aus physiologischen Gründen erforderlich ist, nämlich in den pH-Bereich unter 6,0, vorzugsweise in den Bereich von 5,0 - 6,0. Um den dadurch resultierenden Schwierigkeiten auszuweichen, wird in der europäischen Patentanmeldung EP-A-202 127 vorgeschlagen, den Saugkörperbereich eines derartigen Artikels in zwei Bereiche zu unterteilen, von denen einer die erwünschten Quellstoffe enthält, dafür aber frei von pH-Wert-regulierenden Zusätzen ist und von denen die übrigen Bereiche quellstofffrei sind, statt dessen aber pH-Wert-regulierende Stoffe aufweisen.

Es liegt auf der Hand, daß ein derartiger Aufbau eines hygienischen Zellstoffartikels, beispielsweise einer Windel, technisch aufwendig ist und das Produkt verteuert. Als weiterer Nachteil ist zu nennen, daß das Produkt an denjenigen Stellen an denen sich die Bereiche überlappen auch dicker wird, was zu einer Minderung des Tragekomforts führt. Am wichtigsten ist indes der Umstand, daß der pH-gepufferte Bereich nur auf den quellstofffreien Bereich, in dem sich die Puffer-Substanz befindet, beschränkt ist.

In der FR-A-2.513.875 werden Puffersubstanzen eingesetzt, die den pH-Wert auf $\leq 4,5$ einstellen. Diese Puffersubstanzen wirken aber nicht als Quellstoffe.

Der Erfindung liegt die Aufgabe zugrunde, die bekannten hygienischen Zellstoffartikel, wie Windeln, Krankenunterlagen, Damenbinden, Slipelinlagen oder dergl. dahingehend weiter zu verbessern, daß sie sowohl die erwünschten antimikrobiellen Eigenschaften durch Stabilisierung im leicht sauren pH-Wert-Bereich aufweisen als auch über gute Saug- und Flüssigkeitsspeicher-Eigenschaften durch Zusatz von Quellstoffen verfügen. Die Lösung dieser Aufgabe ist durch die Beobachtung möglich geworden, daß es gelingen kann, die Quellstoffe selbst, welche chemisch betrachtet polymere Säuren sind, als Puffersubstanzen einzusetzen. Sie müssen hierzu mit Alkalimetallen und/oder Ammoniak derart teilneutralisiert werden, daß sich im Zellstoff-Saugkörper bei Benetzung mit Wasser oder einer physiologischen Flüssigkeit der erforderliche pH-Wert zwischen 5,0 und 6,0, vorzugsweise zwischen 5,2 und 5,5 einstellt. Überraschenderweise hat sich dabei ergeben, daß an dem bestehenden Vorurteil in zahlreichen Fällen ganz zu Unrecht festgehalten wird und daß das Flüssigkeitsspeichervermögen, aber auch das Flüssigkeitsansaugvermögen

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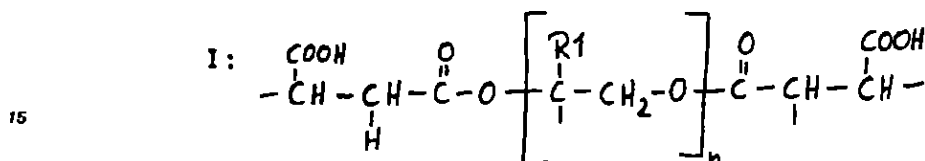
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gewisser synthetischer Quellstoffe unter diesen Bedingungen praktisch durchaus hinreichende Werte aufweist.

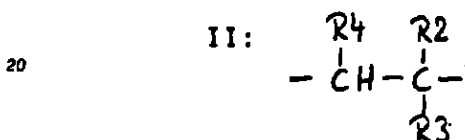
Als besonders geeignet für diesen Zweck haben sich Quellstoffe erwiesen, welche Ppropfpolymere sind mit

- 5 0,5 - 20 Gewichtsprozent chemisch gebundenen Resten der allgemeinen Formel I,
 - 79 - 99 Gewichtsprozent chemisch gebundenen Resten der allgemeinen Formel II, und
 - 0,1 - 2 Gewichtsprozent chemisch gebundenen Resten eines Vernetzers, der aus Monomeren mit wenigstens 2 olefinisch ungesättigten Doppelbindungen hervorgegangen ist;
- wobei bedeuten:

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- 25 n = 2 bis 300
- R1 = Wasserstoff oder Methyl
- R2 = Wasserstoff, Methyl oder Ethyl
- R3 = Carboxyl, Sulfonyl, Phosphonyl, gegebenenfalls verestert mit Alkanol mit 1 - 4 C-Atomen oder eine Gruppe der Formel

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worin R7 eine Sulfonyl- oder Phosphonyl-Gruppe bedeuten,

- R4 = Wasserstoff, Methyl, Ethyl oder Carboxyl.

40 Ppropfpolymere dieser Art lassen sich unter Verwendung von Alkalimetallen oder Ammonium teilneutralisieren und stellen dann Puffersysteme dar, welche die Saugkörper von hygienischen Zellstoffartikeln auf beliebige Werte zwischen 5,0 und 6,0 einzustellen vermögen. Es ist leicht möglich, mit diesen Stoffen pH-Werte von 5,2 oder 5,5 einzustellen, derart, daß diese Werte auch über längere Zeit beim Gebrauch der Zellstoffartikel beibehalten werden. Die Quellstoffe werden, wie andere Quellstoffe auch, in Mengen von, beispielsweise 10 - 50 % dem Zellstoff der hygienischen Zellstoffartikel beigemischt. Selbstverständlich ist es auch möglich, die Saugkörper der Zellstoffartikel nur teilweise, beispielsweise nur zonenweise mit diesen Quellstoffen zu versetzen; in jedem Fall tritt die erwähnte Wirkung ein, in denjenigen Bereichen, in denen sich die Quellstoffe befinden.

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Die erwähnten Ppropfpolymerisate können beispielsweise durch Polymerisation in wässriger Lösung nach dem Verfahren der Gel-Polymerisation hergestellt werden. Dabei werden 15 - 50 %ige wässrige Lösungen der Comonomeren mit bekannten geeigneten Katalysator-Systemen ohne mechanische Durchmischung polymerisiert. Als Beispiel für die Herstellung eines solchen Ppropfpolymerisates wird die folgende Arbeitsanleitung gegeben:

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In einem isolierten Polyethyleneimer von 10 Liter Inhalt werden 5 189 g E-Wasser vorgelegt, 1 000 g Natriumbicarbonat darin dispergiert und langsam 1 888 g Acrylsäure so zudosiert, daß die Reaktionslösung nicht überschäumt. Die Temperatur der Lösung kühlt sich dabei auf 12 - 10 °C ab. Es werden anschließend 100 g des unten angegebenen Umsetzungsproduktes, welches als Ppropfgrundlage dient, zugesetzt. Des weiteren werden 12 g Trimethylolpropantriacyrat und 10 g eines Natriumdilsooctylsulfosuc-

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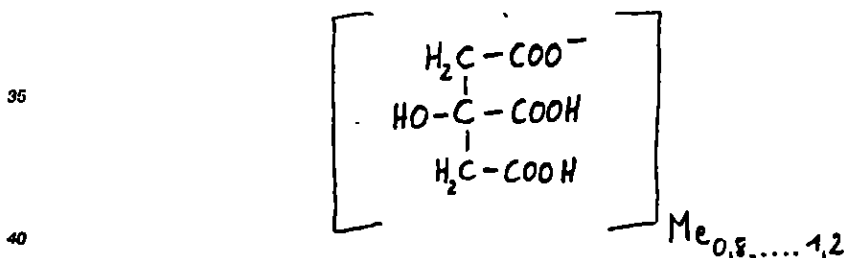
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cinates (Revopol V 21 33 der Firma Revo, Steinau) zugegeben. Bei einer Temperatur von 10-12 °C wird als Initiatoren ein Redox-System, bestehend aus 2,2 g 2,2'-Azobisamidinopropan-Dihydrochlorid, gelöst in 20 g Wasser, 4,4 g Kaliumperoxodisulfat, gelöst in 170 g Wasser und 8 g Natriumpyrosulfit, gelöst in 120 g Wasser, nacheinander zugegeben und verrührt. Die Reaktionslösung wird daraufhin ohne Rühren stehen gelassen, wobei durch Einsetzen der Polymerisation die Temperatur bis auf 85 °C ansteigt. Es entsteht als Reaktionsprodukt ein festes Gel. Dieses wird anschließend mechanisch zerkleinert und bei Temperaturen über 80 °C getrocknet und gemahlen.

Als Pfropfgrundlage dient ein Produkt, welches wie folgt hergestellt wird:
In 345 g eines Blockcopolymeren aus 1,6 mol Propylenoxyd und 0,2 mol Ethylenoxyd mit einer OH-Zahl von 65 werden unter Rühren bei Raumtemperatur 39,2 g Maleinsäureanhydrid eingetragen und diese Mischung unter Rühren auf 80 °C erhitzt. Das Maleinsäureanhydrid löst sich dabei unter schwach exothermer Reaktion auf, es entsteht eine klare, schwach gelblich gefärbte Lösung.

Pfropfpolymersate dieser Art haben den zusätzlichen Vorteil, daß sie unter den genannten Bedingungen Gele mit erhöhter Gelfestigkeit bilden, was auf den höheren Vernetzungsgrad dieser Stoffe gegenüber den meisten bekannten Quellstoffen zurückzuführen ist. Speziell auch diese höhere Gelfestigkeit ist in hygienischen Zellstoffartikeln vorteilhaft, da die Quellstoffe bei Wasseraufnahme festere Gallerten bilden und weitaus weniger zur Klebrigkeit neigen als vorbekannte Quellstoffe.

Wie gesagt, ist es auf die geschilderte Weise möglich, die gewünschten pH-Werte im Saugstoff von hygienischen Zellstoffartikeln leicht und sicher einzustellen und auch über die Gebrauchszeit der Zellstoffartikel zu halten. Dennoch kann es zur Erhöhung der Sicherheit erwünscht sein, den Zellstoffartikeln noch weitere Hilfsstoffe zuzufügen, welche den eingestellten und erwünschten pH-Wert weiter stabilisieren. Als Hilfsstoffe dieser Art können organische oder anorganische Monomere mit wenigstens 2 Säuregruppen eingesetzt werden, die mit Alkalimetallen oder Ammoniak derart teilneutralisiert sind, daß sich bei Benetzung des Saugkörpers mit Wasser oder physiologischer Flüssigkeit ein pH-Wert zu je 5,0 und 6,0, vorzugsweise von 5,2 - 5,5, einstellt. Als anorganisches Monomer kommt insbesondere Phosphorsäure in Betracht, ein Stoff, der einerseits ein gutes Puffervermögen aufweist und andererseits ungiftig ist. Aus der Gruppe der organischen Monomere ist vorzugsweise die Zitronensäure zu nennen; es kommen aber auch zweiwertige Säuren aus der Reihe Malonsäure, Bernsteinsäure, Glutarsäure, Adipinsäure in Betracht oder auch Weinsäure, Fumarsäure, Maleinsäure und vergleichbare Stoffe. Als besonders vorteilhaft hat sich partiell neutralisierte Zitronensäure der Formel



erwiesen, wobei Me ein Natrium-, Kalium- oder Ammonium-Ion bedeutet. Die erwähnten Puffer-Hilfsstoffe können dem Saugstoff in Mengen von 1 - 5 Gewichtsprozent zugesetzt werden.

Die Erfindung wird im folgenden anhand der beigelegten Zeichnung näher erläutert. Es stellen dar:

Fig. 1 eine Draufsicht auf eine Ausführungsform einer Windel;

Fig. 2 einen Querschnitt entlang der Linie II-II der Fig. 1.

Die in der Zeichnung dargestellte Windel ist als Ganzes mit 1 bezeichnet. Die Windel besteht im wesentlichen aus einem Saugkörper 2, bei welchem es sich um eine etwa 0,5 - 10 mm dicke Schicht von Zellstoff-Flocken handelt. Dieser Saugkörper ist auf einer Unterlage 3 angeordnet, welche aus einer Polyäthylenfolie besteht. Auf der beim Gebrauch oberliegenden Seite ist der Saugkörper mit einer Vliesstoff-Schicht 4 abgedeckt, welche die Aufgabe hat, den Saugkörper zusammenzuhalten und dessen Flusen zu verhindern, welche aber der anfallenden und vom Saugkörper aufzunehmenden Flüssigkeit keinen nennenswerten Widerstand entgegensetzt. Der Saugkörper 2 ist von dieser Vliesstoff-Schicht vollständig bedeckt; die Unterlage 3 und die Vliesstoff-Schicht 4 sind im Randbereich 5 der Windel miteinander verbunden, so daß der Saugkörper allseits vollständig von diesen Stoffen eingehüllt ist.

Die Windel 1 hat im dargestellten Ausführungsbeispiel die Form einer Sanduhr, wodurch im Mittelbereich der Windel Ausschnitte 6 entstehen, durch die die Beine des Trägers hindurchreichen können. Die

Windel wird bei Gebrauch dem Träger dadurch angelegt, daß sie zwischen dessen Beinen hindurchgeführt wird und daß die breiteren Abschnitte 7 und 8 über den Bauch- bzw. Rückenbereich des Trägers gelegt werden. In diesem Zustand können die Verschlussbänder 9 am jeweils gegenüberliegenden Teil festgeklebt und die Windel auf diese Weise zu einem hosenartigen Gebilde verschlossen werden. Um einen dichten Beinabschluß zu erreichen, sind am Rande des Mittelbereiches elastische Streifen 10, beispielsweise Gummibänder, angeordnet. Diese Streifen ziehen sich soweit als möglich zusammen und legen die Beinausschnitte eng an die Haut des Trägers an.

Wesentlich im vorliegenden Zusammenhang ist naturgemäß der Saugkörper 2. Dieser Saugkörper besteht in bekannter Weise aus Zellstoff-Flocken, dem die erwähnten teilneutralisierten Quellstoffe sowie auch die ebenfalls erwähnten Hilfsstoffe beigemischt sind. Die Mischung kann dabei quasi-homogen sein; es ist aber auch möglich, nur einzelne Zonen, beispielsweise die besonders beanspruchte Mittelzone, mit diesen Stoffen auszurüsten.

Bezugszeichenliste

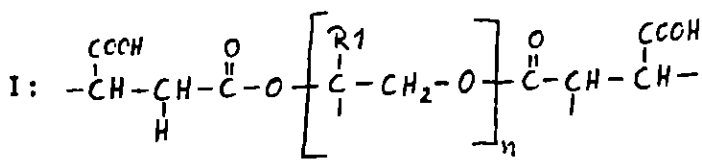
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|----|------|-----------------------|
| 15 | 1 | = Windel |
| | 2 | = Saugkörper |
| | 3 | = Unterlage |
| | 4 | = Vliesstoffschicht |
| 20 | 5 | = Randbereich |
| | 6 | = Ausschnitte |
| | 7; 8 | = breite Abschnitte |
| | 9 | = Verschlussband |
| | 10 | = elastische Streifen |

Patentansprüche

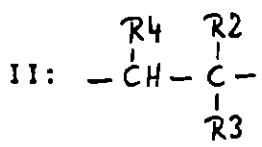
1. Hygienische Zellstoffartikel, wie Windel, Krankenunterlage, Damenbinde, Slipelinlage oder dergl., mit einem oder mehreren Saugkissen aus Zellstoff, mit Zusätzen an Quellstoffen und gegebenenfalls Hilfsmaterialien
sowie einer oberen flüssigkeitsdurchlässigen Abdeckung und einer unteren flüssigkeitsdichten Schicht oder Einlage,
wobei die Quellstoffe polymere organische Säuren sind,
dadurch gekennzeichnet,
daß diese Quellstoffe mit Alkalimetallen und/oder Ammoniak derart teilneutralisiert sind, daß sich im Zellstoff-Saugkörper bei Benetzung mit Wasser oder einer physiologischen Flüssigkeit ein pH-Wert zwischen 5,0 und 8,0, vorzugsweise zwischen 5,2 und 5,5, einstellt.
2. Hygienischer Zellstoffartikel nach Anspruch 1,
dadurch gekennzeichnet,
daß die Quellstoffe Pffropfpolymere sind, mit
0,5 - 20 Gewichts-Prozent chemisch gebundenen Resten der allgemeinen Formel I,
79 - 99 Gewichts-Prozent chemisch gebundenen Resten der allgemeinen Formel II und
0,1 - 2 Gewichts-Prozent chemisch gebundenen Resten eines Vernetzers, der aus Monomeren mit wenigstens zwei olefinisch ungesättigten Doppelbindungen hervorgegangen ist;
wobei bedeuten:

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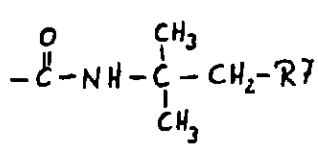


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- n = 2 bis 300
 R1 = Wasserstoff oder Methyl
 R2 = Wasserstoff, Methyl oder Ethyl
 R3 = Carboxyl, Sulfonyl, Phosphonyl, gegebenenfalls verestert mit Alkanol mit 1 - 4 C-Atomen oder eine Gruppe der Formel

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- worin R7 eine Sulfonyl- oder Phosphonyl-Gruppe bedeuten,
 R4 = Wasserstoff, Methyl, Ethyl oder Carboxyl.

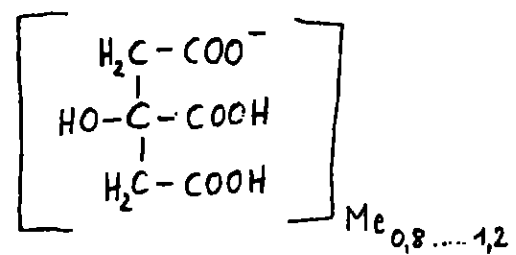
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3. Hygienischer Zellstoffartikel nach Anspruch 1 oder 2
 dadurch gekennzeichnet,
 daß als Hilfsstoffe im Saugkörper organische oder anorganische Monomere mit wenigstens 2 Säuregruppen vorhanden sind, die mit Alkalimetallen oder Ammoniak derart teilneutralisiert sind, daß sich bei Benetzung des Saugkörpers mit Wasser oder physiologischer Flüssigkeit ein pH-Wert zwischen 5,0 und 6,0, vorzugsweise von 5,2 - 5,5, einstellt.

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4. Hygienischer Zellstoffartikel nach Anspruch 3
 dadurch gekennzeichnet,
 daß als Hilfsstoff im Saugkörper 1 - 5 Gewichtsprozent partiell neutralisierte Zitronensäure der Formel

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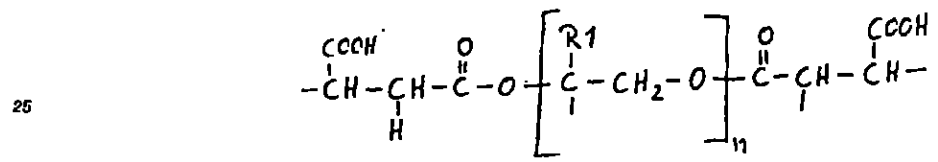
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vorhanden ist, wobei Me ein Natrium-, Kalium- oder Ammonium-Ion bedeutet.

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Claims

1. Sanitary cellulose article such as a diaper, sick-sheet, sanitary towel, protection pad or the like, comprising one or a plurality of absorbent cellulose paddings, additions of swelling agents and possibly auxiliary agents,
 5 as well as an upper liquid-permeable cover and a lower liquid-proof layer or insert, the swelling agents being polymeric organic acids, characterized in that these swelling agents are partially neutralized by means of alkali metals and/or ammonia such that a pH ranging between 5,0 and 6,0, preferably between 5,2 and 5,5, ensues in the absorbent cellulose body when the latter is wetted with water or a physiological liquid.
2. Sanitary cellulose article according to claim 1, characterized in that
 15 the swelling agents are graft polymers having
 0.5 - 20 percent by weight of chemically combined residues of the general formula I,
 79 - 99 percent by weight of chemically combined residues of the general formula II, and
 0.1 - 2 percent by weight of chemically combined residues of a cross-linking agent originating from monomers having at least two olefinically unsaturated double bonds;
 20 I representing:



II representing:
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- n = 2 to 300
 R1 = hydrogen or methyl
 40 R2 = hydrogen, methyl or ethyl
 R3 = carboxyl, sulphonyl, phosphonyl, possibly esterified with alkanol having 1 - 4 C atoms or a group of the formula

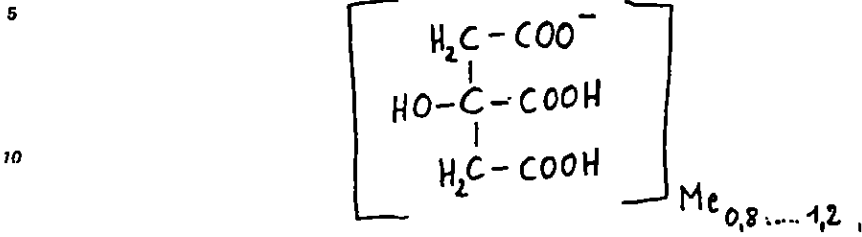


- 50 R7 representing a sulphonyl or phosphonyl group,
 R4 = hydrogen, methyl, ethyl or carboxyl.

3. Hygienic cellulose article according to claim 1 or 2, characterized in that
 55 organic or inorganic monomers having at least 2 acid groups exist as auxiliary agents in the absorbent body, which are partially neutralized by alkali metals or ammonia such that a pH ranging between 5.0 and 6.0, preferably between 5.2 and 5.5, ensues when the absorbent body is wetted with water or a physiological liquid.

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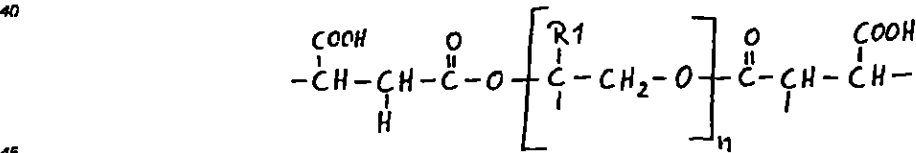
4. Sanitary cellulose article according to claim 3,
characterized in that
1 - 5 percent by weight of partially neutralized citric acid of the formula



15 exists as an auxiliary agent in the absorbent body, Me representing a sodium, potassium or ammonium ion.

Revendications

- 20 1. Article hygiénique en cellulose, comme une linge, alèze, serviette hygiénique, un protège-slips ou analogue, avec un ou plusieurs coussins absorbants en cellulose, avec des additifs en agents gonflants et, s'il y a lieu, des auxiliaires ainsi qu'un recouvrement supérieur perméable aux liquides et une couche inférieure imperméable aux liquides ou un insert inférieur imperméable aux liquides,
- 25 les agents gonflants étant des acides polymères organiques, caractérisés en ce que ces agents gonflants sont partiellement neutralisés à l'aide de métaux alcalins et/ou de l'ammoniac de telle sorte qu'un pH entre 5,0 et 6,0, de préférence entre 5,2 et 5,5, se manifeste dans le corps absorbant en cellulose lors d'un mouillage par de l'eau ou un liquide physiologique.
- 30 2. Article hygiénique en cellulose selon la revendication 1, caractérisé en ce que les agents gonflants sont des polymères greffés avec
- 0,5 - 20 % en poids de restes combinés chimiquement de la formule générale I,
- 35 79 - 99 % en poids de restes combinés chimiquement de la formule générale II, et
- 0,1 - 2 % en poids de restes combinés chimiquement d'un réticulant provenant de monomères avec au moins deux liaisons doubles insaturées à l'oléfine;
- I représentant:



II représentant:

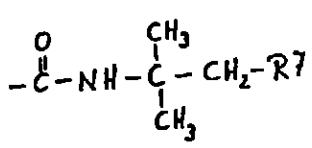


- 55 n = 2 à 300
R1 = hydrogène ou méthyle
R2 = hydrogène, méthyle ou éthyle
R3 = carboxyle, sulfonyle, phosphonyle, s'il y a lieu estérifiés d'alkanol à 1-4 atomes C, ou un

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groupe de la formule

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R7 représentant un groupe de sulfonyle ou phosphonyle,
R4 = hydrogène, méthyle, éthyle ou carboxyle.

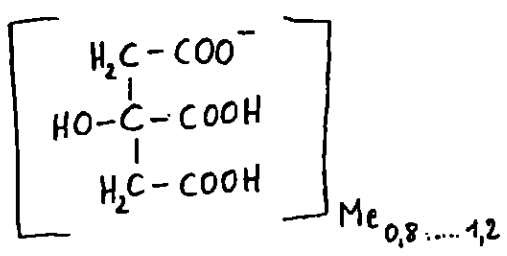
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3. Article hygiénique en cellulose selon la revendication 1 ou 2, caractérisé en ce que des monomères organiques ou inorganiques avec au moins 2 groupes d'acides se trouvent dans le corps absorbant comme auxiliaires, qui sont partiellement neutralisés à l'aide de métaux alcalins ou de l'ammoniac de telle sorte qu'un pH entre 5,0 et 6,0, de préférence de 5,2 à 5,5, se manifeste lors d'un mouillage du corps absorbant par de l'eau ou un liquide physiologique.

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4. Article hygiénique en cellulose selon la revendication 3, caractérisé en ce que 1 à 5 % en poids d'acide citrique partiellement neutralisé de la formule

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se trouve comme auxiliaire dans le corps absorbant, Me représentant un ion de sodium, de potassium ou d'ammonium.

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Fig.1

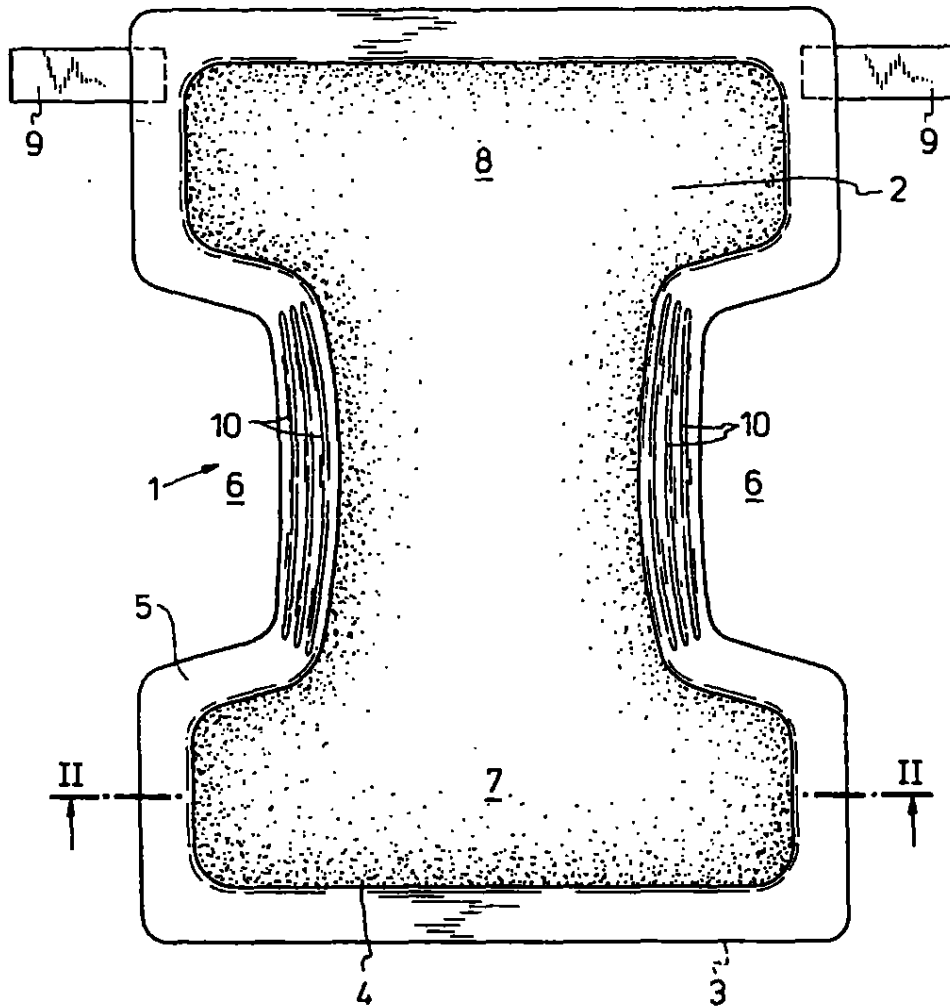
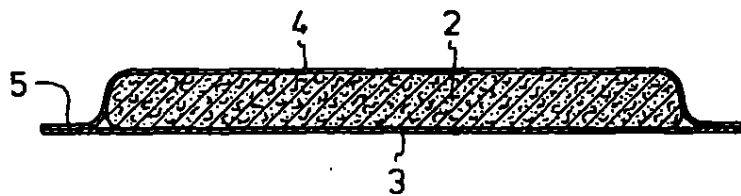


Fig.2



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⑯ BUNDESREPUBLIK
DEUTSCHLAND



DEUTSCHES
PATENTAMT

⑫ Off nl gungsschrift
⑪ DE 3030920 A1

⑤ Int. Cl. 3:
A61 F 13/18
A 41 B 13/02

⑳ Aktenzeichen: P 30 30 920.7
㉑ Anmeldetag: 16. 8. 80
㉒ Offenlegungstag: 22. 4. 82

Behördeneigentlich

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㉕ Sanitäre Hygienemittel, die der Aufnahme Harn und Blut enthaltender Sekrete dienen, mit geruchsverhindernden Eigenschaften

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16.08.80

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Patentanmeldung D 6090

- 11 -

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ZR-FE/Patente

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**"Sanitäre Hygienemittel, die der Aufnahme Harn und Blut
enthaltender Sekrete dienen, mit geruchsverhindernden
Eigenschaften"**

Patentansprüche:

- 5 1. Sanitäre Hygienemittel zur Aufnahme Harn und Blut
enthaltender Sekrete, die in der Absorptionsschicht
als geruchsverhindernde Substanz Ester der Citronen-
säure und/oder Acetylcitronensäure, insbesondere
deren Triester, mit aliphatischen oder alicyclischen
10 Alkoholen mit 1 bis 6 Kohlenstoffatomen im Molekül
enthalten.
2. Sanitäre Hygienemittel nach Anspruch 1, dadurch
gekennzeichnet, daß sie in der Absorptionsschicht
Citronensäuretriethylester enthalten.
- 15 3. Verfahren zur Herstellung der sanitären Hygienemittel
nach Anspruch 1 und 2, dadurch gekennzeichnet, daß
man das Absorptionsmaterial oder die fertige Vorlage
in eine evakuierte Kammer bringt und nach Erzeugung
eines Vakuums die Citronensäure- bzw. Acetylcitronen-
20 säureester bei erhöhter Temperatur bis zum Sättigungs-
druck verdampft.
4. Verfahren zur Herstellung der sanitären Hygienemittel
nach Anspruch 1 und 2, dadurch gekennzeichnet, daß
man das Absorptionsmaterial durch eine Kammer führt,
25 in der die Citronensäure- bzw. Acetylcitronensäureester
gegebenenfalls im Gemisch mit Parfümöl fein zerstäubt
werden.

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Patentanmeldung D 6090

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5. Sanitäres Hygienemittel nach Anspruch 1 und 2 in
Gestalt einer Hygienevorlage, bei der die mit dem
Citronensäure- bzw. Acetylcitronensäureester
imprägnierte, stark saugfähige Absorptionsschicht
5 (1) in der Mitte der Vorlage angeordnet und von
einer nicht imprägnierten Watteschicht oder Schicht
aus gemahlener Zellwolle (2) umgeben ist.

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Henkelstraße 67
4000 Düsseldorf, den 14.8.1980

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z-sü

P a t e n t a n m e l d u n g

D 6090

"Sanitäre Hygienemittel, die der Aufnahme Harn und Blut enthaltender Sekrete dienen, mit geruchsverhindernden Eigenschaften"

Gegenstand der Erfindung sind sanitäre Hygienemittel zur
5 Aufnahme Harn und Blut enthaltender Sekrete, die in der
Absorptionsschicht als geruchsverhindernde Substanz Ester
der Citronensäure und/oder Acetylcitronensäure, insbe-
sondere deren Triester, mit aliphatischen oder alicycli-
schen Alkoholen mit 1 bis 6 Kohlenstoffatomen im Mole-
10kül enthalten.

Als den erfindungsgemäßen sanitären Hygienemitteln mit
geruchsverhindernden Eigenschaften zugrundeliegende
Vorlagen können alle bisher für diese Zwecke einge-
setzten Produkte dienen wie Windeln, Slipenlagen, Damen-
15binden, Tampons. Das diesen sanitären Hygienemitteln
zugrundeliegende absorbierende Material kann aus jedem
Fasermaterial bestehen, das üblicherweise zur Herstellung
derartiger Mittel verwendet wird, wie gesponnener Wolle,
Baumwolle, Cellulose-Chemiefasern, synthetischen Textil-
20fasern, Vliesstoffen, aber auch aus quellfähigen Poly-
meren wie modifizierter Stärke, modifizierter Cellulose
oder saugfähigen Kunststoffpartikeln, die gegebenenfalls
zur besseren Handhabung auf Papier oder andere Lamine
aufgeklebt oder in Netzen, Vliesstoff- bzw. Textilbahnen
25eingelagert sind.

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Patentanmeldung D 6090

- 2 -

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- Für eine wirksame Verhinderung der lokalen Zersetzung oder in der absorbierenden Schicht aufgenommenen Sekrete ist es wichtig, daß eine möglichst gleichmäßige Durchdringung der Absorptionsschicht mit den Estern der
- 5 Citronensäure und/oder Acetylcitronensäure erfolgt. Diese Forderung nach möglichst gleichmäßiger Durchdringung der Absorptionsschicht läßt sich mit den erfindungsgemäß einzusetzenden Produkten unschwierig erfüllen, da sie als Flüssigkeiten bei der Aufbringung in feinsten
- 10 Verteilung, z. B. als Nebeltröpfchen oder aus der Dampfphase keine Probleme aufwerfen. Ein weiterer Vorteil, der sich aus der flüssigen Beschaffenheit der erfindungsgemäß einzusetzenden Produkte ergibt, ist deren leichte Mischbarkeit mit gegebenenfalls zusätzlich aufzubringenden
- 15 Duftstoffen.

- Es ist bereits vorgeschlagen worden, sanitäre Hygienemittel mit Desinfektionsmitteln, medikamentösen Stoffen und Riechstoffen zu imprägnieren, um das Auftreten eines unangenehmen Geruchs soweit wie möglich zu verhindern.
- 20 Zu diesem Zweck hat man Phenole, Quecksilberchlorid, schweflige Säure, in getrennter Anordnung Natriumacetat und Natriumbisulfat sowie unterschiedliche Bakterizide und Fungizide wie Chloramin, Actamer, Hexachlorophen,

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- Bis-(tri-n-alkyl-zinn)sulfosalicylate, Phenylmercuri-
salze und ähnliche in die absorbierenden Schichten
eingebracht. Derartige Zusätze unterdrücken in gewissem
Maß die Entwicklung unangenehmer Gerüche, da sie die
5 für die Entstehung der Gerüche verantwortlichen Mikro-
organismen abtöten. Diese Unterdrückung unangenehmer
Gerüche durch Abtötung für die Zersetzung von Blut und
Harn verantwortlicher Mikroorganismen geht aber mit einer
mehr oder weniger starken Schädigung der körpereigenen
10 Haut- und Vaginalflora einher. Daneben treten bei dem
Einsatz mancher Mittel Hautreizungen, gelegentliche
Unverträglichkeiten, Lichtsensibilisierungen und
toxische Nebenwirkungen unterschiedlicher Stärke auf,
die einem verbreiteten Einsatz hindernd entgegenstehen.
15 Man ist daher weiterhin bestrebt, Mittel aufzufinden,
die die Entstehung unangenehmer Gerüche unterbinden,
ohne daß sie die schädlichen Nebenwirkungen aufweisen.

- Es wurde nun gefunden, daß sanitäre Hygienemittel zur
Aufnahme Harn und Blut enthaltender Sekrete, die in der
20 Absorptionsschicht als geruchsverhindernde Substanz
Ester der Citronensäure und/oder Acetylcitronensäure,
insbesondere deren Triester, mit aliphatischen oder
alicyclischen Alkoholen mit 1 bis 6 Kohlenstoffatomen
im Molekül enthalten, den gestellten Anforderungen
25 weitestgehend gerecht werden.

- Die erfindungsgemäß einzusetzenden Ester der Citronen-
säure lassen sich in bekannter Weise durch azeotrope
Veresterung von Citronensäure mit dem jeweiligen Alkohol
herstellen, wie dies z.B. für den Citronensäure-
30 triethylester in der amerikanischen Patentschrift
20 76 111 (referiert im Chemischen Zentralblatt 1937,
II, Seite 665) beschrieben ist. Die Herstellung der
erfindungsgemäß einzusetzenden Acetylcitronensäure-
ester kann durch Umsetzung der entsprechenden Citronen-
35 säureester mit Acetylchlorid, wie dies für den Acetyl-

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citronensäuretriethylester von Wislicenus in Liebigs
Annalen der Chemie Bd. 129, Seite 192, bzw. durch Um-
setzung der entsprechenden Citronensäureester mit
Essigsäureanhydrid, wie dies gleichfalls für den
5 Acetylcitronensäuretriethylester in der amerikanischen
Patentschrift 2 445 911 (referiert in Chemical Abstracts
1948, Spalte 8818) beschrieben ist, erfolgen.

Als zu veresternde Alkohole kommen z. B. Methanol, Ethanol,
Propanol, Isopropanol, Butanol-1, Butanol-2, 2-Methyl-
10 propanol-1, 2-Methyl-propanol-2, 2-Methyl-butanol-1,
2-Methyl-butanol-4, n-Hexylalkohol, Ethylenglykol,
Propylenglykol, Trimethylenglykol, Hexamethylenglykol,
Glycerin, Erythrit, Sorbit und Cyclohexanol in Frage.

Unter den erfindungsgemäß einzusetzenden Estern der
15 Citronensäure als auch der Acetylcitronensäure kommt den
jeweiligen Triestern die größte Bedeutung zu und unter
diesen zeichnet sich wiederum der Citronensäuretriethyl-
ester durch die stärkste geruchsverhindernde Wirkung
als auch durch die beste anwendungstechnische Eignung
20 aus.

Der Citronensäuretriethylester ist als Lebensmittel-
zusatz zugelassen und somit als unschädlich einzustufen,
selbst bei Überdosierungen können keine Hautreizungen oder
andere Unverträglichkeitserscheinungen auftreten. Da der
25 Citronensäuretriethylester nicht antibakteriell wirksam
ist, kann durch seinen Einsatz auch keine aus medizinischer
Sicht unerwünschte Störung der körpereigenen Haut- bzw.
Vaginalflora eintreten.

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- Wie bereits vorstehend ausgeführt, ist eine möglichst gleichmäßige Durchdringung der absorbierenden Schicht mit den erfindungsgemäß einzusetzenden Mitteln die Voraussetzung dafür, daß keine lokalen Zersetzungs-
5 erscheinungen und damit unerwünschte Geruchsbildung eintreten können. Um eine völlig homogene Imprägnierung zu erreichen, eignet sich am besten ein Verfahren, bei dem das Absorptionsmaterial oder die fertige Vorlage in eine evakuierte Kammer gebracht und nach Erzeugung
10 eines Vakuums der Citronensäure- bzw. Acetylcitronensäureester bei erhöhter Temperatur bis zu seinem Sättigungsdruck verdampft wird. Das Material wird dabei gleichmäßig von dem Citronensäure- bzw. Acetylcitronensäureester durchdrungen und die Konzentrationen in den textilen
15 oder papierartigen Materialien treten mit der Dampfphase ins Gleichgewicht. Die aufzubringende Menge an Citronensäure- bzw. Acetylcitronensäureester ist bei diesem Verfahren durch Verdampfungstemperatur und Vakuum exakt regulierbar. Für die Imprägnierung nach diesem Verfahren
20 hat sich der Citronensäuretriethylester insgesamt als am besten geeignet erwiesen. In einem auf diese Weise völlig homogen imprägnierten sanitären Hygienemittel sind lokale Zersetzungen von Blut oder Harn enthaltenden Sekreten weitestgehend ausgeschlossen.
- 25 Da der Citronensäuretriethylester selbst chemisch relativ inert und geruchsneutral ist, läßt er sich ohne Beeinflussung der Geruchsqualität gut mit Parfümölen mischen. Dies ist von besonderem Vorteil, wenn eine gleichzeitige Parfümierung des sanitären Hygienemittels erwünscht ist.

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Dabei sind der Citronensäuretriethylester und das Parfümöl ohne Schwierigkeit als Mischung applizierbar. Zu diesem Zweck wird das Absorptionsmaterial durch eine Kammer geführt, in der die Mischung aus Citronensäuretriethylester und Parfümöl fein zerstäubt wird, so daß infolge der geringen Tröpfchengröße die Absorptionsmaterialien gleichmäßig benetzt werden. Eine besonders feine Verteilung des Gemisches aus Citronensäuretriethylester und Parfümöl läßt sich durch Anlegen eines elektrischen Feldes an die Zerstäubungskammer erreichen.

Eine besonders vorteilhafte Ausführungsform einer Hygienevorlage (Slip, Binde) ergibt sich, wenn die mit dem Citronensäuretriethylester und gegebenenfalls Parfümöl imprägnierte, stark saugfähige Absorptionsschicht in der Mitte der Vorlage angeordnet (Abbildung Schicht 1), und von einer nicht imprägnierten Watteschicht oder Schicht aus gemahlener Zellwolle (Fluff) umgeben ist (Abb. Schicht 2). Daran anschließend nach außen hin befindet sich ein Hüllvlies (3), eine Wäscheschutzfolie aus Kunststoff oder wasserundurchlässigem Papier (4), ein Klebestreifen (5) und Siliconpapier (6). Die in der stark saugfähigen Absorptionsschicht befindlichen Polymeren mit hohem Saugvermögen, wie z.B. Stärkepfropfpolymerisate werden von dem Citronensäuretriethylester gut benetzt ohne zu quellen. Diese Benetzung des Polymeren durch den Citronensäuretriethylester verhindert jedoch in keiner Weise das Quellvermögen der Saugsubstanz. Der geschilderte Aufbau hat zwei Vorteile, zum einen wird durch die Lage der mit Citronensäuretriethylester benetzten hochsaugfähigen Absorptionsschicht eine Diffusion des Citronensäuretriethylesters zur Wäscheschutzfolie und zum Klebestreifen verhindert, zum anderen befindet sich der geruchsverhindernde Citronensäuretriethylester genau in dem Bereich, wo die Sekrete aufgenommen werden, da bei der geschilderten Ausführungsform die Sekretaufnahme

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fast ausschließlich in der imprägnierten hochsaugfähigen Schicht erfolgt, welche die Flüssigkeit anzieht und festhält. Die Unterbindung der Diffusion ist wünschenswert, da ansonsten eine Wellung der Folie und eine

5 Klebkraftverminderung eintreten kann. Für die Konfektionierung wird die geschilderte Vorlage eingerollt oder eingeschlagen und anschließend einzeln cellophanisiert oder mit einer opaken Folie umhüllt.

10 Nachweis der Hemmwirkung von Citronensäuretriethyl-
ester auf die Harnzersetzung

a) Geruchstest:

4 g gemahlene Zellwolle (Fluff) wurden jeweils mit 0,5 g beziehungsweise 1,5 g Citronensäuretriethyl-
ester besprüht und gut durchmischt. Auf den so präparierten

15 Fluff, sowie auf eine gleiche Menge unbehandelten Fluffs wurden 25 ml frischer Urin gegeben. Es wurde 14 Stunden bei 37°C inkubiert, wobei das Gefäß durch einen luftdurchlässigen Wattestopfen verschlossen

20 war. Anschließend wurden die Proben jeweils 5 verschiedenen Personen zum Geruchstest vorgelegt, wobei die Bezeichnung der Proben keinen Schluß auf eventuelle Zusätze erlaubte. Die Probe ohne Zusatz von Citronensäuretriethyl-
ester wurde in fünf unabhängigen Versuchsreihen jeweils von allen 5 Testpersonen spontan

25 als die weitaus am unangenehmsten riechende identifiziert. Am stärksten wurde der Unterschied zwischen der Probe mit unpräpariertem Fluff und der Probe mit Fluff + 1,5 g Citronensäuretriethyl-
ester empfunden. Die Konzentration von Citronensäuretriethyl-
ester betrug

30 bei dieser Probe auf Urin bezogen 1,5 %. Bei Annahme einer maximalen Menge von 3 ml Urin pro Slipeinlage (etwa das Fassungsvermögen einer Slipeinlage) führt demnach bereits eine Menge von 45 mg Citronensäure-
triethyl-
ester pro Slipeinlage zu einem eindeutigen

35 Ergebnis.

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b) Hemmung der Alkalisierung

Bei der Zersetzung von Urin wird durch die Urease-
tätigkeit Ammoniak freigesetzt, der zu einer Ver-
schiebung des ursprünglich sauren pH-Wertes zur
5 basischen Seite führt. Zur Durchführung des Versuches
wurden wiederum 4 g gemahlene Zellwolle (Fluff) bzw.
4 g Watte jeweils mit 0,5 g bzw. 1,5 g Citronensäure-
triethylester besprüht und gut durchmischt. Auf das
so präparierte Absorptionsmittel, sowie auf eine
10 gleiche Menge unbehandeltes Absorptionsmittel wurden
25 ml frischer Urin gegeben. Diese Proben und eine
Probe Urin ohne Zusatz von Absorptionsmittel wurden
14 Stunden bei 37° C inkubiert, wobei das Gefäß durch
einen luftdurchlässigen Wattestopfen verschlossen war.
15 Anschließend wurden die pH-Werte der einzelnen Proben
gemessen und mit den vor der Inkubierung gemessenen
pH-Werten verglichen. Die bei den Versuchen erhaltenen
Werte sind nachstehender Tabelle zu entnehmen. In
der Tabelle bedeutet U = Urin, F = Fluff, W = Watte,
20 CAT = Citronensäuretriethylester, inkubiert über
14 Stunden = ink.

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Tabelle 1
Hemmung der Alkalisierung

p H - W e r t								
Versuch	U frisch	U ink	U+F ink	U+W ink	U+F+0,5 g CAT ink	U+W+0,5 g CAT ink	U+F+1,5g CAT ink	U+W+1,5gCAT ink
1	6,0	8,7	7,7	-	7,2	-	6,7	-
2	6,7	8,5	7,4	-	7,0	-	6,9	-
3	6,3	7,6	-	7,4	-	6,6	-	6,6

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Wie der vorstehenden Tabelle zu entnehmen ist, wurde in allen Fällen durch den Zusatz von Citronensäure-triethylester die Alkalisierung unterdrückt. Es wurden Differenzen von 0,5 - 1,0 pH-Einheiten beobachtet.

- 5 Im Versuch 2 wurde der pH-Wert des frischen Urins durch Zugabe gealterten Urins heraufgesetzt. Aus der Tabelle ist ferner ersichtlich, daß bereits der Zusatz von Fluff bzw. Watte zu einer Reduzierung der Ureaseaktivität führt.

- 10 Wie den vorstehenden Versuchen zu entnehmen ist, läßt sich durch den Einsatz von Citronensäuretriethylester in den mit Urin versetzten sanitären Hygienemitteln eine Zersetzung und damit die Ausbildung unangenehmer Gerüche weitgehend unterbinden.

- 15 Entsprechend dem Geruchstest a) durchgeführte Versuche, wobei anstelle von Urin eine 1:1 verdünnte wässrige Lösung von Schweineblut eingesetzt wurde, führten gleichfalls zu einer weitgehenden Unterdrückung unangenehmer Gerüche.

- 20 Aus der deutschen Auslegeschrift 24 18 338 war bereits die Verwendung von Estern der Citronensäure und/oder Acetylcitronensäure in wasserfreien kosmetischen Zubereitungen zur Unterdrückung von Körpergeruch bekannt. Es ließ sich aber aus der Tatsache, daß eine nicht antibakteriell wirksame Verbindung beim Aufbringen auf die Haut die Schweißzersetzung reduziert auf keinen Fall der Schluß ziehen, daß diese Verbindung als Zusatzstoff zu textilen und papierartigen Absorptionsmaterialien für Blut und Harn enthaltende Sekrete die Zersetzung dieser Sekrete und die Ausbildung unangenehmer Gerüche
- 30 weitgehend unterbindet.

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Int. Cl.³: A61F 13/18
Anmeldetag: 18. August 1980
Offenlegungstag: 22. April 1982

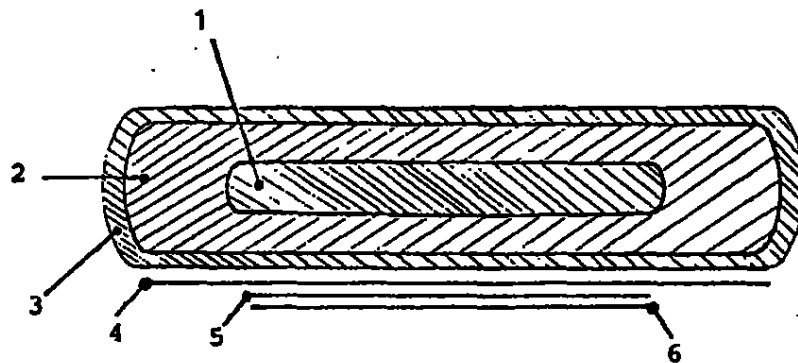
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Abbildung Hygienevorlage



- 1 stark saugfähige imprägnierte
Absorptionsschicht
- 2 Watte, Fluff
- 3 Hüllvlies
- 4 Wäscheschutzfolie aus Plastikfolie
oder wasserundurchlässigem Papier
- 5 Klebestreifen
- 6 Siliconpapier

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(12) **UK Patent Application** (19) **GB** (11) **2 326 348** (13) **A**

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A5R RPK RPV

(56) Documents Cited

GB 2175210 A

EP 0316518 A2

EP 0311344 A2

US 4834438 A

(58) Field of Search

UK CL (Edition P) A5R RPD RPK RPV

INT CL⁸ A61F 13/15 , A61L 15/18 15/22 15/46

ONLINE:WPI

(54) Abstract Title

Absorbent article comprising a pH controlling superabsorbent

(57) The present invention relates to absorbent articles such as diapers, incontinence protectors, sanitary napkins, wound dressings and similar articles which are applied in contact with skin, and concerns methods which make it possible to use an article for an extended period of time without the appearance of unwanted side-effects such as, for instance, growth of undesirable micro-organisms. The absorbent body in the absorbent article comprises a pH-controlling substance in the form of a partially neutralised super-absorbent material in such a manner that the pH in the absorbent article after wetting is in the interval 3.5 - 4.9. Growth of undesirable strains of micro-organisms is prevented and unwanted side-effects resulting from use of the article are reduced.

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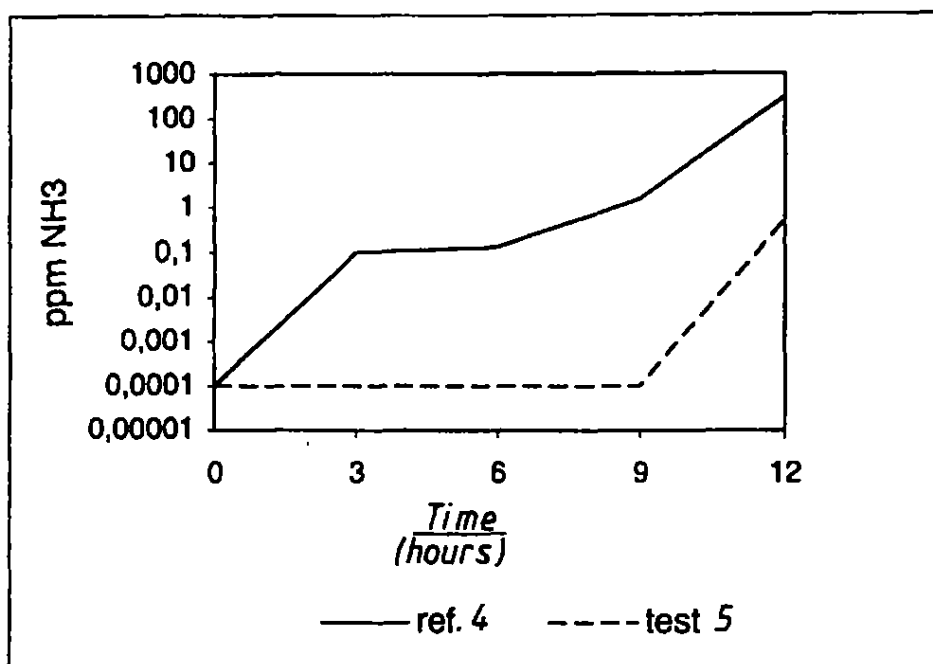


FIG. 1

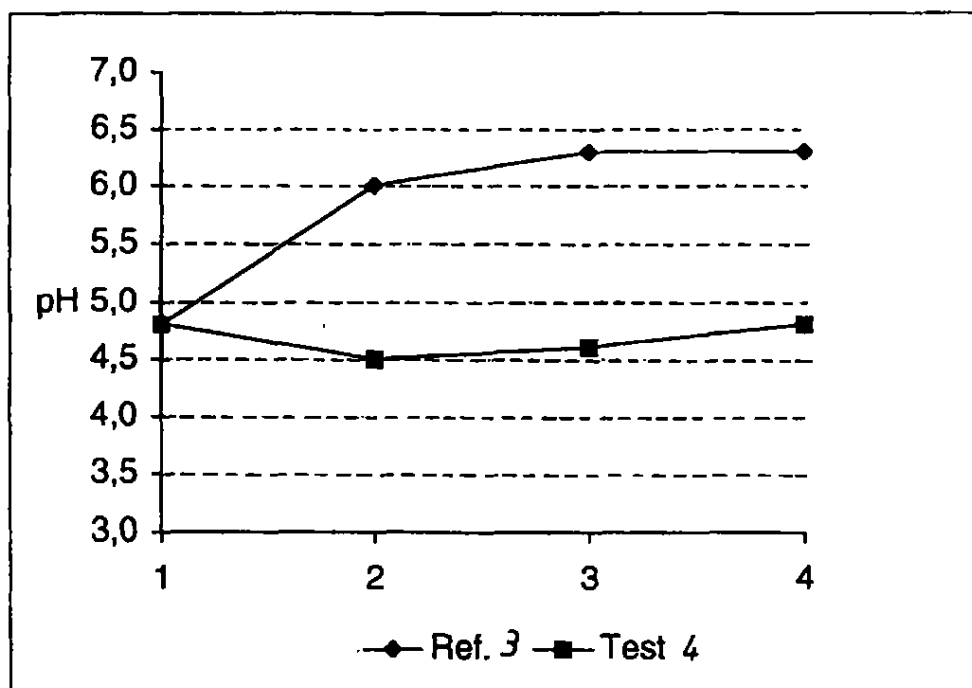


FIG. 2

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TITLE:

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REDUCTION OF UNWANTED SIDE-EFFECTS DURING USE OF ABSORBENT
ARTICLES BY MEANS OF pH-CONTROL

TECHNICAL FIELD:

10

The present invention relates to absorbent articles such as
diapers, incontinence protectors, sanitary napkins, wound
dressings and similar articles which are applied against
skin, and concerns methods aiming at the reduction of
15 unwanted side-effects which sometimes occur during use of
said articles.

BACKGROUND:

20

Absorbent articles of this kind are known in a number of
different types. Conventionally, the absorbent body in
these articles is produced by dry-defibration of cellulose
pulp from, for instance, rolls, bales, or sheets and
converting the pulp into a web of fluffed pulp sometimes
25 with the admixture of what is known as superabsorbents,
which are polymers with the ability to absorb several times
their own weight of water or body fluids.

30

All uses of products which are applied against skin may
lead to unwanted side-effects. These may occur as a result
of occlusion, moisture, mechanical, microbial, and
enzymatic factors which all, to different degrees, interact
and amplify the influence of each other and may cause
different forms of skin irritation and primary or secondary
35 skin infections which sometimes occur in users of said
articles. An increase in pH is a normal phenomenon during
use of absorbent articles in contact with skin. However,
several unwanted side-effects may occur as a result of, or
in connection with, a pH-increase. One example of an
40 unwanted side-effect of this kind is irritational contact

dermatitis which exhibits a connection with the surface-pH of skin. Factors Predisposing Cutaneous Irritation, Wilhelm K-P et al, Dermatologic Clinics 8, No. 1, 1990.

- 5 Another example of unwanted effects is the activity of enzymes such as lipases and proteases which exhibit a strongly pH-dependent activity which increases with increasing pH. The skin starts to decompose and becomes sensitive to mechanical forces and bacterial attacks.
- 10 Etiologic Factors in Diaper Dermatitis: The Role of Urine, Berg R.W. et al, Pediatric. Dermatology. 3, No. 2, 1986.

Another example of unwanted side-effects is that some bacteria such as Proteus can metabolise substances in urine and other body fluids and produce odorous substances such as ammonia and amines, which also raises the pH. At a high pH, the equilibrium for many odorous substances is shifted so that more volatile components are formed, resulting in a stronger odour than at a low pH.

- 20 An absorbent article such as a diaper, or the like provides an environment for micro-organisms which comprises access to moisture, nutrients, and heat. An unwanted side-effect of this is that growth of bacteria is promoted in such an environment. High numbers of bacteria constitute a risk of the appearance of infections. Moreover, a high presence of bacteria constitutes an increased risk for the creation of unpleasant odours caused by the formation of different substances, resulting from biological or chemical decomposition of components in body fluids such as, for instance, urine or menses.
- 30

- Micro-organisms which may be associated with the occurrence of problems when using products in contact with skin may be of different types. Examples of micro-organisms which cause odour and those which constitute a risk for urinary tract
- 35

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infections are *Proteus mirabilis*, *Proteus vulgaris*,
Escherichia coli, *Enterococcus* and *Klebsiella*.

5 Examples of micro-organisms which are associated with skin-
infections and other skin problems are *Candida albicans* and
Staphylococcus sp. and *Streptococcus* sp.

RELATED ART:

10 It is known that a low pH is advantageous in order to
reduce the occurrence of negative effects on skin.

15 Different ways of solving the described problems have been
suggested. In the American patent US 3,794,034 the
importance of the pH in an absorbent article is described
as well as the impregnation of an absorbent article with
buffering substances which aid in keeping the pH in the
20 article between 3.5 and 6.0, which is advantageous both for
inhibiting the growth of unwanted bacteria and, in
connection therewith, the creation of unwanted odours, and
for avoiding negative effects on skin.

25 In the European patent 0,311,344 pH-control in an absorbent
article is disclosed, wherein the buffering properties are
obtained by using a partially neutralised superabsorbent
material. In order to achieve sufficient inhibition of the
growth of unwanted bacteria in the article, a separate
bacteria inhibiting substance has also been added. The
European patent EP 0,316,518 discloses buffering of pH in
30 an absorbent article by using a polymeric organic acid.

35 One drawback in using bacteria suppressing agents, as
described in EP 0,311,344, is that these agents are often
selective and may be associated with risks, for instance in
the form of allergenic properties or negative ecological
consequences in garbage handling. Furthermore, the use of

this type of agents may involve a risk that resistant strains of micro-organisms arise.

5 In EP 0,316,518 an absorbent article is disclosed, comprising a pH-controlling substance in the form of a partially neutralised superabsorbent material. It is stated that pH in the absorbent article is in the interval 5 - 6. However, this is not a sufficiently low pH in order to obtain a sufficient inhibition effect on the micro-organisms which are present since the majority of micro-organisms require a pH below 5 in order to be affected to a significant degree.

15 One difficulty when evaluating the influence of different components on the pH in absorbent articles of the aforementioned kind is that the degree of acidity in cellulose fluff pulp varies depending on the production method. Chemical cellulose pulp (CP) varies between pH 6 - 8.5 and chemical thermomechanical cellulose pulp (CTMP) varies between 5.5 - 8.5. Variations outside said intervals also occur.

OBJECT OF THE INVENTION:

25 The object of the present invention is to achieve an absorbent article of the kind mentioned in the introduction which makes it possible to use the article during a longer period of time without the appearance of undesired side effects such as unpleasant odour, increased risk of infections or negative skin effects which are due to the growth of micro-organisms resulting from an unwanted raise in skin-pH, or from other reasons.

DESCRIPTION OF THE INVENTION:

5 An absorbent article of the kind mentioned in the introduction, wherein the problems connected with using the article for an extended period of time have been substantially removed, has been achieved through the invention with an absorbent body in the absorbent article comprising a pH-controlling substance in the form of a partially neutralised superabsorbent material and in that 10 pH in the absorbent article after wetting is in the interval 3.5 - 4.9, whereby growth of unwanted strains of micro-organisms is restricted and the occurrence of unwanted side effects resulting from the use of the article is reduced.

15 It has been shown that if the absorbent body in an absorbent article comprises a pH-controlling substance in the form of a partially neutralised superabsorbent material which after wetting creates a pH in the absorbent article 20 which is in the interval 3.5 - 4.9, and preferably 4.1 - 4.7, a significant inhibition effect on the growth of unwanted micro-organisms is obtained. The inhibition effect is based on the fact that many micro-organisms have an activity which is strongly pH-dependent and decreases with 25 decreasing pH, which means that a decrease in pH leads to a decrease in activity in most micro-organisms which, in turn, leads to a decrease of bad smell as well as negative effects on skin in the form of skin-irritation and primary or secondary skin-infections and a generally lower risk of 30 infections.

Enzymes, such as lipases and proteases have an activity which is strongly pH-dependent and decreases with decreasing pH, which means that a decrease in pH will also 35 lead to a decrease in enzymatic activity and an accompanying reduction in negative skin effects.

An absorbent body containing absorbent material and absorbed fluid is a heterogeneous system from a pH point of view. The system may contain superabsorbent material, fibres and liquid containing several kinds of ions. In order to obtain reproducible pH-values, measurements must be made in several places in the absorbent body and the mean value calculated.

An absorbent body in accordance with the invention may also comprise other absorbent materials besides a partially neutralised superabsorbent material, for instance fluffed cellulose pulp. It has proven advantageous to use a partially neutralised superabsorbent material as above in combination with fluffed cellulose pulp having a pH below 7, preferably below 6 which gives a further improved effect.

A suitable fluffed cellulose pulp may consist of a chemical thermo-mechanical cellulose pulp having a pH = 2.5 - 8.5, preferably 2.5 - 6.5 and most preferably 2.5 - 5.5, or of a chemical cellulose pulp having a pH = 2.5 - 8.5, preferably 2.5 - 8.0 and most preferably 2.5 - 7.0.

In order to obtain a suitable degree of acidity in the cellulose pulp, its pH may be controlled during the production process, for instance by adding an acidifying substance. This added substance may, for instance, consist of SO₂-water. In this way, it is also possible to neutralise NaOH which may occur in the pulp. Another way of achieving a suitable degree of acidity in the cellulose pulp is to add a suitable acid after production of the pulp.

A suitable, partially neutralised superabsorbent material may, for instance, consist of a cross-linked poly-acrylate of the kind which is described in the European patent EP 0

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391 108 in the name of Cassella AG. Other types of superabsorbent material than the above indicated, and having corresponding properties, may be used. A suitable proportion of superabsorbent material in the article is 5 - 100%, preferably 15-50%, and most preferably 15-50%. The proportion of superabsorbent material which has been stated to be preferred relates to areas of the article which will absorb the major part of the fluid and, consequently, does not concern end-portions or edge-portions or similar parts of the article since such parts thereof mostly do not significantly contribute to the absorptive function of the article.

Examples of the relation between the degree of neutralisation and pH in the superabsorbent material are given below.

	Degree of neutralisation %	pH
20	18	4.0
	25	4.3
	30	4.5
	35	4.7
	45	5.0
25	60	5.5

From the table it can be learned that the degree of neutralisation should normally be lower than 45% and preferably 35%. However, the degree of neutralisation should preferably be higher than approximately 20%.

An absorbent body in accordance with the invention, comprising a partially neutralised super-absorbent material in accordance with the invention may have somewhat lower absorption capacity when compared to a corresponding absorbent body containing a conventional super-absorbent

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material. Such a lowering of the absorption capacity may be compensated by increasing the amount of absorbent material to a corresponding degree.

5 An absorbent body in accordance with the invention, comprising a partially neutralised super-absorbent material may also comprise some type of conventional bacteria-inhibiting substance such as parabens or benzoic acid. Such bacteria inhibitors normally exhibit an increased effect at
10 a lower pH.

SHORT DESCRIPTION OF DRAWINGS:

15 The invention will in the following be described in more detail, with reference to a number of examples which are shown in the appended figures.

Fig. 1 shows in a diagram the formation of ammonia in a reference product compared with a product in accordance with the invention.
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Fig. 2 shows in a diagram the surface-pH of the skin during use of a test product containing a conventional absorption body, compared with the use of a corresponding test product in accordance with the invention.
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30 DESCRIPTION OF EXAMPLES:

The following examples are intended to give a closer illustration of the effect in absorbent articles having an absorbent body comprising a combination of a partially
35 neutralised super-absorbent material and cellulose pulp

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having a pH of 2.5 - 8.5 compared to conventional materials of a corresponding type.

TEST LIQUIDS:

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Test liquid 1

A solution of 0.9% sodium chloride.

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Test liquid 2

Synthetic urine according to the description in, among other, EP 0,565,606 which can be obtained from Jayco Pharmaceuticals Co., Pennsylvania. The composition is 2 g/l KCl; 2 g/l Na₂SO₄; 0.85 g/l (NH₄)H₂PO₄; 0.15 g/l (NH₄)₂HPO₄; 0.19 g/l CaCl₂ and 0.23 g/l MgCl₂. The pH in this composition is 6.0 - 6.4.

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Test liquid 3

Synthetic urine containing the following substances: KCl, NaCl, MgSO₄, KH₂PO₄, Na₂HPO₄, NH₂CONH₂. The pH in this composition is 6.0 - 6.5.

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Test liquid 4

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Sterile synthetic urine to which has been added a growth medium for micro-organisms. The synthetic urine contains mono- and divalent cat- and anions and urea and has been prepared in accordance with the information in Geigy, Scientific Tables, vol 2, 8th ed. 1981 p. 53. The growth medium for micro-organisms is based on information of Hook- and FSA-media for entero-bacteria. The pH in this mixture is 6.6.

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TEST METHODS:

Method 1, preparation of absorbent bodies for test.

5 Absorbent bodies were prepared using a slightly modified
sample former according to SCAN C 33:80. Fluffed pulp and
super-absorbent material of the desired type were weighed
and a homogeneous mixture of fluffed pulp and super-
absorbent material was subsequently introduced into a flow
10 of air having a negative pressure of approximately 85 mbar,
through a pipe having a diameter of 5 cm and being equipped
at the bottom with a metal net having a thin tissue placed
thereon. The mixture of fluffed pulp and super-absorbent
material was gathered onto the tissue on the metal net and
15 thereafter constituted the absorbent body. The absorbent
body was weighed and compressed to a bulk of 6-12 cm³/g. A
number of absorbent bodies referred to as Reference product
1, Reference product 2, test product 1, test product 2,
test product 3, test product 4, etc. having different
20 compositions as described below were made. The amount of
absorbent material in the single core and dual core
absorbent bodies, respectively, was adjusted so that the
single cores and dual cores had approximately the same
absorption capacity.

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Method 2, measurement of pH in cellulose pulp.

The pH in the cellulose pulp in the different test products
was measured by determining the pH in a water extract from
30 the pulp in accordance with SCAN P 14:65. 1.0 g air dry
cellulose pulp was placed in a 100 ml glass container and
20 ml distilled water was added. After mixing, a further 50
ml of distilled water was added and the mixture was stirred
for approximately 30 s and was left for 1 hour. The liquid
35 was poured off and pH was determined with a glass electrode

at 20-30°C. Two samples were prepared and the mean value was calculated.

Method 3, measurement of pH in an absorbent body.

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10 An absorbent body having a diameter of approximately 50 mm was prepared according to method 1. A predetermined amount of Test liquid 1, 2 or 3 was added, 10 ml to a single core absorbent body and 20 ml to a dual core absorbent body, whereafter the absorbent body was left to swell for 30 minutes. Thereafter, pH was measured in the absorbent body using a surface electrode, Flat-bottomed Metrohm pH-meter, Beckman Ø12 or Ø72. Parallel measurements were performed on at least two different absorbent bodies. The pH was determined at 10 locations on each absorbent body and the mean value was calculated.

Method 4, measurement of bacteria inhibition in absorbent bodies.

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Absorbent bodies were prepared in accordance with method 1. Single core, as well as dual core absorbent bodies were prepared. Test liquid 4 was prepared. Bacteria suspensions of each of *Escherichia coli* (E.c.), *Proteus mirabilis* (P.m.), *Enterococcus faecalis* (E.f.) were cultivated in nutritional bouillon 30°C overnight. The graft cultures were diluted and the bacterial count was determined. The cultures were mixed in different proportions so that the final mixed culture contained approximately 104 organisms per ml test liquid 4. Test liquid 4 was added to a sterile sputum container 70.5 x 52 mm, volume 100 ml, and the absorbent body was placed upside-down in the container and was left to absorb liquid for 5 minutes, whereafter the container was turned and incubated at 35 °C for 0; 6 and 12 hours, respectively whereafter the bacterial count in the absorbent body was determined. The nutritional medium used

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was TGE agar for measurement of the total amount of bacteria and Drigalski agar for specific determination of *Escherichia coli* and *Proteus mirabilis*, and Slanetz Bartley agar for specific determination of *Enterococcus faecalis*.

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Method 5. measurement of ammonia content.

Single core absorbent bodies were prepared in accordance with method 1. Test liquid and micro-organisms were added in accordance with method 5 whereafter the containers were incubated at 35°C for 0; 3; 6 and 12 hours, whereafter samples were taken from the containers using a hand pump and a so called Dräger-pipe. The ammonia content was obtained as a colour change on a scale graded in ppm or volume-percent.

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Method 6. measurement of the surface-pH of skin.

Test products were prepared by applying a backing of approximately 25 g/m² polyethylene and a topsheet of approximately 20 g/m² polypropylene nonwoven to absorbent bodies according to Ref. 3 and test 4, respectively. Test liquid 3 was added to the topsheet and was absorbed into the test product. The test products which were obtained in this manner were applied to the forearms of a test person and were left there for 24 hours. The procedure was repeated twice. The surface-pH of the skin at the place of contact was measured before application and after 24, 48 and 72 hours with Courage + Khazaka skin-pH-meter with a flat-bottomed Mettler-Toledo glass electrode 403/120.

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TEST PRODUCTS:

Reference product 1: Single core absorbent body having a total weight of 1 gram, prepared from a conventional super-absorbent

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material and a conventional chemical thermo-mechanical cellulose pulp with the ratio 15/85 weight-%.

- 5 Test product 1: Single core absorbent body having a total weight of 1 gram, prepared from a partially neutralised super-absorbent material with pH = 4.2, in accordance with the invention, and a chemical thermo-mechanical cellulose pulp with pH = 5.8 and with the ratio 15/85 weight-%.
- 10
- 15 Test product 2: Single core absorbent body having a total weight of 1 gram, prepared from a partially neutralised super-absorbent material with pH = 4.2, in accordance with the invention, and a chemical thermo-mechanical cellulose pulp with pH = 3.7 and with the ratio 15/85 weight-%.
- 20
- 25 Reference product 2: Dual core absorbent body. The upper core (uc) had a total weight of 1.2 grams and was prepared from a conventional super-absorbent material and a conventional chemical thermo-mechanical cellulose pulp with the ratio 12/88 weight-%. The lower core (lc) had a total weight of 1.1 grams and was prepared from a conventional super-absorbent material and a conventional chemical cellulose pulp with the ratio 12/88 weight-%.
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- 5 **Test product 3:** Dual core absorbent body. The upper core (uc) had a total weight of 1.3 grams and was prepared from a partially neutralised super-absorbent material having a pH = 4.5, in accordance with the invention, and a chemical thermo-mechanical cellulose pulp having a pH = 5.8 and with the ratio 15/85 weight-%. The lower core (lc) had a total weight of 1.2 grams and was prepared from a partially neutralised super-absorbent material having a pH = 4.5, in accordance with the invention, and a chemical cellulose pulp having a pH = 6.3 and with the ratio 15/85 weight-%.
- 10
- 15
- 20 **Reference product 3:** Single core absorbent body having a total weight of 1 gram, prepared from a conventional super-absorbent material and a conventional chemical cellulose pulp, with the ratio 15/85 weight-%.
- 25 **Test product 4:** Single core absorbent body having a total weight of 1 gram, prepared from a partially neutralised super-absorbent material with pH = 4.2, in accordance with the invention, and a conventional chemical cellulose, with the ratio 15/85 weight-%.
- 30
- 35 **Reference product 4:** Single core absorbent body having a total weight of 1 gram, prepared from a conventional super-absorbent material and a chemical thermo-

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mechanical cellulose pulp with pH = 6.7, with the ratio 15/85 weight-%.

5 Test product 5: Single core absorbent body having a total weight of 1 gram, prepared from a partially neutralised super-absorbent material with pH = 4.2, in accordance with the invention, and a chemical thermo-mechanical cellulose pulp with pH = 6.7 and with the ratio 15/85 weight-%.

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15 Test product 6: Dual core absorbent body. The upper core (uc) had a total weight of 1.3 grams and was prepared from a partially neutralised super-absorbent material having a pH = 4.6, in accordance with the invention, and a chemical thermo-mechanical cellulose pulp having a pH = 5.8 and with the ratio 15/85 weight-%. The lower core (lc) had a total weight of 1.2 grams and was prepared from a partially neutralised super-absorbent material having a pH = 4.6, in accordance with the invention, and a chemical cellulose pulp having a pH = 6.3 and with the ratio 15/85 weight-%.

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30 TEST RESULTS:

Example 1

35 Table 1 shows that in a single core, conventional absorbent body according to reference product 1, good growth of

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micro-organisms prevails. The measurement was performed in accordance with Method 4.

Table 1:

time	Esherichia coli	Proteus mirábilis	Enterococcus faecalis
0 hours	3,3	3,1	3,7
6 hours	7,0	6,4	7,1
12 hours	9,2	9,1	8,3

Example 2

Table 2 shows that in a single core absorbent body according to test product 1, good inhibition of the growth of micro-organisms is obtained. The measurement was performed in accordance with Method 4.

Table 2:

time	Esherichia coli	Proteus mirábilis	Enterococcus faecalis
0 hours	3,2	3,3	3,4
6 hours	5,5	3,2	4,8
12 hours	7,3	4,0	6,1

Example 3

Table 3 shows that in a single core absorbent body according to test product 2, good inhibition of the growth of micro-organisms is obtained. The measurement was performed in accordance with Method 4.

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Table 3:

time	Esherichia coli	Proteus mirábilis	Enterococcus faecalis
0 hours	3,4	3,3	3,5
6 hours	3,2	2,6	3,6
12 hours	2,8	2,0	3,5

Example 4

Table 1 shows that in a dual core, conventional absorbent body according to reference product 2, good growth of micro-organisms prevails. The measurement was performed in accordance with Method 4.

Table 4:

time	Esherichia coli		Proteus mirábilis		Enterococcus faecalis	
	uc*	lc**	uc*	lc**	uc*	lc**
0 hrs	3,4	3,4	3,4	3,4	3,4	3,4
6 hrs	6,8	7,0	6,6	6,7	6,7	6,2
12 hrs	9,0	9,0	9,1	9,0	8,0	7,8

*uc = upper core, **uk = lower core

Example 5

Table 5 shows that in a single core, absorbent body according to test product 3, good inhibition of the growth of micro-organisms is obtained. The measurement was performed in accordance with Method 4.

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Table 5:

time	Esherichia coli		Proteus mirábilis		Enterococcus faecalis	
	uc*	lc**	uc*	lc**	uc*	lc**
0 hrs	3,4	3,4	3,4	3,4	3,4	3,4
6 hrs	5,1	5,6	3,3	4,2	4,4	4,5
12 hrs	7,3	7,4	4,0	4,0	5,9	4,8

*uc = upper core, **lc = lower core

Example 6

Fig. 1 shows that efficient delay of the development of ammonia is obtained in a single core absorbent body according to test product 5 when compared to a single core, conventional absorbent body, according to Reference product 4. The measurement was performed in accordance with Method 5.

Example 7

Fig. 2 shows that the surface-pH of skin after a period of use of a test product containing an absorbent body in accordance with the invention, test product 4, is stabilised at a lower level than after use of a corresponding test product containing a conventional super-absorbent material, according to Reference product 3, after addition of Test liquid 3. The measurement was performed in accordance with Method 6.

Example 8

5 Table 6 shows that pH, when measured in a single core absorbent body, test product 1, in accordance with the invention, after addition of test liquid, lies within the effective pH-interval 3.5 - 4.9. The measurement was performed in accordance with Method 3.

Table 6:

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	Test liquid 1	Test liquid 2	Test liquid 3
pH	4,29	4,42	4,54

Example 9

15 Table 7 shows that pH, when measured in a dual core absorbent body, test product 6, in accordance with the invention, after addition of test liquid, lies within the effective pH-interval 3.5 - 4.9. The measurement was performed in accordance with Method 3.

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Table 7:

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	Test liquid 1	Test liquid 2	Test liquid 3
pH uc*	4,72	4,83	4,80
pH lc*	4,75	4,73	4,73

*uc = upper core, **lc = lower core

30 The invention shall not be considered to be restricted to the embodiments described herein. Accordingly, a number of further variants and modifications are conceivable within the scope of the appended claims.

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CLAIMS:

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1. An absorbent article, intended to be worn in contact with the skin of a wearer, said article comprising a pH-controlling substance in the form of a partially neutralised super-absorbent material,

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characterized in that the pH in the article, after wetting and during use of the article in contact with skin, is in the interval 3.5 - 4.9, preferably 4.1 - 4.7.

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2. An absorbent article according to claim 1, characterized in that said article comprises at least one further absorbent material.

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3. An absorbent article according to claim 2, characterized in that the article comprises chemical thermo-mechanical cellulose pulp (CTMP).

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4. An absorbent article according to claim 3, characterized in that the chemical thermo-mechanical cellulose pulp has a pH from 2.5 - 8.5, preferably 2.5 - 6.5 and most preferably 2.5 - 5.5.

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5. An absorbent article according to claim 4, characterized in that said pH has been obtained by the addition of an acidifying agent.

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6. An absorbent article according to claim 4, characterized in that said pH has been obtained by the addition of an acidifying agent in a separate step after the pulp manufacturing process.

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7. An absorbent article according to any one of claims 2-6, characterized in that the article comprises chemical cellulose pulp (CP).

8. An absorbent article according to claim 7,

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c h a r a c t e r i z e d i n that said chemical
cellulose pulp has a pH from 2.5 - 8.5, preferably
2.5 - 8.0 and most preferably 2.5 - 7.0.

- 5 9. An absorbent article according to claim 1,
c h a r a c t e r i z e d i n that said pH has been
obtained in the pulp manufacturing process by the
addition of an acidifying agent.
- 10 10. An absorbent article according to claim 1,
c h a r a c t e r i z e d i n that said pH has been
obtained by the addition of an acidifying agent in a
separate step after the pulp manufacturing process.
- 15 11. An absorbent article according to claim 1
substantially as described in any one of Test Products
1 to 6.

[54] ODOR REDUCTANT BODY WASTE PAD

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[22] Filed: Feb. 27, 1973

[21] Appl. No.: 336,270

Related U.S. Application Data

[63] Continuation of Ser. No. 131,884, April 7, 1971, abandoned.

[52] U.S. Cl. 128/290 R

[51] Int. Cl. A61F 13/16

[58] Field of Search ... 128/284, 287, 290, 296, 270, 128/285

[56] References Cited

UNITED STATES PATENTS

1,950,286	3/1934	Barkow	128/290 R
1,950,957	3/1934	Wilhelm	128/290 R
2,467,884	4/1949	Elias	128/270 X
3,004,895	10/1961	Schwartz	128/287
3,067,745	12/1962	Burgeni et al.	128/270
3,093,546	6/1963	Atkinson	128/290 R
3,329,145	7/1967	De Merre	128/290 R
3,491,759	1/1970	Samuel	128/290 R

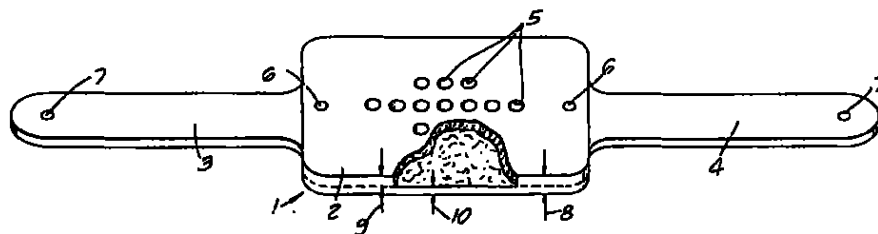
Primary Examiner—Charles F. Rosenbaum

Attorney, Agent, or Firm—J. L. Jones, Sr.

[57] ABSTRACT

A substantial proportion or all of the total thickness of an unused single use, disposable body waste fluid absorbent pad, such as a sanitary napkin and a baby diaper, combines a water soluble, weakly acidic buffered solid composition having a pH range of 3.5 to 6.0, with a waste fluid absorbent pad. The absorbent pad of wood pulp is impregnated with a dry buffered non-hygroscopic, non-toxic, solid, acid composition having an aqueous pH range of 3.5 to 6.0. The wood pulp pad structure density can range from the macerated loose random fiber of typical density 1.5–2.5 lbs/cu. ft. of the commonly sold commercial fluffed wood pulp absorbent pad sanitary menstrual napkins, to that of a 9–10 pound weight absorbent tissue paper sheet typically embodied in the menstrual napkin of the U.S. Pat. No. 3,532,097, issued Oct. 6, 1970. The controlled acid pH of the buffered absorbent pad, when the pad is wet with body waste fluids, e.g., menstrual fluids or urine of infants, inhibits the rapid formation of free ammonia gas and volatile amine compounds from urea, uric acid, amino acids and peptones by bacterial and enzyme action, and forms nonvolatile salts of the basic compounds. The buffered pH range is not irritating to the user's skin.

11 Claims, 4 Drawing Figures



ODOR REDUCTANT BODY WASTE PAD

This application is a continuation of Ser. No. 131,884 filed Apr. 7, 1971 and now abandoned.

BACKGROUND OF THE INVENTION

It is well known that some menstruating females emit odorous menstrual fluids. Emitted fluids can also rapidly form odorous products on further proteolytic reaction. It is established that some of the most perceptible odors are due to chemically basic amine type compounds, which are volatile. The characteristic amine type odors are embarrassing to menstruating females.

The urine impregnated diapers of infants are well known for having and developing an ammonical odor on storage. The widespread use of single use, disposable baby diapers is restricted by the persistent ammonical odor of the discarded, used diapers, prior to their final disposal outside the baby's household. In addition, the ammonical urine products can induce a common rash on the baby's torso, due to the alkaline pH of the urine in persistent contact with the baby's skin.

My buffered acid pH body waste odor prevention pad can inhibit the formation of embarrassing odors by absorbing any free ammonia and amines present in freshly excreted body waste fluids; and also by further inhibiting the rapid formation of ammonia and volatile amine compounds from urea, uric acid, amino acids and the like by bacterial and enzyme action in the waste fluids.

SUMMARY OF THE INVENTION

A substantial portion or all of the total thickness of a single use, disposable body waste fluid absorbent pad, such as a menstrual sanitary napkin or a baby diaper, has a water soluble, weakly acidic, buffered solid composition having an aqueous pH range of 3.5 to 6.0 disposed in the dry reservoir absorbent pad of the napkin and the diaper. The dry, buffered pH reservoir absorbent pad is formed of wood pulp impregnated with a dry, buffered, non-toxic, non-hygroscopic, solid acid composition having a typical pH range of 3.5 to 6.0. The bleached wood pulp pad structure can range from macerated, loose random fiber of typical density 1.5-2.5 lb/cu ft of the commonly sold commercial fluffed wood pulp absorbent pad in sanitary menstrual napkins, to that of a 9-10 pound weight absorbent tissue paper sheet embodied in the menstrual mapkin of the U.S. Pat. No. 3,532,097 issued Oct. 6, 1970, and also in the diaper pad of U.S. Ser. No. 63,749, filed Aug. 14, 1970. The controlled pH range of the buffered pad inhibits the rapid formation of ammonia and volatile amines from the urea, uric acid, amino acids and peptones in the body waste fluids, by bacterial and enzyme action.

The acidic buffers composition also neutralizes and converts to a relatively nonvolatile, nonodorous salt any ammonia or amine which is initially present in the freshly excreted waste fluids or which is formed later by bacterial or enzyme action. The buffered pH of the pad is in the acidic range which is not irritating to the skin.

Included in the objects of this invention are:

To provide a body waste fluid absorbent pad having a dry, solid buffered weakly acidic chemical reservoir composition suitable for inhibiting the formation of ammonia and volatile amine odors from the absorbed

waste fluids, and also for neutralizing any basic compounds in the freshly excreted waste fluids.

To provide a dry, body waste fluid absorbent pad having a buffered pH reservoir composition capable of absorbing ammonia and amines contained in waste fluids absorbed on a pad.

To provide a dry, nontoxic, acidic pH reservoir pad, buffered to a pH range of 3.5 to 6.0, and suitable for use in body waste fluid absorbent pads, and which will not irritate the body skin.

To provide a dry body waste fluid absorbent pad suitable for neutralizing and forming non-volatile salts of ammonia and amines and other basic chemical compounds present in the body waste fluids absorbed on the pad.

Further objects and advantages of this invention will become apparent in the following description, to be read in conjunction with the following drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective partial sectional view of a menstrual sanitary napkin containing a buffered acidic pH absorbent pad of this invention.

FIG. 2 is a perspective partial elevational view of another menstrual napkin modification, further illustrating the position of a buffered acidic pH absorbent pad.

FIG. 3 is a perspective view of a disposable single use baby diaper having a buffered acidic pH absorbent pad.

FIG. 4 is a sectional view through 4-4 of FIG. 3, further illustrating the placement of the buffered, acidic pH absorbent diaper pad of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

It is well known that menstruating females can emit odors that are embarrassing to them. The odors can arise as the result of proteolytic decomposition of blood and tissue waste in menstrual fluids, which are further decomposed into products which yield ammonia and volatile amine compounds. The odors of the ammonia and amines are socially unpleasant. Likewise, mothers object to the odor of ammonia in the urine impregnated, single use, disposable infant diaper after they are removed from the infant, and before the diapers are removed from the household.

The waste menstrual fluid and baby urine have a common problem of odor generation. Waste fluid odor generation can be reduced and can be inhibited by preventing bacterial and enzymatic decomposition in the waste products. The urea, creatinine, uric acid in urine are further converted into volatile ammonia in a wet diaper, due to bacterial and enzymatic action. Likewise, the proteins, amino acids, urea and nitrogen containing tissue excreta in menstrual fluids, are converted by proteolytic and enzymatic action into simpler molecules, including some volatile ammonia and amines. The relatively high temperature of the sanitary napkin in use next to the body skin further promotes the microbial incubation process, and the rapid rate of these proteolytic and enzymatic processes.

I have found that the biological conversion processes which lead to the common problem of amine and ammonia formation in these body waste fluids absorbent pads can be inhibited by controlling the pH of the absorbent pads receiving these wastes. By controlling the pH of the absorbent pad structure material to provide a buffered acidic reservoir of pH range 3.5 to 6.0, the

formation of substantial amounts of free volatile ammonia and amine compounds is prevented. The buffered pH acidic reservoir functions two-fold. First, it inhibits bacterial growth in the proteolytic degradation of the excretory products, since bacterial growth rate is generally decreased in acid media. Secondly, the ammonia and amines that form, or which are initially excreted in the waste fluids, are immediately neutralized by the buffer composition, forming nonvolatile salts. The pH of the buffering composition is controlled over a range compatible with the normal human skin.

Human urine normally ranges from pH 5.5-6.5, becoming alkaline or near alkaline after meals. The skin of newborn babies (seven days old) has a pH less than 5.0 (Behrendt and Green The measurement of Anderson (Brit. J. Derm., 63, 283-96) and Martin Beare et al (Brit. J. Derm., 70, 233-41) both show that the skin of normal children is acidic. According to Martin Beare et al, normal children less than three years of age have skin pH values ranging from 5.86 to 6.78. Significantly, the higher pH value of 6.78 was in the perianal area which can be contaminated at that age with traces of urine and feces. The other skin areas of the body were significantly more acidic. Anderson's pH measurements of other skin areas of young children were significantly more acidic, ranging from pH 4.87 to 5.53. The skin of adult females was found to have an average pH of 5.50 by Draize (J. Invest. Derm., 77-85). Thus an acidic pH range of 4.5 to 6 is typically normal for the skin of babies or females.

This invention teaches body waste fluid pads impregnated with nontoxic, water soluble, weakly acidic buffered, dry, solid, acid-salt compositions having a buffered pH range of 3.5 to 6.0, when wet with an aqueous body waste fluid. The waste fluids, urine and menstrual fluid, impregnating the pad will be incubated at substantially body temperature while secured on the person, or at room temperature while awaiting final disposal in the household. The buffered acidic pH of the waste fluid while incubating in the impregnated pad will inhibit the bacterial and enzymatic process leading to formation of the volatile ammonia and amine odors, since acidic pH media generally inhibit bacterial growth processes.

Some of the nontoxic, food type, solid, weak acids useful in the buffered pH compositions of this invention are citric, tartaric, gluconic, glutaric, levulinic, glycolic, succinic, malic, fumaric, and acid phosphate salts. Other similar nontoxic solid, weak acids can be used. Preferably, the buffered acid compositions should not be hygroscopic or deliquescent. The preferred weak acids useful in the buffered compositions should not be the typical short chain aliphatic acids such as acetic or butyric, due to their being liquids, and their volatility and odor. Likewise, the long chain fatty acids such as myristic, palmitic and stearic acids form undesirable surfactant salts or soaps. Obviously toxic acids, such as boric and oxalic, are undesirable.

The buffered acid compositions can typically be simply formed by adding Na OH or Na₂CO₃ solutions to the concentration of pure acid solutions in amounts to provide a desired buffered acid solution in the range of pH = 4.5 to 6.0. The lower pH values will provide a greater buffering capacity for the absorbent pad.

The buffered acid compositions can be uniformly dispersed in the absorbent wood pulp, either in the random macerated wet or dry wood pulp form, or on the

thin (9-10 lb) absorbent tissue as it is being sheeted out and dried on the paper forming machine. The wood pulp stock can be bleached white stock, for either the macerated pulp or the tissue sheet. The buffered composition can be added to the pulp base for the macerated pulp, as a desired aqueous concentration of the buffered solution. The solution is sprayed on the pulp as it is sheeted into the relatively thick, non-calendared, pulp sheet, which is dried to a sheet stock suitable for storage, and then disintegrated into macerated pulp for absorbent pads.

The buffered composition solution can also be sprayed on the wet tissue stock sheet as it is made on the paper sheeting machine, just prior to final drying of the tissue paper stock. Thus, the dry macerated pulp composition, having a buffered, dry, solid, non-toxic water soluble composition impregnated therein, is suitable for use in absorbent pads for sanitary napkins and diapers. The absorbent pad can also be a menstrual napkin comprised of multiple ply of absorbent tissue sheet stock, as U.S. Pat. No. 3,532,097 and the pending U.S. patent application on diaper pads, Ser. No. 63,749, filed Aug. 14, 1970. In either the macerated wood pulp or the tissue sheet absorbent pad construction, the desired concentration of dry, solid acidic composition can be achieved.

Dry, solid, acidic buffer compositions of sodium citrate and citric acid have been uniformly dispersed in bleached white macerated pulp and bleached white, absorbent tissue paper stock. Typically, 2 wt. percent of a dry citric acid-potassium citrate buffer composition, having an aqueous pH value of 4.0 as a 10 wt. percent solution, was separately sprayed on macerated paper pulp and on 10 lb. weight tissue paper, and dried. The dried buffered paper stock was formed into diapers and napkins in accordance with the earlier reference teachings on diaper and napkin construction.

Blind use tests of both diapers and napkins utilizing the above modified paper stock were made. The female napkin users and the infants' caretakers were unaware of the diaper and napkin modification employed in the respective use tests.

Female napkin users were supplied with buffered napkin modifications and also identical appearing napkins which were not buffered modifications. The napkins supplied to users were numbered in a code unknown to the users, indicating the buffered and non-buffered modifications. The users were asked to indicate the odorous and non-odorous napkins, immediately after the napkin's use and also after incubating the napkin for 24 hours at room temperature in a plastic envelope. Typically, the napkins identified by the user after both time intervals as non-odorous, or less odorous, was the buffered napkin, having the buffer pH controlled composition impregnantly disposed therein.

Likewise, the infant caretakers were asked to indicate the odorous and non-odorous diapers, also supplied as coded buffered and non-buffered modifications. The diapers were examined for odor immediately after use and also after incubating at room temperature, when infant feces did not interfere with the odor test. Typically, the caretaker correctly identified the non-odorous, or less odorous, diapers as the buffered diaper, having the buffer pH controlled composition impregnantly disposed in the diapers.

Typically, the diaper's absorbent pad can be impregnated pregated with 1 wt percent of a buffer composi-

tion, such as NaH_2PO_4 having an aqueous pH value of 4.1 to 4.5 in a 5 percent aqueous solution. Likewise, sodium dihydrogen phosphate (NaH_2PO_4) is a suitable buffer composition for sanitary napkin modifications of this invention.

It is desirable to optimize the concentration of dry, solid acidic buffer composition in the absorbent pad at the lowest concentration value consistent with minimum ammonia and amine odor concentration during the absorbent pad use. The minimum optimal buffer concentration is desirable to provide a low raw material cost, adapting this invention to widespread use. In addition, the low buffer concentration minimizes any potential skin irritation effects. It should be noted that well known and widely used food acids are the preferred acids of choice in the buffer compositions, reducing the toxicity problem to nil.

Referring to FIG. 1 in detail, the menstrual napkin 1 has a menstrual fluid absorptive section 2 and a pair of straps 3 and 4, as disclosed in my copending patent application filed as of this date titled INTEGRAL STRAP TISSUE NAPKIN. The multiple reservoir apertures 5 receive menstrual fluid flow. The adhesive plug securing means 6, 6 and 7, 7 bond the multiple ply tissue paper sheets of the napkin together. The absorptive section 2 has a total thickness 8, comprising the primary absorptive section thickness 9 and the secondary absorptive section thickness 10. All or a fraction of the total absorptive section thickness 8 comprises multiple ply of tissue paper sheets having the nontoxic, water soluble, weakly acidic, buffered, dry solid composition, having an aqueous pH of 3.5 to 6.0 impregnantly disposed therein. Preferably the buffer impregnated tissue sheets are disposed at least adjacent the surface of the sanitary napkin which first receives the menstrual fluid excreta, as are required to minimize odor.

Referring to the conventional menstrual napkin 20 in FIG. 2, the shaping cover sheet 21, of open gauze or scrim, forms the front strap 23 and the rear strap 22. The partial sectional view discloses the total absorptive section thickness 26 has partial absorptive section thicknesses 24 and 25. The absorptive section thickness 24, which is to be disposed so as to directly receive the menstrual fluid excreta, has the buffered, dry solid composition, whose pH range is 3.5 to 6.0, impregnantly disposed therein. Likewise a portion of the section thickness 25, or all of 25 may also be impregnated with the buffer composition as required to reduce the excreta odor. The relative value of thicknesses 24 and 25 are those values which are required.

Referring to FIGS. 3 and 4 in detail, the infant diaper 30, has the overlying plastic membrane margins 31 and 32, formed by overwrapping and sealing the thin plastic membrane sheet 33 on to the edge margins of absorptive pad 34. The enlarged partial sectional view of FIG. 4 illustrates the porous cover sheet 35, which is disposed directly adjacent the infant in diaper use. The relative thickness values of absorptive sections 36 and 37 can be adapted to provide maximum reduction of ammonia and amine odor, by adjusting the thickness of buffer impregnated absorptive section 36 to the required value. Section 36 can range up to 100 percent of the total absorptive pad thickness 38, thus decreasing section 37 to zero percent.

Other odor reductant body waste pad variations can be made without departing from the scope of this invention. Many modifications and variations of my im-

provements in an odor reductant waste pad can be made in light of my teachings. It is therefore understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. A single use, disposable, human body waste fluid absorbent pad combination comprising:

a waste fluid absorbent pad having cellulose fibers disposed therein, and adapted in size and shape to being externally worn on the human body and to receiving excreted human body waste fluid; and, a nontoxic, nonvolatile, water soluble, weakly acidic, dry solid buffer composition selected from the solid acids and lithium, sodium, potassium salts of citric, tartaric, gluconic, glutaric, levulinic, glycolic, succinic, malic, fumaric, and phosphoric acids, said buffer composition having an aqueous pH range of 3.5 to 6.0, said buffer composition impregnantly disposed in said cellulose fibers disposed in said absorbent pad in a buffer composition concentration adapted to form salts of all the volatile chemically basic waste fluid excreta products absorbently disposed in said cellulose fibers during use.

2. A single use, disposable, human body waste fluid absorbent pad combination comprising:

a waste fluid absorbent pad having cellulose fibers disposed therein, and adapted in size and shape to being externally worn on the human body and to receiving excreted human body waste fluid; and, a nontoxic, nonvolatile, water soluble, weakly acidic, dry solid buffer composition selected from the solid acids and solid lithium, sodium and potassium salts of citric, tartaric glycolic, succinic, fumaric, malic acids, and phosphoric acids, said buffer composition having an aqueous pH range of 3.5 to 6.0, said buffer composition impregnantly disposed in said cellulose fibers disposed in said absorbent pad in a buffer composition concentration adapted to form salts of all the volatile chemically basic waste fluid excreta products absorbently disposed in said cellulose fibers during use.

3. A single use, disposable human body waste fluid absorbent pad combination comprising:

a waste fluid absorbent pad having cellulose fibers disposed therein, and adapted in size and shape to external wear on the human body and to receiving excreted human body waste fluid; and, a nontoxic, nonvolatile, water soluble, weakly acidic, dry solid buffer composition selected from the dry, solid compositions of the acids and lithium, sodium and potassium salts of citric, tartaric, gluconic, glutaric, levulinic, glycolic, succinic, malic, fumaric and phosphoric acids, said buffer composition having an aqueous pH range of 3.5 to 6.0, said buffer composition uniformly impregnantly disposed in said cellulose fibers disposed in said pad and adapted to receive said waste fluid, the concentration of said buffer composition adapted to form non-volatile salts of all the volatile chemically basic waste fluid excreta products disposed on said pad fibers.

4. A single use, disposable human body waste fluid absorbent pad comprising:

a waste fluid absorbent pad having cellulose fibers disposed therein, and adapted in size and shape to external wear on the human body and to receive

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human body waste fluid excreted on one face of the fiber pad; and,
a nontoxic, nonvolatile, water soluble, weakly acidic, dry, solid buffer composition selected from the solid acids and lithium, sodium and potassium salts of citric, tartaric, glycolic, succinic, fumaric, malic acids, and phosphoric acids, said buffer composition having an aqueous pH range of 3.5 to 6.0, said buffer composition uniformly impregnantly disposed in said cellulose fibers disposed in said pad and adapted to receive said waste fluid, the concentration of said buffer composition adapted to form nonvolatile salts of all the volatile chemically basic waste fluid excreta products disposed on said pad fibers.
5. A single use, disposable, human body waste fluid absorbent pad comprising:
a waste fluid absorbent pad having cellulose fibers disposed therein and adapted in size and shape to being externally worn on the human body and to receiving excreted human body waste fluid; and
a nontoxic, nonvolatile, water soluble, weakly acidic, dry solid buffer composition, having an aqueous pH range of 3.5 to 6.0, uniformly impregnantly disposed in said cellulose fibers disposed in said absorbent pad in a composite buffer concentration adapted to form salts of all the volatile chemically basic waste fluid excreta products absorbently disposed in said cellulose fibers during use.
6. In the product of claim 5, the modification wherein said waste fluid absorbent pad having cellulose fibers disposed therein is a menstrual waste fluid sanitary napkin pad adapted to external body wear.

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7. In the product of claim 5, the modification wherein said waste fluid absorbent pad having cellulose fibers disposed therein is a baby diaper waste fluid absorbent pad adapted to external body wear.
8. In the product of claim 5, the modification wherein said buffered, dry solid composition is uniformly concentrated in said cellulose fibers disposed in the structure of said waste fluid absorbent pad.
9. A single use, disposable human body waste fluid absorbent pad comprising:
a waste fluid absorbent pad having cellulose fibers disposed therein, and adapted in size and shape to external wear on the human body and to receive excreted human body waste fluid on one face of the fiber pad; and
a nontoxic, nonvolatile, water soluble, weakly acidic, dry, solid buffer composition, having an aqueous pH range of 3.5 to 6.0, impregnantly disposed in said cellulose fibers disposed in the pad face to be worn adjacent to said human body, the concentration of said buffer composition adapted to form nonvolatile salts of all the volatile chemically basic waste fluid excreta products disposed on said pad fibers.
10. In the product of claim 9, the modification wherein said waste fluid absorbent pad having cellulose fibers disposed therein is a menstrual sanitary napkin pad and adapted to external body wear.
11. In the product of claim 9, the modification wherein said waste fluid absorbent pad having cellulose fibers disposed therein is a baby diaper absorbent pad adapted to external body wear.
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United States Patent

Bryce

[15] 3,707,148

[45] Dec. 26, 1972

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[54] IMPREGNATED DIAPER	2,542,909	2/1951	De Wet.....128/290 R
[72] Inventor: Douglas Maxwell Bryce, Long Eaton, England	2,602,042	7/1952	Abbott.....424/28
	2,643,969	6/1953	Mahon.....128/284 X
	2,837,462	6/1958	Morin.....128/290 R
[73] Assignee: Boots Pure Drug Company Limited, Nottingham, England	3,004,895	10/1961	Schwartz.....128/287 X
	3,024,207	3/1962	Shaw.....128/290 R
	3,082,118	3/1963	Shaw et al.128/284 X
[22] Filed: June 1, 1970	3,198,828	8/1965	Matter.....424/27
[21] Appl. No.: 42,522	3,340,875	9/1967	Dudley et al.....128/290 R
	3,490,454	1/1970	Goldfarb et al.....128/290 R

[30] Foreign Application Priority Data
June 5, 1969 Great Britain.....28,480/69

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[52] U.S. Cl.....128/284
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[58] Field of Search.....128/284, 286, 287, 290, 296, 128/156, 270; 424/27-28, 76

[57] ABSTRACT

Ammonia absorbing products are described which comprise a non-volatile ammonia absorbing agent having a pK value of between 1.8 and 4.5. The agent may be carried in or on a sheet carrier or it may be included in a water permeable sachet. The products are of use as, or as part of, infants' napkins.

[56] References Cited

UNITED STATES PATENTS

2,418,907 4/1947 Schreiber.....128/290 R

13 Claims, No Drawings

IMPREGNATED DIAPER

This invention relates to products designed to absorb the ammonia formed in absorbent materials used to absorb body effluents. We describe the invention mainly in terms of napkins for babies but the invention is equally applicable to, for example, incontinence pads.

The management of infants and others is frequently complicated by the incidence of a rash which is primarily due to the chemical irritation of the skin by ammonia liberated from urine and faeces in the napkin. A major cause of the ammonia in the discharge is degradation of urea in the urine by bacterial ureases produced by faecal organisms such as *Proteus spp.* which are usually present. The irritated skin is ideally suited to support secondary microbiological infections leading to severe irritation, pain and restlessness.

Attempts have been made to reduce the incidence of napkin rash by a number of methods. Thus one method is to treat the napkins during the laundering process with an antibacterial agent such as cetrinide or hexachlorophane with the intention of killing the bacteria which are already present on the napkin and the residuum of the agent left on the napkin is intended to suppress the bacteria when the faeces and urine are passed. Another method is to treat the napkins with vinegar in the final laundry rinse with the intention of absorbing the ammonia as it is formed. Boric acid has also been used to impregnate towel napkins but it is not an efficient absorbent for ammonia and furthermore its use in this manner has been highly criticized since boric acid can be extremely toxic when in direct contact with the skin. Yet another method is to treat the napkins with an anti-ureatic agent, i.e., an agent which inhibits the action of the urease so that ammonia is not formed. For example, napkins have been treated with copper acetylacetonate. Such agents are sometimes used with various additives but in all instances the amounts involved are extremely small. For example, 0.15 mg copper acetylacetonate has been added to a 15g napkin. A further method is to treat laundered napkins with an anti-bacterial agent. None of the methods has been widely adopted because either it is unsatisfactory or it is dependent on treatment in a commercial laundry.

We have now found it possible to reduce or prevent the incidence of napkin rash by providing certain ammonia absorbing products for use as or in association with napkins. In preferred embodiments of the invention the ammonia absorbing agent is provided in such a way that it does not come into direct contact with the skin except as an innocuous solution.

According to the present invention we provide an ammonia absorbing product which comprises a non-volatile ammonia absorbing agent having a pK value of between 1.8 and 4.5 carried, in an amount of at least 1.5 gram per square meter of the product, in or on a sheet carrier or included in a water permeable sachet.

The sheet carrier can be in a number of forms. Thus one example is an ordinary napkin, e.g., a towel napkin or a disposable napkin. Another example is a strip of paper which may be impregnated with the ammonia absorbing agent or a strip of cellulose tape to which the ammonia absorbing agent is secured with an adhesive.

Suitable ammonia absorbing agents which may be used in accordance with the present invention include

pharmaceutically acceptable organic acids, which are usually monomeric, such as citric, malic, tartaric, maleic, fumaric, malonic and succinic acids, cellulose derivatives of polybasic acids such as cellulose phosphate, oxidized cellulose, cation exchange resins in the H form or silicic acid gels. The preferred range of pK values for these agents is 2.5 to 4.5.

There are a number of embodiments of the present invention and these include the following ammonia absorbing products:

1. A towel napkin acting as the carrier may be impregnated with the ammonia absorbing material but this is not always very desirable because the impregnation process must be repeated after washing the napkin and this task could not be effectively performed by the layman. Such towels may have a surface area of up to 0.8 square meter, for example they often measure 60 × 60 cm., and may be impregnated with an aqueous solution of, for example, malic acid to deposit at least 0.5 g. and preferably 3 to 4 g. of acid per napkin.

2. The ammonia absorbing agent may be incorporated in a disposable napkin. A disposable napkin is of absorbent material intended to hold the urine. It may comprise a sponge but generally the absorbent material is a textile have a non-woven base that generally consists of or contains a large proportion of cellulose fibers and is generally referred to as cellulose wadding. In such a napkin the wadding is generally 3 mm. thick and usually 5 mm. or more. An ammonia absorbing product of the present invention in which the carrier is in the form of a disposable napkin may simply comprise the absorbent base material and the ammonia absorbing agent but generally the napkin is reinforced on at least one side but may be reinforced on both sides or may in fact be located in a reinforcing envelope. The reinforcement may be integral with the fibrous base, this being achieved, for example, by bonding the surface or surfaces of the fleece. Reinforcement may be performed and then applied to the textile base, for example it may be a net that is applied to the base. Preferably there is a net on both sides of the napkin. In the production of such napkins any reinforcement may be applied to the napkin after the textile base has been formed into the desired shape or the reinforcement may be present on a textile sheet material that is to be cut to shape to form the napkin. The product in which the carrier is in the form of a disposable napkin may be formed initially as a continuous sheet (for example in a continuous roll) but in use it generally has the dimensions of a napkin in which event it should carry at least 0.5 g. of the acid. Disposable napkins are generally substantially rectangular in shape with one side about 1 1/4 to 2 1/4 times the length of the other side. Thus the long side may be from 20 to 40 cm. but preferably 25 to 35 cm. and usually about 30 cm. while the short side may be from 10 to 25 cm. preferably from 15 to 20 cm. and usually about 18 cm.

The incorporation of the ammonia absorbing agent into a disposable napkin may be accomplished in a number of ways to produce the ammonia absorbing product. The agent may be an integral part of the absorbent material, for example, having been impregnated into the material or coated onto it, or it may be present in granular form dispersed evenly throughout the absorbent material. If the ammonia ab-

sorbing agent is a cation exchange resin in sheet form it may be incorporated as such in the body of the napkin. Where the ammonia absorbing agent is in a fibrous form, e.g., cellulose phosphate it may be included in the napkin in the form of woven or non-woven sheets which may be prepared by standard techniques. Such sheets often contain large amounts of other fibers, e.g., cellulose fibers.

3. The ammonia absorbing agent may be carried in or on a disposable napkin liner to produce an ammonia absorbing product. Such liners are intended to allow the urine to pass through to an absorbent material, e.g., towelling, behind it. Liners are generally fairly thin permeable textile sheet materials and may be woven, knitted or, most usually, non-woven. They may be, for example, less than 1 mm. thick and are often of cellulose fibers. Liners are usually not more than 25 x 25 cm. but they may be produced in continuous lengths and carry the ammonia absorbing agent to give a product of the invention in continuous sheet form. Each liner should carry at least 0.5 g of the agent.

4. The ammonia absorbing agent may be carried on a base material in strip or sheet form to give an ammonia absorbing product suitable, e.g., for insertion between a napkin liner and a napkin or a pocket or folds in a towel napkin. Such strips or sheets may also be incorporated in disposable napkins and facilitate the manufacture of the finished product incorporating an ammonia absorbing agent. They may also be integrated with napkin liners. The strips may be manufactured from a continuous roll of material which may be woven, knitted or non-woven and which is from 1 to 25 cm. wide and individual lengths can be cut as required. Non-woven material for this purpose is preferably a paper, for example being made mainly from short cellulose fibers, e.g., less than 10, and preferably less than 5, mm in length, generally by a process in which water is drained from an aqueous slurry of the fibers on a screen. The material is usually thin, e.g., less than 1 mm thick.

Thin material carrying the ammonia absorbing agent may be combined with thicker absorbent at any stage in the manufacture of the final absorbent article. For example a continuous sheet of wadding may have paper carrying the agent continuously laid against it or the wadding may be continuously formed around the thin material and the resulting laminate cut to desired shape subsequently or wadding and the thin material may be cut to shape and then laid together.

When the ammonia absorbing agent is distributed over paper that is within the final absorbent article, as opposed to being a liner, this paper is generally present primarily to provide the ammonia absorbing agent. The paper may be substantially coextensive with the main absorbent, e.g., the wadding of the article or it may cover some areas only of the wadding or other absorbent material. Thus the paper may be in the form of narrow strips which are laid against or into the wadding. For example the paper may be in the form of a strip from 1 to 25 cm. wide.

It is particularly preferred that the housewife should be able repeatedly and easily to produce napkins that are capable of absorbing ammonia and this can be achieved by providing the housewife with a roll of the paper carrying the absorbent agent with the result that

she can tear off a suitable length of paper to prepare each napkin or to provide her with a container, e.g., a box, containing interleaved sheets of the paper.

The ammonia absorbing agent may be incorporated with the sheet carrier in any convenient manner. For example acids that are soluble in water or other convenient solvents may be impregnated as a solution into absorbent sheet carrier, optionally as the last stage in the manufacture of the carrier which is then dried to give a uniformly impregnated material. For example, aqueous solutions of citric or tartaric acid may be used.

Certain acids which are used as ammonia absorbing agents in the invention may conveniently be applied as a coating on a thin material. Thus the material may be dipped into molten acid or molten acid may be sprayed on to it. The acid then solidifies as it cools. It may be desirable to include a plasticizer for the acid in the melt in order to produce a more flexible coated material.

5. The ammonia absorbing product may be formed by sealing a quantity of the ammonia absorbing agent in a water permeable sachet, formed from, for example, polyvinyl alcohol. Such a sachet may be inserted for example in a pocket or within the folds of a towel napkin; or it may be incorporated within an absorbent napkin. Each sachet preferably contains at least 0.5 g. of the agent, and preferably at least 1 g., and usually at least 2 g. or even 3 g. of the agent.

The urine and faecal discharge in soiled napkins normally contains up to 0.65% w/w of ammonia but when treated with urease the total ammonia content rises to an average of 1.2% w/w. This concentration of ammonia is the maximum which one would reasonably expect in practice. A soiled napkin which has absorbed the average volume of 150 ml. of urine may therefore produce up to 1.8 g. of ammonia. The amounts of various acids required to neutralize the potential ammonia content of urine were found by titrating ammonia to pH 5.5. using a glass electrode pH meter and the results are summarized in the following table.

Acid	Wt. of acid (g.) equiv. to 1g. NH ₃ titrated to pH 5.5
Citric	4.2
Malic	3.4
Maleic	4.6
Malonic	3.6
Succinic	3.8
Tartaric	4.2
Fumaric	3.5

We prefer to use citric or malic acid as the ammonia absorber and we have found that in practice the incidence of napkin rash caused by the presence of relatively large quantities of ammonia is reduced by using about 4 g. of citric acid or 3.5 g. of malic acid with a napkin.

The time a soiled napkin is in contact with the skin will have some bearing on the incidence of napkin rash and in laboratory experiments it was found possible to prevent the evolution of ammonia over a period of 6 hours, during which period the napkins were lightly pressed occasionally, by treating the napkin with only 2.5% w/w of malic acid based on a 20 g. napkin.

By including at least 0.5 g. of the ammonia absorbing agent in a napkin or at least 1.5 g. per square meter of an absorbent material which may be cut to the dimensions of a napkin, it is possible to absorb a significant amount of the ammonia that will be evolved during normal usage. The optimum amount naturally depends upon the particular agent being used. When the agent is an ion exchange resin the amounts are of course greater than when the agent is an acid such as malic acid.

In practice we generally have at least 1 g. and often at least 2 g. or even at least 3 g. of organic acid in each napkin. For a disposable napkin measuring 30 x 18 cm. these quantities are equivalent to about 20 g., 40 g. and 60 g. per square meter respectively, the area being the surface area of one side of the napkin. By using such amounts it is possible substantially to eliminate the evolution of ammonia collected in the napkin during normal usage over a 6 hour period.

It is to be understood that the ammonia absorbing material may be used in conjunction with the other additives for reducing napkin rash, e.g., bactericides and enzyme inhibitors which are pharmaceutically acceptable and also compatible with the ammonia absorbers. Typical of such bactericides are phenylmercuric salts such as phenylmercuric nitrate and phenylmercuric acetate. Bronopol has also been found to be useful in conjunction with, e.g., malic or citric acid and the amount of acid may be reduced. Bronopol is 2-bromo-2-nitropropane-1,3-diol.

In constructing a napkin from an absorbent material containing the ammonia absorbing agent, it is of course necessary to consider the dermatological effect of the particular agent being used. It is preferred that the agent should be dermatologically acceptable, that is to say that it should be non-irritant and non-toxic both in solid form and solution but it is adequate in most constructions of napkins if it is merely dermatologically acceptable in solution in urine. Thus if it is dermatologically unacceptable and is enclosed in a water soluble sachet or absorbed on a strip of paper it will only come into contact with the skin when in solution after absorbing ammonia and this would be satisfactory.

The following non-limitative examples illustrate the invention:

EXAMPLE 1

A rectangular portion of cellulose wadding (20 g.; 30 cm. x 18 cm.) was treated with a solution of citric acid (4g.) in isopropanol and dried. The treated wadding was covered with a 30 cm. x 18 cm. rectangular piece of cotton wool (5 g.) and used as a disposable napkin with the cotton wool in contact with the skin.

Similar napkins were prepared using water or ethanol as the solvent for the citric acid.

EXAMPLE 2

Disposable napkins were made in a similar way to that described in Example 1 but using tartaric acid (4 g.), malic acid (3.5 g.) or fumaric acid (3.5 g.) to impregnate the cellulose wadding.

EXAMPLE 3

A disposable napkin was prepared from a rectangular portion of cellulose wadding (20 g.; 30 cm. x 18 cm.) and above the wadding was placed at equal distances four strips of absorbent paper 25 cm. x 2.5 cm., each strip being impregnated with an aqueous solution of malic acid so that each strip contained 1 g. of acid. The absorbent wadding and treated strips were enclosed in a fabric envelope and when treated with 100 ml. of artificial urine containing urease the evolution of free ammonia was prevented for a period in excess of 6 hours.

EXAMPLE 4

A disposable napkin was prepared from a rectangular portion of cellulose wadding (20 g.; 30 cm. x 18 cm.) and above the wadding was placed at equal distances four strips of absorbent paper 25 cm. x 2.5 cm., each strip containing 0.5 g. of malic acid and 0.625 mg. of Bronopol. The absorbent wadding and the treated strips were enclosed in a fabric envelope.

EXAMPLE 5

A continuous length of absorbent paper was impregnated with a solution of malic acid and Bronopol at a rate of 66 g/m² malic acid and 83 mg/m² Bronopol, and was dried. Parts of this were treated in different ways. One part was cut into sheets 20 cm. x 15 cm. which were interleaved and packed in a box. One part was cut longitudinally into strips 20 cm. wide and perforated every 15 cm., each strip then being wound as a roll. Another part was cut into strips 2.5 cm. wide, part of this then being cut into 15 cm. lengths and part being wound on a roll.

One napkin can be made up using 6 of these strips 2.5 cm. x 20 cm. Thus they may be placed in the folds of an ordinary towel napkin or in a specially prepared pocket therein, or they may be placed between a napkin liner and a napkin or they may be attached to a napkin liner for use in conjunction with a napkin or they may be incorporated in a disposable napkin.

EXAMPLE 6

2 g. of malic acid and 2.5 mg. of Bronopol were enclosed within a sachet made from polyvinyl alcohol. This sachet was placed in the folds of a towel napkin. In place of the 2 g. of malic acid and the Bronopol there was also made a sample comprising 4 g. of malic acid. Citric acid could be used for these examples in place of the malic acid.

EXAMPLE 7

Disposable napkins were made as described in Example 1 but replacing the malic acid with 10 g. of granules of Zeokarb 225 resin (Trade Name) or a similar quantity of Amberlite IRC 50 resin (Trade Name) in the H⁺ form. The granules were sprinkled evenly across the full area of the cellulose wadding absorbent. When the napkins absorbed 100 ml. each of a synthetic urine containing urea and urease, free ammonia was present after 30 minutes as shown by a pH of 9 compared with an original pH of 5.5.

I claim:

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1. A baby's napkin comprising a material that will absorb liquid, at least 2 grams of a monomeric organic acid as an ammonia absorbing agent and having a pK value of from 1.8 to 4.5, and 2-bromo-2-nitropropane-1,3-diol.

2. A napkin according to claim 1 in which the material that will absorb liquid is towelling.

3. A napkin according to claim 1 in which the material that will absorb liquid is cellulose wadding at least 3 mm thick.

4. A napkin according to claim 1 in which the ammonia absorbing agent is impregnated into or coated onto the material that will absorb liquid.

5. A napkin according to claim 1 including a napkin liner and in which the ammonia absorbing agent is in or on the napkin liner.

6. A napkin according to claim 1 in which the ammonia absorbing agent is in or on paper.

7. A napkin according to claim 1 in which the ammonia absorbing agent is in a water permeable sachet.

8. A napkin according to claim 1 in which the ammonia absorbing agent is a monomeric organic acid selected from the group consisting of citric acid, malic acid, maleic acid, malonic acid, succinic acid, tartaric acid and fumaric acid.

9. A napkin according to claim 1 additionally comprising a urease.

10. A napkin according to claim 1 in which the ammonia absorbing agent is in or on a sheet carrier.

11. A sheet carrier suitable for use in a napkin according to claim 10 and comprising a permeable textile base less than 1 mm thick and having one dimension of from 20 to 40 cm and the other dimension of from 10 to 25 cm and comprising at least 2 g of a monomeric organic acid as ammonia absorbing agent and having a pK value of 1.8 to 4.5, and 2-bromo-2-nitropropane-1,3-diol.

12. A sheet carrier suitable for use in a napkin according to claim 10 and comprising a roll of a permeable textile less than 1 mm thick, the roll being less than 25 mm wide, and comprising at least 40 grams per square meter of a monomeric organic acid as an ammonia absorbing agent and having a pK value of from 1.8 to 4.5, and 2-bromo-2-nitropropane-1,3-diol, the textile being capable of serving as a napkin liner.

13. A sheet carrier suitable for use in a napkin according to claim 10 and comprising a strip of paper from 1 to 25 cm wide and less than 1 mm thick and formed from short cellulose fibers and comprising at least 40 grams per square meter of a monomeric organic acid as an ammonia absorbing agent and having a pK value of from 1.8 to 4.5 and 2-bromo-2-nitropropane-1,3-diol.

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