

**Industria y Comercio**

SUPERINTENDENCIA

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PETITORIO

SUPERINTENDENCIA Y COMERCIO
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 Dependencia: 2029 DIVISION DE NUEVAS CREACIONES

**FORMULARIO UNICO DE SOLICITUD DE PATENTE
 PCT
 ENTRADA EN FASE NACIONAL**

1	SOLICITUD DE:			
	☒ Patente de Invención.	☐ Patente de Modelo de Utilidad.		
	☐ Capítulo I.	☒ Capítulo II.		
2	SOLICITANTE (71)	Nombre: SCA HYGIENE PRODUCTS AB sociedad constituida y existente bajo las leyes de Suecia. Dirección: S-405 03 Goteborg, Suecia. Domicilio: Goteborg, Suecia.	IDENTIFICACION C.C. ☐ NIT ☐ C.E. ☐ Otro ☐ Cual _____ Número: _____	
3	REPRESENTANTE APODERADO	Nombre: EMILIO FERRERO Dirección: Carrera 4ª. No. 72-35 Teléfono: 347 36 11 Fax:: 217 92 11 E-mail: <u>clientes@camyo.com.</u> Domicilio: Bogotá, Colombia.	IDENTIFICACION C.C. ☒ NIT ☐ C.E. ☐ Otro ☐ Cual _____ Número: <u>438.019</u> T.P. <u>31.929</u>	
4	INVENTOR (ES) (72)	1- Sussan SANDBERG Gubbekullavägen 15, S-439 35 Onsala Suecia. 2- Bo ANDREASSON Parkgatan 29, S-852 38, Sundsvall, Suecia.		
5	PCT (86) Solicitud Internacional No. <u>PCT/SE01/00612</u> Fecha: <u>22 de marzo de 2001</u> Publicación Internacional No. <u>WO 01/77437 A1</u> Fecha : <u>18 de octubre de 2001</u>			
6	Título (54) <u>MÉTODO DE ADSORCIÓN DE POLIMEROS CATIONICOS Y ANIONICOS</u> <u>SOBRE LA SUPERFICIE DE PARTICULAS Y PAPEL O PRODUCTO NO</u> <u>TEJIDO QUE CONTIENE TALES PARTICULAS</u>			
7	Clasificación Internacional (51) <u>D21H 21/18</u>			
8	Prioridad SI ☒ NO ☐	(33) País de Origen <u>SE.</u>	(32) Fecha <u>6 de abril de 2000</u>	(31) Número de Solicitud <u>0001268-2</u>

9

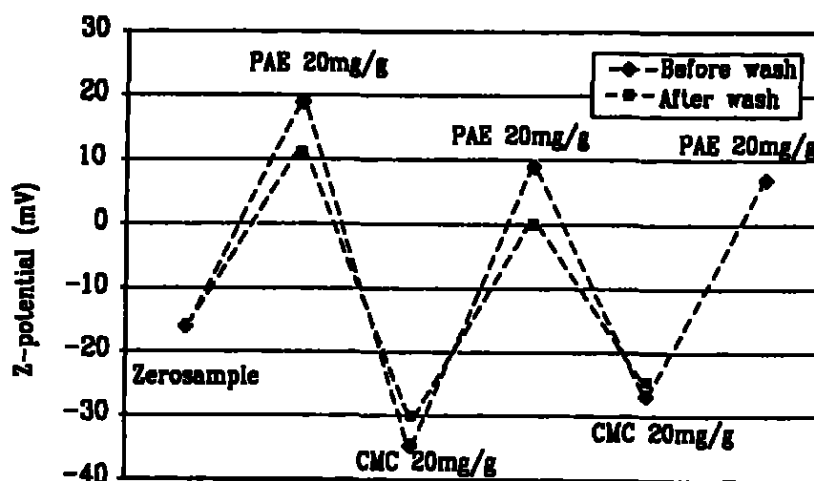
Comprobante de pago No.: 02-65.102 Fecha: 30 de septiembre de 2002

10

Anexos:

- ☒ Comprobante de pago de la tasa de presentación de la solicitud por 378.000.00.
- ☐ Comprobante de pago por reivindicación de prioridad.
- ☒ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☒ Poderes, si fuere el caso.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones.
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Copia del examen preliminar efectuado por la IPEA.
- ☐ Traducción del examen preliminar efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☒ Arte final 12x12
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ Otros

11

FIGURA CARACTERISTICA:**FIG. 1**

12

Solicito la concesión de la patente,

NOMBRE: EMILIO FERRERO

FIRMA: 

C.C. 438.019 de Usaquén T.P. 31.929

af

For patents, utility models, industrial designs,
trademarks, commercial names, trade emblems,
slogans.

Para patentes, modelos de utilidad, diseños
industriales, marcas de fábrica, nombres
comerciales, enseñás, lemas comerciales.

REPRESENTACION Y PODER

REPRESENTATION AND
POWER OF ATTORNEY

11256
C 31

I (we), the undersigned / Yo (nosotros), abajo firmado (s)
SCA HYGIENE PRODUCTS AB

of / domiciliado (s) en 405 03 Goteborg,
SWEDEN

por el presente nombramos a EMILIO FERRERO, tpa. 31929;
GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA DE PAEZ,
tpa. 23555 y GERMAN CAVELIER, tpa. 832, domiciliados en la
Carrera 4ª N° 72-35, Bogotá, Colombia, en obediencia a lo
dispuesto en el parágrafo 1º del Artículo 543 del Código de
Comercio, el primero como principal y los demás como
suplentes, en su orden, como mis (nuestros) representantes en
todos los asuntos de propiedad industrial con facultad para
recibir notificaciones y nombrar apoderados judiciales o
extrajudiciales. El primer representante suplente reemplazará al
principal en caso de ausencia o impedimento temporal o
definitivo de aquél. La misma regla se aplicará cuando el
segundo representante suplente haya de reemplazar al primero,
el tercero al segundo. En tales casos, el representante
principal, o el primero, o segundo suplente, en su caso, o ambos,
declararán su intención de no ejercer la representación
mediante declaración autenticada por Notario Público en
Colombia, o por Notario u otro Funcionario Público, o Cónsul
de Colombia, en el extranjero; y si se tratare de impedimento,
en el certificado respectivo. Si alguno de los nombrados faltare
definitivamente, el siguiente tomará su lugar. Cuando cesare la
ausencia o impedimento del representante principal, o de su
primero o segundo suplentes, en su caso, podrán ejercer la
representación, en su orden, uno u otros según el caso,
sumiéndola por el solo hecho de ejercerla, cesando en ese
momento el ejercicio de la representación por el primero,
segundo o tercer suplente en su caso.

demás, confiero (conferimos) poder a los abogados arriba
nombrados, para obtener la protección de mi (nuestra)
propiedad industrial y contra la competencia desleal, a cuyo
efecto autorizo (amos) a los dichos apoderados para que me
(nos) representen ante cualesquiera entidades o personas,
erzan o no jurisdicción, especialmente ante las del orden
administrativo, contencioso-administrativo y judicial, así como
tribunales de arbitramento, en todo lo concerniente a los
siguientes asuntos: a) Obtención de patentes de invención,
modelos de utilidad, y diseños industriales; el registro de
marcas de fábrica, colectivas, defensivas, de servicio, lemas
comerciales, nombres comerciales, enseñás, variedades
vegetales y denominaciones de origen; su renovación, traspaso,
cambio de nombre o domicilio, cancelación voluntaria; y el
registro de licencias de uso de esos derechos; b) Las acciones de
competencia desleal, protección del consumidor, oposiciones u
observaciones, cancelación administrativa y judicial, nulidad,
medidas cautelares, concesión de licencias, la tutela, la
obtención de secretos industriales, y en general los juicios
civiles, penales, administrativos o contencioso-administrativos
relacionados con estos derechos; acciones y procesos que
promovamos o se nos promuevan. Y para que en todos los
casos arriba determinados, puedan sustituir este mandato,
mediante, conciliar, admitir los hechos del proceso, desistir,
cancelar, recibir, renunciar, y ratificar los actos de agentes
licuados.

In due compliance with the terms of paragraph 1st. of article 543
of the Commercial Code, do hereby appoint EMILIO FERRERO,
tpa. 31929; GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA
DE PAEZ, tpa. 23555 and GERMAN CAVELIER, tpa. 832,
domiciled at Carrera 4ª N° 72-35, Bogotá, Colombia, the first as
principal and the others as alternates, in the order of their
appointment, as our representatives for all industrial property
matters with faculty to receive notifications and to appoint
attorneys in and out of Court. The first alternate shall replace
the principal in case of his absence or of temporal or definitive
impediment. The same rule will apply when the second
alternate representative is to replace the first one, or when the
third is to replace the first or second alternates in their turn, or
both of them, second. In such cases, the principal
representative, or the first or second alternates in their turn, or
both of them, shall state their intention not to act as
representatives through a declaration given before a Notary
Public in Colombia, or before a Notary or another Public Official
or a Colombian Consul abroad; and in case of impediment, the
appropriate certificate shall suffice. If any of the appointees
were to be definitely absent, the following alternate shall take
his place. When the absence or impediment of the principal
representative, or of the first or second alternate in their turn
ceases, the representation can be taken again in their sequence,
by the principal, the first or second alternate depending on case,
and the mere fact or its exercise will suffice. The exercise of the
representation by the first, second or third alternates in their
turn shall end at such time.

In addition, we grant a Power of Attorney in favor of the
above-named attorneys-at-law so that they may obtain the
protection of my (our) industrial property and against the
unfair competition, for which purpose I (we) authorize the said
attorneys to represent me (us) before any authorities or persons,
with or without jurisdiction, specially those administrative,
administrative contentious and judicial, as well as before
Arbitration Court, in all matters concerning the following: a)
Obtainment of patents, utility models and industrial designs;
the registration of trademarks, collective, defensive and service
marks, slogans, commercial names, trade emblems, vegetal
varieties and denominations of origin; its renewal, assignment;
change of name or domicile, voluntary cancellation; and the
registration of licenses of use of the above rights; b) Actions of
unfair competition, protection to the consumer, oppositions or
observations, administrative or Court cancellation, nullity,
infringement, and the action for writ
mandamus, for the purpose of obtaining, and in general the
civil, penal and administrative actions relating to those rights;
actions and suits instituted by me (us) or against me (us). And
that in all the above matters they may substitute this Power of
Attorney, compromise, admit the facts of the case,
desist, cancel, receive, resign and ratify acts done by
representatives without a power of attorney.

JUAN MANUEL EOT, REGINA
NOTARIO

Given and signed this / Dado y firmado hoy
Gothenburg 19 February 1999

In/en

TRADUCCION No: 1707199
MARIA ELVI A MARTELO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2879 Min. Justicia

Signature

Firma

Bengt Forshult
Head of Patent Department

SCA Hygiene Products AB

CAVELIER ABOGADOS
PROFESORES (MINUTA) 12.1.12.5

LEGALIZACION.

LEGALIZATION

El Señor Cónsul de Colombia debe expedir un certificado consular sobre (1) la existencia legal de la compañía que otorga el poder, (2) que ésta ejerce su objeto social, y (3) que las personas que otorgan el poder están autorizadas para darlo. A este efecto les solicitamos que muestren al Señor Cónsul las pruebas que acreditan esos hechos (1), (2) y (3).

The Colombia Consul must issue a consular certificate, on (1) the legal existence of the company which grants the Power-of-Attorney, (2) that it is in actual exercise of its company purposes, and (3) that the persons who execute the Power of Attorney is authorized to do so. To this effect, please show the Consul the evidence to prove the above facts (1), (2) and (3).

NO SE ASUME RESPONSABILIDAD DEL TEXTO
2009 FEB 14 A 11:50
DE LEGALIZACIONES
SECRETARIA DE GOBIERNO

TRADUCCION No. 1707/99
MARIA ELVIRA MARQUELO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2879 Min. Justicia

I, the undersigned, RICKARD STRÖM, Notary Public of Gothenburg, Sweden, do hereby certify,

that Bengt Forshult

has personally signed this document overleaf, and

according to a Power of Attorney, dated 1998-08-11, signed by GUNNAR ANDERSSON and SVEN-ERIK WINLÖF, who are duly authorized

to sign jointly for and on behalf of

HYGIENE PRODUCTS AKTIEBOLAG - Org.No. 556007-2356

According to a Swedish Certificate of Registration, dated 1998-07-20, Bengt Forshult is duly authorized

to sign such a document on behalf of the company.

Gothenburg, this 25th day of February 1999

Exp. No.: 79234

Fee: SEK 350:-

MINISTERIO DE RELACIONES EXTERIORES

Exp. No.: 79234
Fee: SEK 350:-

COMO NOTARIO SEXTO DEL CIRCULO DE BOGOTA, HAGO CONSTAR QUE LA FOTOCOPIA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA

NO. 3066 01 OCT 2002

The Ministry for Foreign Affairs in Stockholm, hereby certifies that

Mr. Rickard Ström, Notary Public of Gothenburg, has issued and signed the foregoing attestation in his official capacity

Fee Stockholm this 2nd day of March

Kr 120/- PAID 1977

Handwritten signature: Bengt Forshult

MARIA SMITH RUEDA Encargada de las Funciones Consulares

Handwritten signature: Maria Smith Rueda

Fecha 1999-03-05

No. 022

que el señor Bengt Forshult
ejercía para la representación de la Sociedad SCA Hygiene Products Aktiebolag
según se ha acordado en los documentos que tuve a la vista.

PAGADO
Impuesto de Timbre
Dólares US\$ 7
Dólares US\$ 100

EL CONSUL DE COLOMBIA

CERTIFICA:

que el señor Bengt Forshult

NOTA PARA EL SEÑOR CONSUL DE COLOMBIA: Según los artículos 65 del C. de P.C. y 480 del C. de Co., si el poderdante es una sociedad, el Señor Cónsul debe certificar que tuvo a la vista las pruebas de su existencia, que ejerce su objeto social y que quien confiere el poder es su representante:



WITODERE-173 (MINOTA 121.125)

COMME
JUAN DEL T

9:

CION
IAD

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JEFL
S2A

TRADUCCION No: 1707199
MARIA ELVIRA MARTELO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No 2879 Min. Justicia

MINISTERIO DE RELACIONES
EXTERIORES

Maria Smith Rueda
202032
Cuya firma aparece en el
DOCUMENTO DESEMPENA
LAS FUNCIONES INDICADAS

MINISTERIO DE RELACIONES
EXTERIORES
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ANULADO
JEFE DE LEGALIZACIONES
SANTAFE DE BOGOTA D.C.
NO SE ASUME
RESPONSABILIDAD DEL TEXTO
Cuya firma aparece en el
DOCUMENTO DESEMPENA
LAS FUNCIONES INDICADAS

COMO NOTARIO SEXTO DEL CIRCULO
EL BOGOTA, HAGO CONSTAR QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA
01 OCT 2001
MEDINA



EL CONSULADO DE COLOMBIA EN
ESTOCOLMO, SUECIA

Fecha.....1999-07-01..... No: 001329

Previa la confrontación correspondiente DA
FE de que la firma que aparece en este docu-
mento es similar a la REGISTRADA aquí por

Inger Höglberg, M. Tel. 0800 123 456
Superiores, Suecia

M. Smith
MARIA SMITH RUEDA
Encargada de las Funciones Consulares



PAGADO

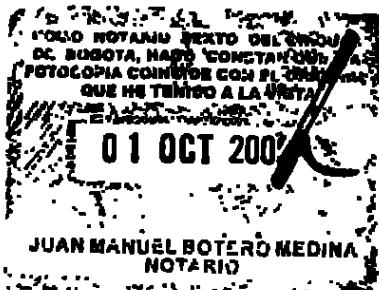
Impuesto de Timbre

Diez dólares US\$ 7

Derechos Consulares

Quince dólares US\$ 15

TRADUCCION No: 1729799
MARIA ELVIRA MARTELO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2879 Min. Justicia



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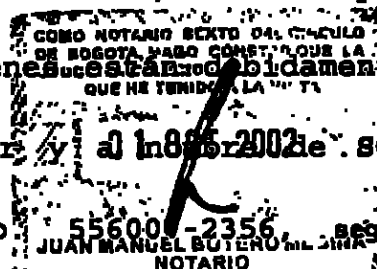
TRADUCCIÓN OFICIAL No. 17.07/99 preparada por María Elvira Martelo, Traductora Oficial aprobada por el Ministerio de Justicia por Resolución 2879 de 1995 y reconocida por el Ministerio de Relaciones Exteriores.

(A continuación se traducen los sellos y legalizaciones de un documento escrito en inglés y español, por el cual SCA HYGIENE PRODUCTS AB otorga poder a EMILIO FERRERO, GONZALO PERDOMO, LUZ CLEMENCIA DE PAEZ Y GERMAN CAVELIER). Dado y firmado el 19 de febrero de 1999 en Gothenburg. (Firma ilegible) Bengt Forshult, Jefe del Departamento de Patentes.

Yo, el abajo firmante RICKARD STRÖM, Notario Público de Gothenburg, Suecia, por el presente certifico,

que Bengt Forshult

ha firmado personalmente el documento anterior y

que de acuerdo con el poder de fecha 1998-08-11, firmado por GUNNAR ANDERSSON y SVEN-ERIK WINLÖF, quienes  están debidamente

autorizados para firmar conjuntamente por y a nombre de SCA

HYGIENE PRODUCTS AKTIEBOLAG - Org. No. 55600-2356, según

Certificado de Registro Sueco de fecha 1998-07-20, Bengt Forshult está

debidamente autorizado para firmar dicho documento a nombre de la compañía.

Gothenburg, 25 de febrero de 1999.

Ex oficio: (Firma ilegible), RICKARD STRÖM (Sello notarial).

Exp. No.: 79234

Derechos: SEK 350:--

No. 3066

El Ministerio de Relaciones Exteriores en Estocolmo por el presente certifica que el Sr. Rickard Ström, Notario Público de Goteborg, ha expedido y firmado la declaración anterior en su capacidad oficial.

Derechos Estocolmo, 25 de marzo

Kr. 120 PAGADOS de 1999

(Firma ilegible) Inger Högberg. (Sello en tinta) Ministerio de Relaciones Exteriores.

(En español) Certificación de la capacidad legal de Bengt Forshult y de la existencia legal de SCA HYGIENE PRODUCTS AKTIEBOLAG expedida el 5 de marzo 1999 por el Consulado de Colombia en Estocolmo bajo el No. 022. (Firma) M. Smith. MARÍA SMITH RUEDA, Encargada de las Funciones Consulares. Sello consular en tinta. Pagados impuesto de timbre y derechos consulares.

(En español) Certificación de la firma de Inger Högberg, Ministerio de Relaciones Exteriores, Suecia expedida el 01 de julio de 1999 por el Consulado de Colombia en Estocolmo bajo el No. 001329. (Firma) M. Smith. MARÍA SMITH RUEDA, Encargada de las Funciones Consulares. Sello consular en tinta. Pagados impuesto de timbre y derechos consulares.

COMO NOTARIO SEXTO DEL CIRCULO DE BOGOTA, HAGO CONSTAR QUE LA FOTOCOPIA COINCIDE CON EL ORIGINAL
01 OCT 2002
MARIA SMITH RUEDA
NOTARIO

(Al anverso) Legalización de la firma que antecede expedida por

el MINISTERIO DE RELACIONES EXTERI RES bajo el No. 119916 del 14 de febrero del 2000, firmado por el Jefe de Legalizaciones.

Es traducción fiel y completa de la cual se deja copia en esta oficina para su confrontación.

COLO 11256-801-014-7

Id. 108

Feb. 15/00

Maria Elvira Martelo
TRADUCCION No. 110799
MARIA ELVIRA MARTELO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2879 Min. Justicia

MINISTERIO DE RELACIONES EXTERI RES
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CIVIL MARTELO
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LAS FUNCIONES INDICADAS

COMO NOTARIO DEL CIRCULO
DE BOGOTA, HAGO CONSTAR QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA
01 OCT 2002
JUAN MANUEL BOTERO MEDINA
NOTARIO

NO SE ASUME
RESPONSABILIDAD DEL TEXTO
2000 FEB 15/00
Jefe de Legalizaciones
SANTAFÉ DE BOGOTÁ D.C.

COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE LA FIRMA

[Handwritten signature]

CONCIDE(N) CON LA FIRMA REGISTRADA POR EL (ELLOS) EN ESTA NOTARIA

SANTAFE DE BOGOTA, 16 FEB 2000



COMO NOTARIO SEXTO DEL CIRCULO DE BOGOTA, HAGO CONSTAR QUE LA FOTOCOPIA CONCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA

01 08 2002

JUAN MANUEL SUTERO MEDINA
NOTARIO

COPIA DE LA FIRMA

2002

2002

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 October 2001 (18.10.2001)

PCT

(10) International Publication Number
WO 01/77437 A1

(51) International Patent Classification²: D21H 21/18, 23/10, 27/00 // 21/20

(21) International Application Number: PCT/SE01/00612

(22) International Filing Date: 22 March 2001 (22.03.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0001268-2 6 April 2000 (06.04.2000) SE

(71) Applicant (for all designated States except US): SCA HYGIENE PRODUCTS AB [SE/SE]; S-405 03 Göteborg (SE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): SANDBERG, Susann [SE/SE]; Gubbekullavägen 15, S-439 35 Onsala (SE). ANDRIASSON, Bo [SE/SE]; Parkgatan 29, S-852 38 Sundevall (SE).

(74) Agent: GÖTEBORGS PATENTBYRÅ DAHLS AB; Sjöporten 4, S-417 64 Göteborg (SE).

(81) Designated States (national): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

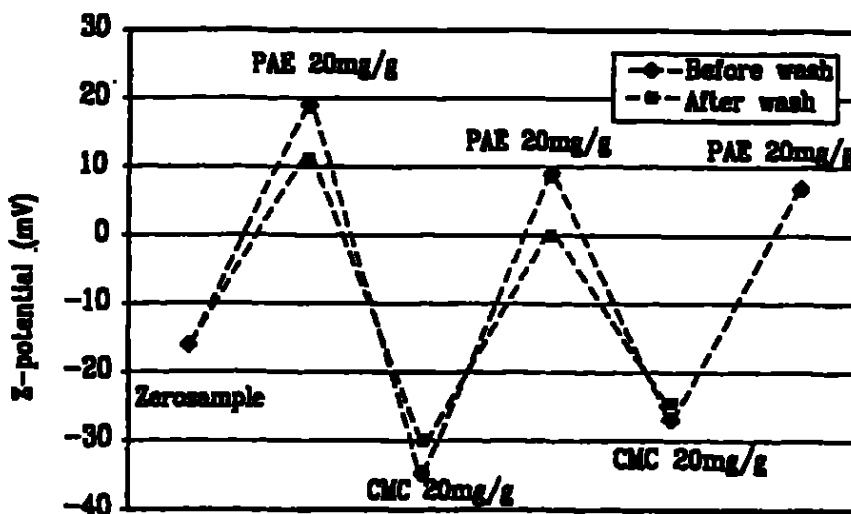
(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF ADSORPTION OF CATIONIC AND ANIONIC POLYMERS ON THE SURFACE OF PARTICLES AND PAPER OR NONWOVEN PRODUCT CONTAINING SUCH PARTICLES



(57) Abstract: Method of producing a particle or group of particles intended for use in paper- and/or nonwovensmaking and having a coating of at least two, preferably at least three, outside each other located thin layers of alternating cationic and anionic polymers, at which the particle or group of particles is treated in consecutive steps with solutions of the alternating cationic and anionic polymers. The amount of the respective polymer to be added in each step is controlled by charge measurements of the treatment solution or a liquid containing the particles or group of particles and the polymer solution, after the treatment in each step in order to determine that substantially all polymer is adsorbed to the particle surface. It is also referred to a paper- or nonwoven product containing fibres and/or fillers produced according to the method. It is further referred to paper products containing increased amounts of wet strength agent and to tissue paper having improved wet strength.

WO 01/77437 A1

Claims

1. Method of producing a particle or group of particles intended for use in paper- and/or
5 nonwovenmaking having a coating of at least two, preferably at least three, outside each
other located thin layers of alternating cationic and anionic polymers, at which the
particle or group of particles is treated in consecutive steps with solutions of the
alternating cationic and anionic polymers,
characterized in
10 that the amount of the respective polymer to be added in each step is controlled by
charge measurements of the treatment solution or a liquid containing the particles or
group of particles and the polymer solution, during and/or after the treatment in each
step in order to determine that substantially all polymer is adsorbed to the particle
surface.
15
2. Method as claimed in claim 1,
characterized in
measuring the Z-potential of the particles or groups of particles during and/or after the
treatment in each step in order to determine the amount of cationic/anionic polymer
20 adsorbed to the particle surface.
3. Method as claimed in claim 1 or 2,
characterized in
that the particle is a fiber.
25
4. Method as claimed in claim 3,
characterized in
that the fiber is a cellulosic fiber.
- 30 5. Method as claimed in claim 3,
characterized in
that the fiber is a synthetic or regenerated fiber.
- 35

12. Tissue paper based on wood pulp cellulose with no admixture of other types of fibers, such as synthetic reinforcing fibers, characterized in that it has a wet tensile index of at least 6,5, preferably at least 7,0 and more preferably at least 7,5 Nm/g.
- 5
13. Tissue paper as claimed in claim 12, characterized in that it contains at least three, outside each other located thin layers of alternating cationic and anionic polymers.
- 10

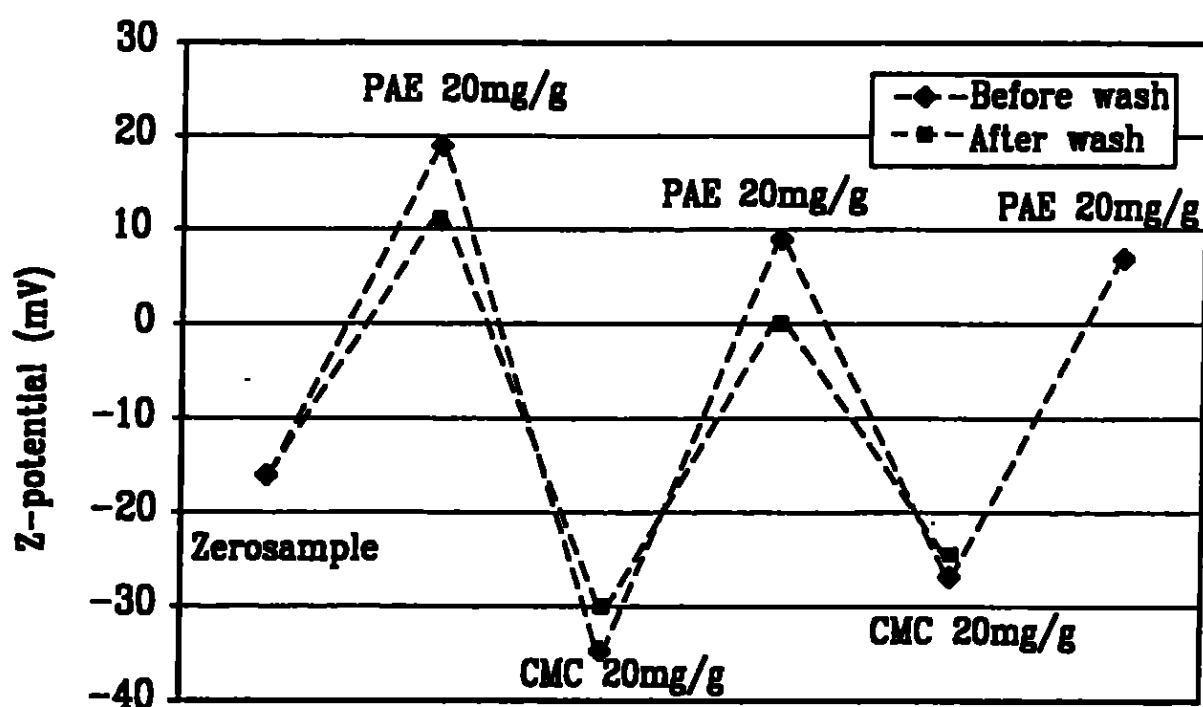


FIG.1

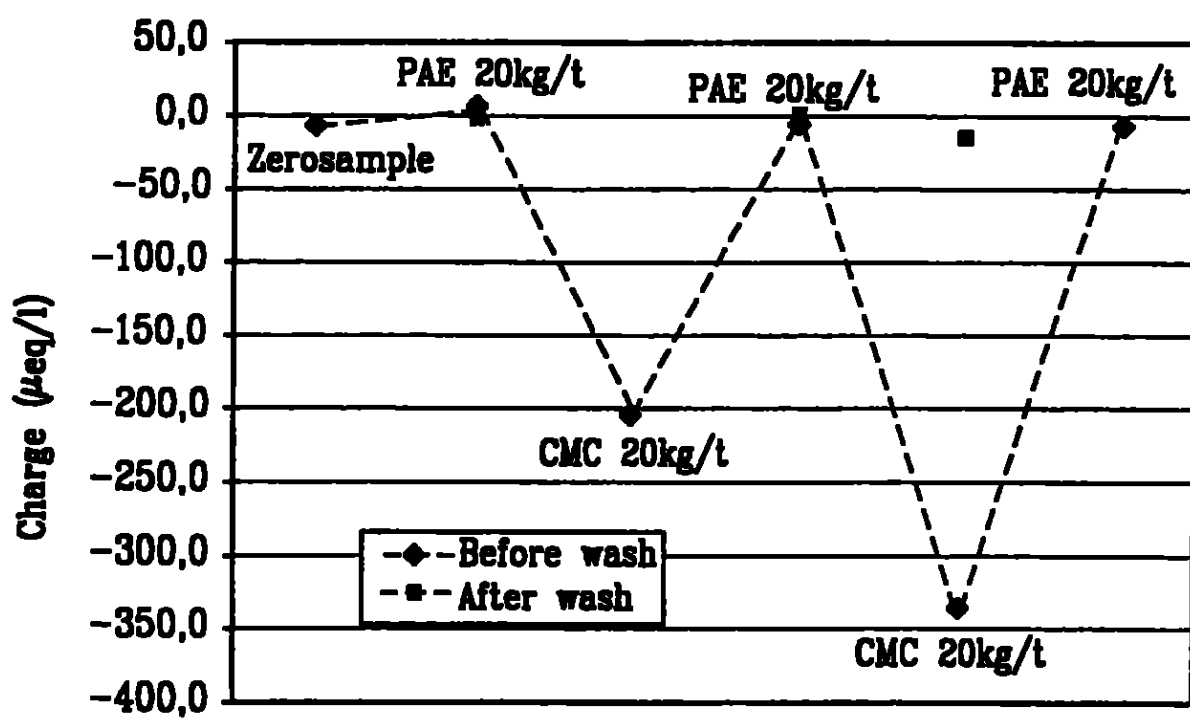


FIG.2

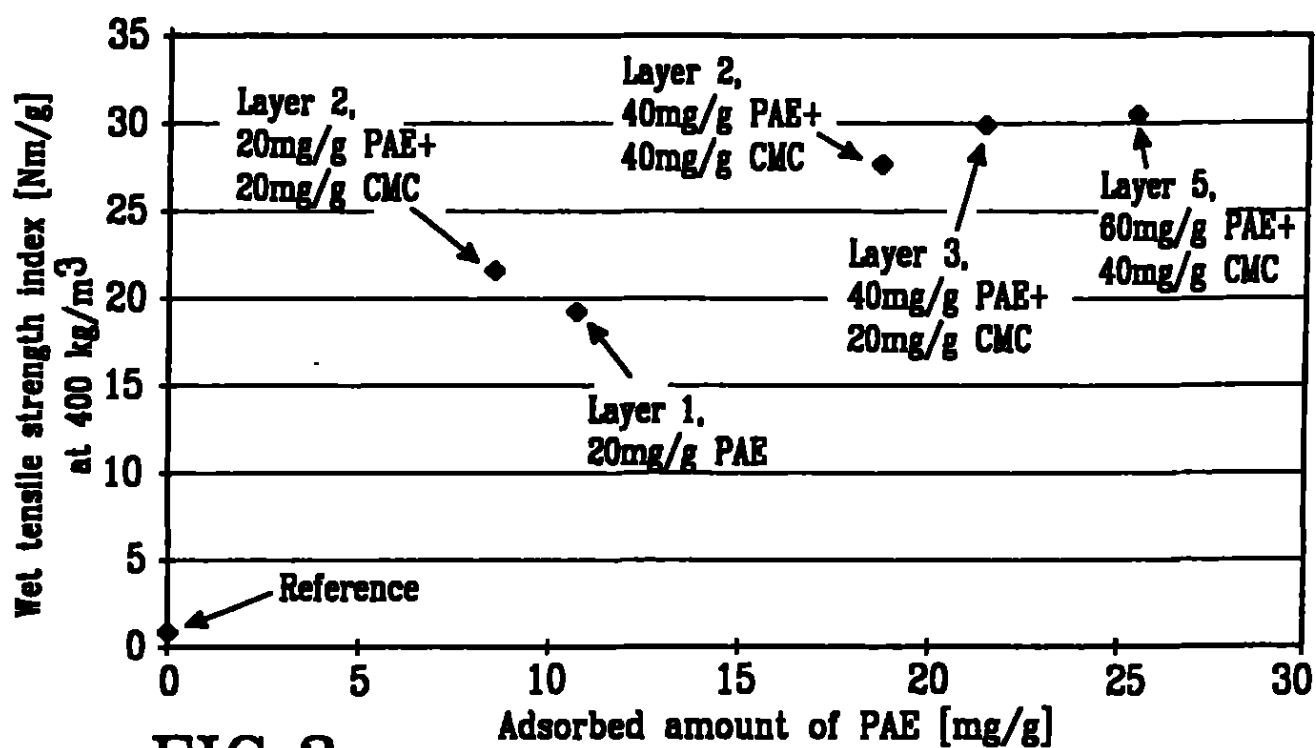


FIG.3

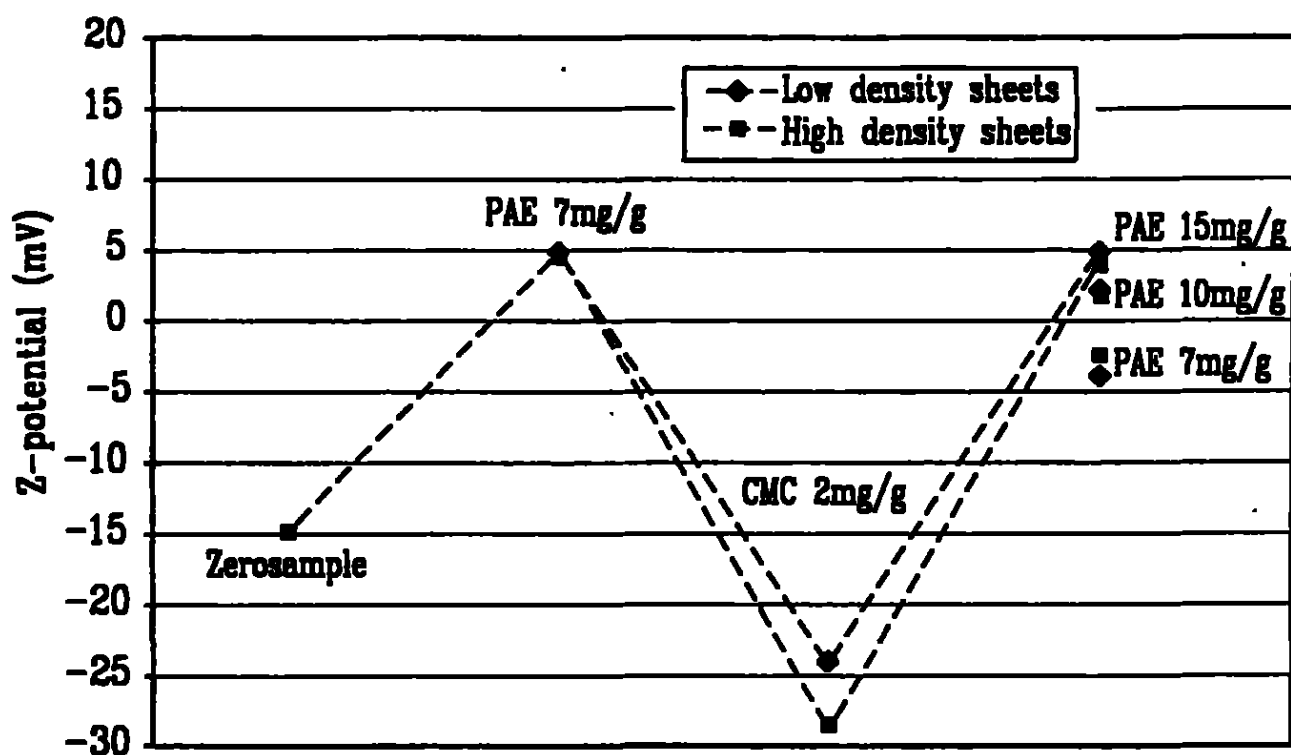


FIG.4

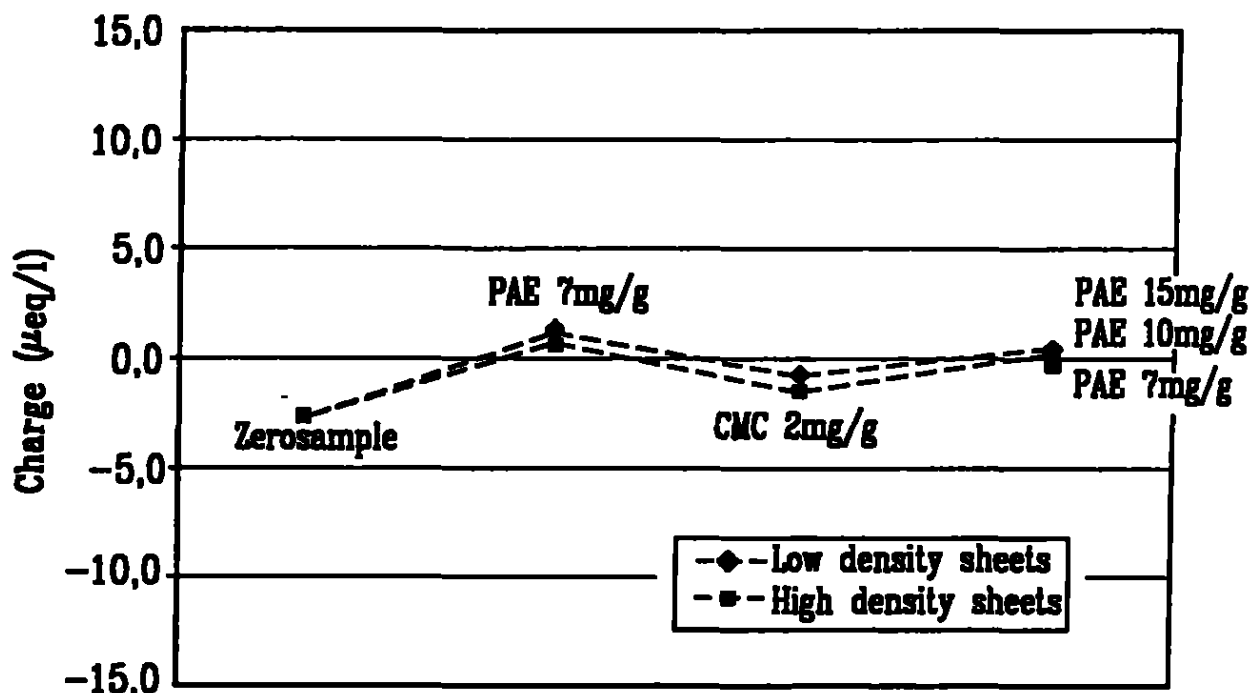


FIG. 5

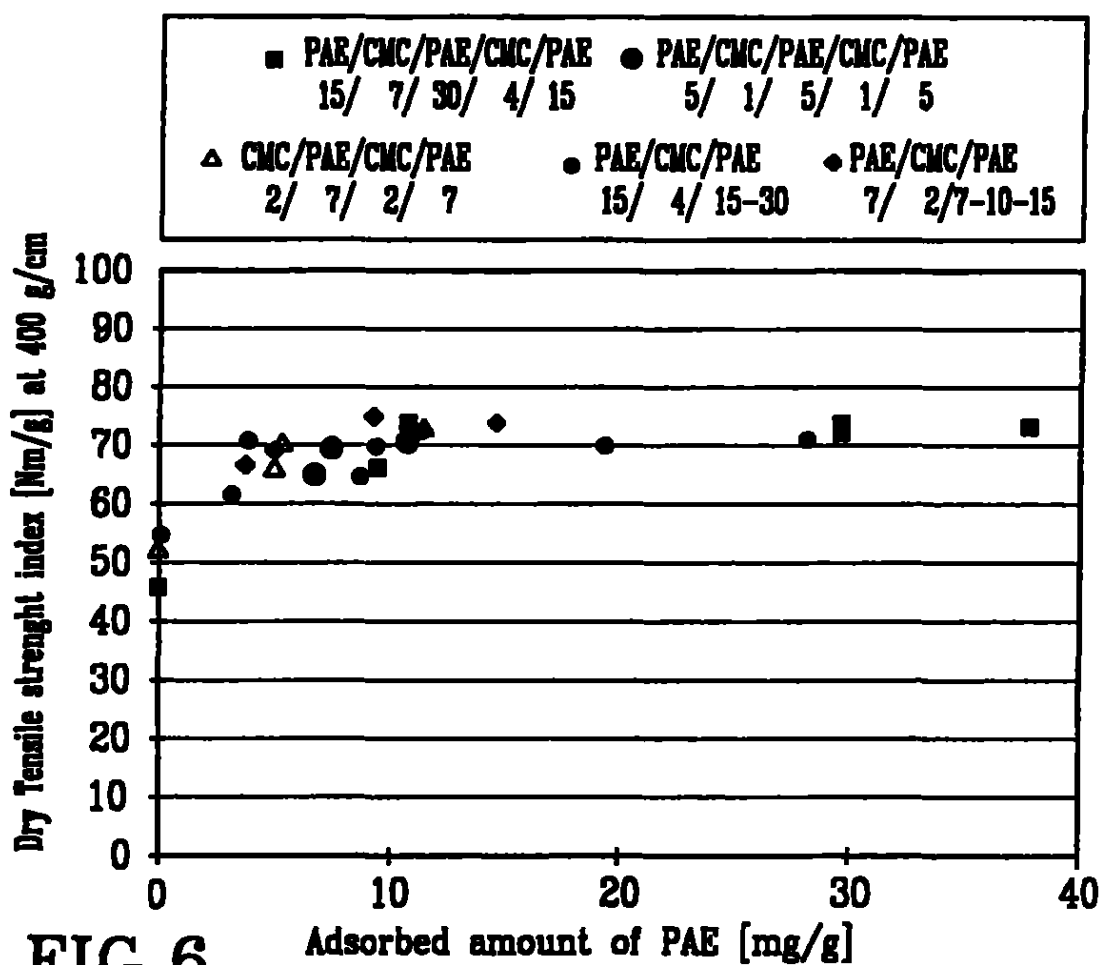


FIG. 6

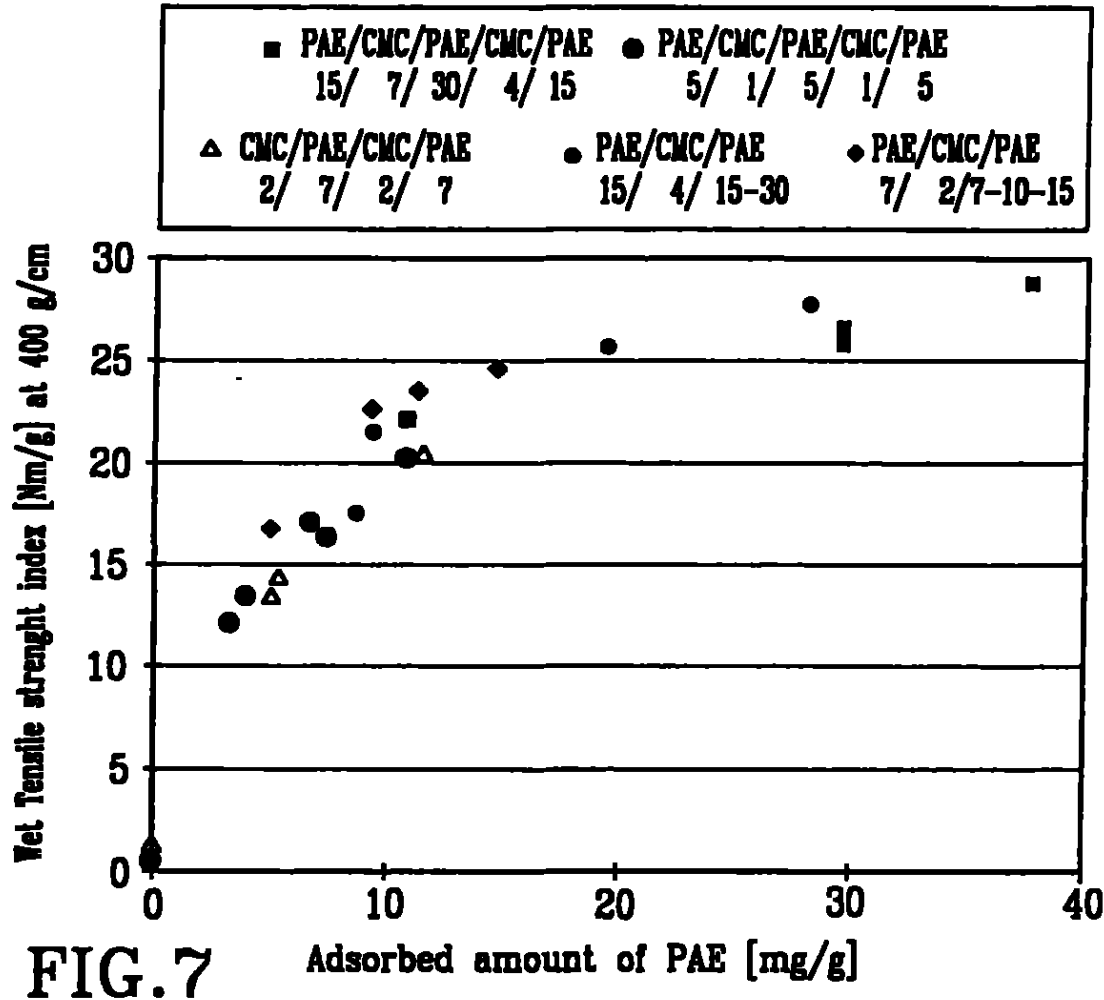


FIG.7

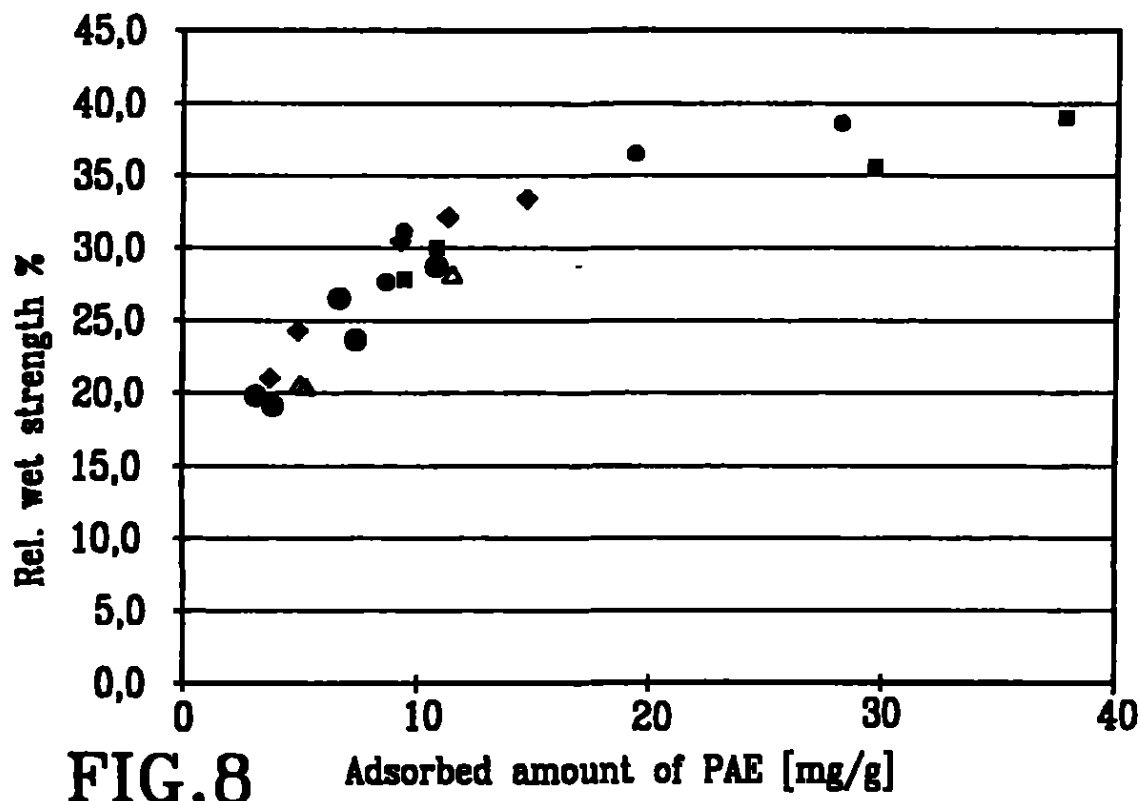


FIG.8

1
INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 01/00612

A. CLASSIFICATION OF SUBJECT MATTER				
IPC7: D21H 21/18, D21H 23/10, D21H 27/00 // D21H 21/20 According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols)				
IPC7: D21H				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
SE,DK,FI,NO classes as above				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
A	EP 0835957 A2 (FORT JAMES CORPORATION), 15 April 1998 (15.04.98), claim 1, 9; abstract --	1-13		
A	WO 9945201 A1 (KIMBERLY-CLARK WORLDWIDE, INC.), 10 Sept 1999 (10.09.99), page 33, claims 1-3 --	1-13		
A	US 5783041 A (RICHARD T. UNDERWOOD), 21 July 1998 (21.07.98), abstract --	1-13		
A	WO 9532335 A1 (MINERALS TECHNOLOGIES INC.), 30 November 1995 (30.11.95), abstract --	1-13		
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; border: none;"> * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "F" earlier application or patent but published on or after the international filing date "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; vertical-align: top; border: none;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to substantiate the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family </td> </tr> </table>			* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "F" earlier application or patent but published on or after the international filing date "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to substantiate the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "F" earlier application or patent but published on or after the international filing date "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to substantiate the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family			
Date of the actual completion of the international search		Date of mailing of the international search report		
9 July 2001		11 -07- 2001		
Name and mailing address of the ISA Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer Barbro Nilsson/ED Telephone No. +46 8 782 25 00		

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 01/00612

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0560556 A1 (OJI PAPER COMPANY LIMITED), 15 Sept 1993 (15.09.93), page 4, lines 33-35, line 55 - page 5, line 1; claim 1 --	12
P,A	WO 0032702 A1 (SCA HYGIENE PRODUCTS AB), 8 June 2000 (08.06.00), pages 6-7; claims 1, 9; abstract	1-11
P,X	 ----- --	12-13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE01/00612

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 12 in part
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

see next sheet

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

- I Claims 1-11 comprising a method and paper or nonwoven products**
- II Claims 12-13 comprising tissue paper**

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT**International application No.
PCT/SE01/00612****Box I.2**

Present claim 12 relates to a tissue paper defined by reference to a desirable characteristic or property, namely a wet tensile index over at least 6,5 Nm/g. The claim cover all tissue papers having this characteristic or property, whereas the application provides support within the meaning of Article 6 and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such paper. In the present case, the claim so lacks support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claim, which appear to be supported and disclosed, namely relating to a paper produced with the method according to the invention.

INTERNATIONAL SEARCH REPORT
Information on patent family members

02/07/01

International application No.
PCT/SE 01/00612

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
EP	0835957	A2	15/04/98	NONE		
WO	9945201	A1	10/09/99	AU	3312499 A	20/09/99
				BR	9908420 A	26/12/00
				CN	1292838 T	25/04/01
				EP	1068390 A	17/01/01
				US	5935383 A	10/08/99
US	5783041	A	21/07/98	AU	2667297 A	07/11/97
				WO	9739189 A	23/10/97
WO	9532335	A1	30/11/95	AU	702265 B	18/02/99
				AU	2438495 A	18/12/95
				BR	9507737 A	19/08/97
				CA	2190827 A	30/11/95
				CN	1148877 A	30/04/97
				CZ	9603360 A	14/05/97
				EP	0797704 A	01/10/97
				FI	964626 A	19/11/96
				HU	77823 A	28/08/98
				HU	9603207 D	00/00/00
				IL	113721 A	11/04/99
				JP	10505883 T	09/06/98
				NO	964740 A	11/12/96
				NZ	285321 A	27/04/98
				PL	317223 A	17/03/97
				RU	2138592 C	27/09/99
				SK	147396 A	06/08/97
EP	0560556	A1	15/09/93	DE	69314202 D,T	14/05/98
				JP	2826586 B	18/11/98
				JP	5253160 A	05/10/93
				JP	5277053 A	26/10/93
				JP	2630164 B	16/07/97
				JP	5285083 A	02/11/93
				CA	2093985 A	16/10/93
				JP	5286100 A	02/11/93
				JP	6017364 A	25/01/94
				JP	2621742 B	18/06/97
				JP	6017365 A	25/01/94
WO	0032702	A1	08/06/00	AU	1903500 A	19/06/00
				SE	9804123 A	31/05/00

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

GÖTEBORGS PATENTBYR DAHLS AB
Sjöporten 4
S-417 64 Göteborg
SUEDE

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

LEID

Date of mailing
(day/month/year)

19.06.2002

Applicant's or agent's file reference
p15905pc/js

IMPORTANT NOTIFICATION

International application No.
PCT/SE01/00612

International filing date (day/month/year)
22/03/2001

Priority date (day/month/year)
08/04/2000

Applicant

SCA Hygiene Products AB

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



European Patent Office
D-80299 Munich
Tel. +49 89 2399 - 0 Tlx 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Jacobus Prues, S

Tel. +49 89 2399-8113



PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference p15805pc/js		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/SE01/00612	International filing date (day/month/year) 22/03/2001	Priority date (day/month/year) 06/04/2000	
International Patent Classification (IPC) or national classification and IPC D21H21/18			
Applicant SCA Hygiene Products AB			
1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of 5 sheets, including this cover sheet. ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). These annexes consist of a total of 3 sheets.			
3. This report contains indications relating to the following items: - I ☒ Basis of the report - II ☐ Priority - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability - IV ☐ Lack of unity of invention - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement - VI ☐ Certain documents cited - VII ☐ Certain defects in the international application - VIII ☐ Certain observations on the international application			
Date of submission of the demand 12/10/2001		Date of completion of this report 19.06.2002	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80288 Munich Tel. +49 89 2399 - 0 Tlx 523656 epmu d Fax +49 89 2399 - 4485		Authorized officer Nestby, K Telephone No. +49 89 2399 8625 	

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/SE01/00612

I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-16 as originally filed

Claims, No.:

1-12 with telefax of 17/05/2002

Drawings, sheets:

1/4-4/4 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/SE01/00612

- ☐ the drawings, sheets:
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):
- (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-8, 10-12
	No:	Claims	9
Inventive step (IS)	Yes:	Claims	1-8, 10-12
	No:	Claims	9
Industrial applicability (IA)	Yes:	Claims	1-12
	No:	Claims	

2. Citations and explanations
see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. According to Rule 6.3(b)(i) PCT the examiner must conclude that the features of the preamble of claim 1 are "part of the prior art". In fact, such a method is disclosed in EP-A-0 835 957, WO-A-88/45201 and WO-A-85/32335 (hereafter referred to as D2, D3 and D4, respectively).
In addition to the features of the preamble of claim 1, some of the features of the characterizing part of claim 1 are also disclosed in D2 (see claim 1 of D2), i. e. "the amount of the respective polymer to be added in each step is controlled by charge measurements of the treatment solution or a liquid containing the particles or group of particles and the polymer solution, after the treatment ...".

The features which distinguish the method of claim 1 from that disclosed in D2 is thus that charge measurements is carried out during and/or after the treatment in each step, thereby assuring that all polymer (which is added in each step - see page 5, second paragraph of the description) is adsorbed to the particle surface.

The subject-matter of claims 1 to 8 is therefore novel (Article 33(2) PCT).

The advantage of the distinguishing features is that no excess of polymer remains after each step, therefore, no overdose of polymer is necessary in the following step in order to obtain a zero net charge. Overdosing is a disadvantage both from economical, environmental and process stability point of view.

The solution to this problem proposed in claim 1 (as well as in claims 2 to 8 describing particular embodiments of the present application) is considered as involving an inventive step (Article 33(3) PCT) for the following reasons:

Firstly, said prior art problem is convincingly solved. Secondly, there is no hint in the available background art documents towards this solution.

2. Since the features of the characterizing portion of claim 1 are typical method features, the effect of which is not detectable in the produced particle, it

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/SE01/00612

follows that the produced particle or a paper containing said produced particle cannot be distinguished from a particle or a paper containing a particle produced by said prior art method as described in D2, D3 or D4.

Consequently, the paper or nonwoven product of claim 9 is not novel (Article 33(2) PCT).

3. The paper or nonwoven product of claims 10, 11 contains fibres, filler or other particles having at least three layers. It is assumed that the feature "fibres, filler particles or other particles having" (which is present in claim 10) has been "forgotten" in claim 12 (Art. 6 PCT - unclarity). Since the cited documents disclose only two polymer layers, the subject matter of claims 10 to 12 is novel (Article 33(2) PCT).
- 3.1 The applicant alleges that it would not be feasible to arrive at three or more layers by following the teaching of the prior art, i. e. "it is only by controlling the addition of the cationic and anionic polymers in each step so that all polymers is adsorbed to the particle surface, that it is possible to achieve three or more layers." The examiner has no reason to believe that said allegation is wrong.

The subject matter of claims 10 to 12 of the present application can hence be considered as involving an inventive step (Article 33(3) PCT).

Nevertheless, by using the expression "it contains at least 1.5 ..." in lines 4-6 of claim 10, it would appear that it is the paper or nonwoven product ("it") and not necessarily the filler particles which contain said amount of wet strength agent (Art. 6 PCT - lack of clarity).

Please note that D2 discloses anionic and cationic (wet) strength agents.

PATENT COOPERATION TREATY

25

From the INTERNATIONAL BUREAU

PCT

INFORMATION CONCERNING ELECTED OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

To:

GÖTEBORGS PATENTBYRÅ DAHLS AB
Sjöporten 4
S-417 64 Göteborg
SUÈDE

2001 - 10
CA

Date of mailing (day/month/year) 03 December 2001 (03.12.01)		IMPORTANT INFORMATION	
Applicant's or agent's file reference P15905PC/CA			
International application No. PCT/SE01/00612	International filing date (day/month/year) 22 March 2001 (22.03.01)	Priority date (day/month/year) 06 April 2000 (06.04.00)	
Applicant SCA HYGIENE PRODUCTS AB et al			

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

EP : AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE,TR
National : AU,BG,CA,CN,CZ,DE,GB,IL,JP,KP,KR,MN,NO,NZ,PL,RO,RU,SE,SK,US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

AP : GH,GM,KE,LS,MW,MZ,SD,SL,SZ,TZ,UG,ZW
EA : AM,AZ,BY,KG,KZ,MD,RU,TJ,TM
OA : BF,BJ,CF,CG,CI,CM,GA,GN,GW,ML,MR,NE,SN,TD,TG
National : AE,AG,AL,AM,AT,AZ,BA,BB,BR,BY,BZ,CH,CO,CR,CU,DK,DM,DZ,EE,ES,FI,GD,GE,GH,GM,HR,HU,ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MW,MX,MZ,PT,SD,SG,SI,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 38(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer: Claudio BORTON Telephone No. (41-22) 338.83.38
--	--

PATENT COOPERATION TREATY

PCT

NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

GÖTEBORGS PATENTBYRÅ DAHLS AB
Sjöporten 4
S-417 64 Göteborg
SUÈDE2001-10-23
PCT/SE01/0061

Date of mailing (day/month/year) 18 October 2001 (18.10.01)		IMPORTANT NOTICE	
Applicant's or agent's file reference P15905PC/CA			
International application No. PCT/SE01/00612	International filing date (day/month/year) 22 March 2001 (22.03.01)	Priority date (day/month/year) 06 April 2000 (06.04.00)	
Applicant SCA HYGIENE PRODUCTS AB et al			

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
KP, KR, US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AE, AG, AL, AM, AP, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EA, EE, EP, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OA, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ,

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 18 October 2001 (18.10.01) under No. WO 01/77437

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

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**Method of adsorption of cationic and anionic polymers on the surface of particles
and paper or nonwoven product containing such particles**

Technical field

- 5 The present invention refers to a method of producing a particle or group of particles intended for use in paper- and/or nonwovenmaking having a coating of at least two, preferably at least three, outside each other located thin layers of cationic and anionic polymers, at which the particle or group of particles is treated in consecutive steps with solutions of the cationic and anionic polymers. It also refers to a paper or nonwoven
10 product containing such particles or groups of particles. It further refers to paper products containing increased amounts of wet strength agent and to tissue paper having improved wet strength.

Background of the invention

- 15 The increased use of recovered fibers in paper production and the use of components with poorer bonding properties, such as mineral fillers, have increased the need for more effective dry and wet strength agents in the paper. Traditionally two different methods have been used for adding strength improving chemicals to the paper, viz. by adding chemicals at the wet end of the paper process or by surface application by
20 means of a size press. Wet end addition is usually more effective than surface application counted per kg utilized product. In order to maintain the addition made in the wet end in the paper sheet, wet end chemicals are mainly exclusively cationic, and for making them less sensitive to dissolved and colloidal materials and the increased concentration of electrolytes caused by the increased closing of the systems, their
25 cationic charge is usually increased. This leads in turn to a decreased saturation adsorption of the additive chemicals to the fibers, which leads to a reduced maximum effect of the additive chemicals. This involves that there is a need both for new methods of applying strength-improving chemicals to the paper, and new chemical systems.
- 30 Besides there is an increased need for improving the opacity of the finished paper. Since the today most frequently used strength agents contribute negatively to the opacity the need for new methods of developing strength in the paper is further reinforced.

Such a way would be to utilize size presses to a higher extent, but this would however lead to large reductions of the manufacturing capacity and the production economy since the paper has to be dried once further depending on the rewet it is exerted to in the size press.

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This involves that there is a great need for new ways of treating fibers and other particles contained in the paper, such as filler particles, in the wet end of the paper machine.

- 10 It is known to build up thin multilayers of electro active polymers on an electrostatically charged substrate for use in optics, such as sensors, friction reduction etc. This is described in for example in *Thin Solid Films*, 210/211 (1992) 831-835 and in *Thin Solid Films*, 244 (1994) 806-809. The substrate is herewith immersed alternatingly in diluted solutions of a polycation with an intermediate rinsing in order to remove rests
15 of the previous polyion which is not bonded to the substrate. The thickness of each deposited layer is described to be between 5-20Å. There is no indication that the treated substrates could be particles, such as fibers or filler particles.

- 20 In US 5,338,407 there is disclosed a method for improving the dry strength properties of paper, at which an anionic carboxy methyl guar or carboxy methyl hydroxy ethyl guar and a cationic guar is added to the furnish. These two components are either added in mixture or separately. There is no indication that the treatment is made under such conditions that a double layer is built up on the fibers with one component in one layer and the other component in the other layer.

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- In the US patents 5,507,914 and 5,185, 062 there are disclosed methods for improving the dewatering properties and the retention of paper by adding anionic and cationic polymers to the pulp. There is no indication that the treatment takes place under such conditions that a double- or multilayer is created on the pulp fibers with the anionic
30 component in one layer and the cationic component in the other layer.

Dual surface treatment of filler particles with anionic and cationic polymers is disclosed in EP-A-0 850 879, WO 95/32335, US-A-4,495,245 and US-A-4,925,530. There is no indication that the treatment takes place under such controlled conditions that a double-

or multilayer is created on the pulp fibers with the anionic component in one layer and the cationic component in the other layer.

5 In the international patent application PCT/SE99/02149 there is disclosed a method as stated in the introduction above and according to which particles or groups of particles are produced which have a coating of at least two, preferably at least three, outside each other located thin layers of interacting polymers. The particles or groups of particles are treated in consecutive steps with solutions of the interacting polymers, and the
10 respective polymer is added only in such an amount in each step that substantially all polymer is adsorbed to the particle surface. This is accomplished by removing excess of the previous polymer between each treatment step alternatively by adding the respective polymer only in such an amount in each step that substantially all polymer is adsorbed to the particle surface.

15 *The object and most important features of the invention*

The object of the present invention is to provide a method according to above and which offers a way to ensure that each polymer for forming the respective layer on the surface of the particles or group of particles is added only in such an amount in each step that substantially all polymer is adsorbed to the particle surface. This has according
20 to the invention been accomplished by the fact that the amount of the respective polymer to be added in each step is controlled by electric charge measurements of the treatment solution or a liquid containing the particles or group of particles and the polymer solution, after the treatment in each step in order to determine that substantially all polymer is adsorbed to the particle surface.

25

In order to determine the amount of cationic/anionic polymer adhered to the particle surface the Z-potential of the particles or groups of particles may be measured.

30 The particles or groups of particles may be of optional type, however fibers, e g cellulosic fibers, regenerated fibers and different types of synthetic fibers, and filler particles are mainly concerned.

The interacting polymers are preferably alternating cationic and anionic polyelectrolytes, but they may also be so called zwitter ions.

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According to one embodiment of the invention the particles are cellulose fibers for papermaking and at least one of the polymers is a strength additive such as a wet and/or dry strength agent.

- 5 The invention also refers to a paper- or nonwoven product, which contains fibers and/or filler particles produced by the method described above. The term paper used herein refers to all types of paper, such as tissue paper, graphical paper, linerboard, wiping material etc. The nonwoven material could be of optional type.
- 10 The invention further refers to paper products containing increased amounts of wet strength agent and to tissue paper having improved wet strength.

Description of drawings

- 15 Fig. 1 shows the results of Z-potential measurements of cellulose fibres treated in consecutive steps with cationic and anionic polymers in the form of PAE (polyamino-amide-epichlorhydrine) and CMC (carboxy methyl cellulose).

Fig. 2 shows the result of charge measurements of the colloidal phase before and after washing the fibers in the trial of Fig. 1.

- 20 Fig. 3 shows the wet strength tensile index of 30 gsm paper sheets made from the treated fibers vs. adsorbed amount of PAE.

Fig. 4 shows Z-potential of the fibres after addition of PAE / CMC / PAE.

Fig. 5 shows the charge of the colloidal phase from PCD measurements after addition of PAE / CMC / PAE.

Fig. 6 shows the dry tensile strength index vs. adsorbed amount of PAE.

- 25 Fig. 7 shows the wet tensile strength index vs. adsorbed amount of PAE.

Fig. 8 shows relative wet strength vs. adsorbed amount of PAE.

Description of the invention

- 30 According to the present invention particles or groups of particles, e g fibers or filler particles, are treated with alternating cationic and anionic polymers in order to build up thin multilayers of the interacting polymers on the particle surface.

- The particles are treated in consecutive steps with solutions of the alternating cationic and anionic polymers, at which the treatment time for each step is sufficient for
35 forming a layer of the desired molecular thickness. For particles or groups of particles

having an anionic surface, which for example is the case for cellulosic fibers, the first layer should be a cationic polymer, and vice versa. By adding the polymers in consecutive steps and letting them form several layers on the particle surface, it is possible to adsorb higher amounts of polymer to the particle surface than is possible when adding them in one step intermixed forming only one layer.

The addition is controlled in such a way that substantially no excess amount of the respective polymer is added in each step, so that substantially all polymer is adsorbed to the particle surface. This is made by measuring the electric charge of the treatment solution or the liquid in which the treated particles or groups of particles are contained. After having allowed the polymer to adsorb to the particle surface a certain period of time the electric charge of the solution should be close to zero. The charge measurements are made with streaming potential measurement, e g with a PCD instrument (Particle Charge Detector).

In order to determine the amount of cationic/anionic polymer adhered to the particle surface the Z-potential is measured according to the method described below.

The method according to the invention for building the desired multilayers is based on electrostatic attraction between oppositely charged polyelectrolytes. By treating the particles in consecutive steps with a solution containing polyions of opposite charge and permit these spontaneously to adsorb to the particle surface, multilayers of the stated kind are built up. In principle all types of polyelectrolytes may be used.

According to one embodiment the method is used for adsorbing strength additives to cellulosic fibers used for papermaking. Since the cellulose fiber has an anionic surface the first polymer to be adsorbed is a cationic polymer. This may for example be polyaminoamide-epichlorhydrine (PAE) or glyoxylated polyacryl amide (G-PAM). This layer will make the fibre surface cationically charged. In a next step an anionic polymer, e g CMC (carboxy methyl cellulose), is added. The fiber surface will then turn anionic again. Then the next layer of cationic polymer can be added and so on.

Through such a treatment cellulose fibers higher amounts of strength additives,

e g PAE or G-PAM, can be adsorbed to the fiber surface than is possible with conventional techniques, which will result in improved strength properties of the paper produced.

It is of course also possible to make new types of surface modifications to particles or groups of particles through consecutive adsorption of thin layers of interacting polymers according to the invention. By for example treating fibers with consecutive layers of hydrophobic, charged polyelectrolytes it would be possible for example to develop new types of hydrophobizing chemicals for the hydrophobization of paper. It would also be possible to build up "intelligent" surface layers on fibers, which alter the properties with temperature, pH, salt content etc.

Further applications are ion-exchanging fibers where "membranes" with ion-exchanging properties are provided on the fiber surface, wet strength agents where the added polymers are reactive with the fibers and with each other, in order to provide permanent bonds between the fibers and for the production of highly swelling surface layers, where the added chemicals form swollen gel structures on the fiber surface for use in absorbent hygiene products. Another possible application are new types of fibers for printing paper, where the adsorbed polymers change colour when they are exerted to an electric, magnetic or electromagnetic field. Such polymers are available today.

The fibers that are treated with the method according to the invention can be of optional kind, natural as well as synthetic fibers. Mainly cellulosic fiber are concerned. However it would be possible to treat synthetic fibers, for example for giving them a more hydrophilic surface.

Also groups or agglomerates of fibers or particles can be treated according to the method.

Examples of suitable anionic and cationic polyelectrolytes which may be used in the method according to the invention are given below.

Anionic polyelectrolytes: Anionic starch with different degrees of substitution, anionic guar, polystyrene sulfonate, carboxy methyl cellulose with different degrees of substitution, anionic galactoglucomannan, polyphosphoric acid, polymethacrylic acid,

polyvinyl sulphate, alginate, copolymers of acryl amide and acrylic acid or 2-acrylic amide-2-alkylpropane sulphonic acid.

Cationic polyelectrolyte: Cationic galactoglucomannan, cationic guar, cationic starch, polyvinyl amine, polyvinyl pyridine and its N-alkyl derivatives, polyvinyl pyrrolidone, chitosan, alginate, modified polyacryl amides, polydiallyl dialkyl, cationic amide amines, condensation products between dicyane diamides, formaldehyde and an ammonium salt, reaction products between epichlorohydrine, polyepichlorohydrine and ammonia, primary and secondary amines, polymers formed by reaction between ditertiary amines or secondary amines or dihaloalkanes, polyethylene imines and polymers formed by polymerisation of -(dialkylaminoalkyl)acrylic amide monomers.

Example 1

The polymers used during the tests are listed in Table 1 below.

Table 1.

Name	Polymer	Supplier	D.S.*	Viscosity (mPas)
Kenores 1440	Polyaminoamide-epichlorohydrin, (PAE)	EKA Chemicals		
Parez 631 NC	Glyoxalated polyacrylamide, (G-PAM)	Cytec Industries		
Cekol 50000G	Carboxymethyl cellulose, (CMC)	Metsä Speciality Fibres	0.78	7200 (1% conc)
Finnfix BW			0.4-0.6	100-700 (4% conc.)

* D.S. = degree of substitution

The PAE and G-PAM was diluted in deionized water to an active content of 10 g/l before use. The different CMC's were dissolved in deionized water by dispersion using a hand mixer, to a suitable concentration between 5 and 10 g/l depending on the viscosity.

The pulp used was a dried fully bleached TCF, Celeste 85, from SCA Östrand. The pulp was beaten to 25°SR and was diluted with tap water to a concentration of 3 g/l. The pH during the trials was 7.5 and the conductivity was set to 1200 μ S/cm using NaCl.

Three, four and five layers of alternating PAE and CMC were made. The addition of the additives were controlled by measuring the electric charge with Z-potential and PCD instruments. In some tests G-PAM was used instead of or together with PAE. The addition sequence is listed in Table 2 below.

Table 2.

5		Addition (mg/g)								
	Trial	PAE	CMC	PAE	CMC	PAE	G-PAM	CMC	PAE	G-PAM
10	1	20	20	20	20	20				
	2	15	7	30	4	15				
	3	15	4	15						
	4	15	4	30						
	5	7	2	7						
	6	7	2	10						
	7	7	2	15						
15	8	5	1	5	1	5				
	9		2	7	2	7				
	10						7	2	7	
	11						7	2		7
	12	7						2		7

Adsorption time for the additives were 10 minutes.

Furnish preparation

In trial 1 the PAE and CMC additions were considerably overdosed, 20 mg/g pulp. The pulp was then dewatered, washed with deionized water and dewatered again between each step in order to remove the excess of PAE and CMC. This was repeated until five layers were made, starting and ending with PAE, see Table 2 above.

In trials 2-12 the PAE and CMC additions were successively optimised to more realistic levels. Both three, four and five layers were made, see Table 2. The addition of the additives were made with no washing step in between, always controlled by measuring the charge with Z-potential and PCD instruments. Three trials using G-PAM instead or together with PAE were performed in order to evaluate another wet strength additive using the multilayering technique.

Sheet preparation

30 g/cm² sheets were formed in a dynamic sheet former. The sheets were pressed between blotters and then dried under restrained conditions. Two sheets of each sample point were formed and pressed to two different densities, ~350 and ~450 kg/m³. Finally

the sheets were cured for 10 minutes at 105°C. The tensile strength was then interpolated to a density of 400 kg/m².

Charge determinations

5 *Fibre charge determination using a Z-potential instrument*

The Z-potential of the fibres was measured with a streaming potential instrument (Magendans SZ2, supplied by Müttek) [Penniman, J.G., *Comparison of pulp pad streaming potential measurement and mobility measurement*. Tappi Journal, 1992 75 111-115 and Jaycock, M.J.; *Assumptions made in the measurement of zeta-potential by streaming current/potential detectors*. Paper Technology, 1995 36 35-38.19, 20; Barron, W., *et al.*, *The streaming current detector: a comparison with conventional electrokinetic techniques*. Colloids and Surfaces, 1994 88 129-139; Sanders, N.D. and J.H. Schaefer, *Comparing papermaking wet-end charge-measuring techniques in kraft and groundwood systems*. Tappi Journal, 1995 78 142-150.

10 The potential is measured between two electrodes, one screen electrode placed close to the fibre pad, which is formed when pumping it against a screen, and the second electrode is a ring electrode situated on the lower part of the fibre pad. Conductivity is then measured between these two electrodes and a calculated value of the Z-potential (ζ) is presented.

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Colloidal charge determination using a PCD

A PCD 03 (Particle Charge Detector) supplied by Müttek measures a voltage difference induced by a moving charged medium, e.g. colloidal substances in a white water. High molecular mass polymers and colloidal substances attach to the Teflon surfaces of the equipment. The oscillating piston moves and induces a potential difference that is detected [Jaycock, M.J., *Assumptions made in the measurement of zeta-potential by streaming current/potential detectors*. Paper Technology, 1995 36 35-38 ; Barron, W., *et al.*, *The streaming current detector: a comparison with conventional electrokinetic techniques*. Colloids and Surfaces, 1994 88 129-139 and Sanders, N.D. and J.H. Schaefer, *Comparing papermaking wet-end charge-measuring techniques in kraft and groundwood systems*. Tappi Journal, 1995 78 142-150.20-22].

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The results are presented, as the charge in µeq/l, calculated from the amount of reference polymer needed to titrate to zero charge. With PCD it is the charge of the colloidal phase that is measured.

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Tensile strength evaluation

Strength evaluation of the sheets was performed according to the standard methods SCAN P 44:81 for dry tensile strength. For wet tensile strength the test pieces were tested according to SCAN P 58:86. A deviation from these methods was that the width
 5 of the test pieces was 15 mm. Soaking time of the test pieces before tensile strength test was 15s. The tensile strength results are presented as geometrical mean values of

machine and cross direction, $\frac{\sqrt{MD \cdot CD}}{\text{grammage}} \text{ Nm / g .}$

Analysis of strength additives in sheets***10 Total nitrogen content***

PAE and G-PAM adsorption in the sheets was analysed by measuring the total nitrogen content in the sheets. The method is based on flash combustion and is called Dumas
 Total Nitrogen Analysis and the measuring instrument used is Carlo Erba Instrument
 NA 1500 supplied by CE Termo Quest. A manual is supplied together with the
 15 instrument.

Ion Exclusion Chromatography

In some tests PAE and G-PAM adsorption in the sheets was analysed by ion exclusion chromatography.

1 g of paper sample is hydrolysed with 1.0 M NaOH. The hydrolysis is done at 100 ° C for
 20 24 hours. The PAAE resin is then hydrolysed to DETA and Adipate (see formula below). The solution is neutralised with an ion exchanger and the resulting adipic acid is analysed with ion exclusion chromatography. The wet strength resin is treated and analysed in the same way to calculate the amount of adipic acid in the actual resin. This result is then used to calculate the amount of PAE resin in paper.

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- 5 Ion exclusion chromatography is mainly used for analysis of weak inorganic and organic acids. The chromatographic column is packed with a stationary phase consisting of a sulfonated polystyrene/divinylbenzene based cation exchanger. Depending on the degree of crosslinking of the polystyrene/divinylbenzene resin, different organic acids may diffuse into the stationary phase to a greater or lesser degree. This mechanism together with ion exchange is used for chromatographic separation of organic acids in solution.
- 10 Suppressed conductivity is used for detection. The equipment used for the analysis is described below:

Columns:	2 x Dionex ICE-AS1 columns in series
Suppressor:	Dionex AMMS-ICE
15 Detector	Dionex PED (Conductivity mode)
Eluent:	1.0 mM Heptafluorobutyric acid; 0.8 ml/min

- The working range for the method is 0.01- 1.0 % in paper (calculated as dry PAE resin) and the relative standard deviation for a paper sample with 0.3 % PAE (dry resin) is 3.8 %.
- 20

Trial 1

- In trial 1 both PAE and CMC were added in excess according to the addition sequence of Table 2. This was done to ensure saturated fibres. During this trial Z-potential and PCD measurements were performed to control both the adsorption of polymers and the desorption of polymers in the intermediate washing step.
- 25

- Fig. 1 shows the Z-potential of the fibres during trial 1, before and after washing of the fibres. As can be seen the Z-potential is not largely influenced by washing the fibres. A small decrease in the observed Z-potential can be detected when washing the PAE treated fibres and a small increase when washing the CMC treated fibres, which presumably is due to the additive desorption during the washing step.
- 30

- Fig. 2 shows the results of charge measurements of the colloidal phase (PCD measurements) during trial 1, before and after washing of the fibres. Fig. 2 shows that
- 35

when adding PAE / CMC in excess a large amount of the added polymer stays in the colloidal phase instead of adsorbing to the fibres. In the washing step the excess is removed.

- 5 Fig. 3 shows the wet tensile index of the sheets versus the adsorbed amount of PAE. When five layers were made the wet tensile index levels out, even though the adsorption of PAE increases. The explanation to this is not clear. Anyway it is clear that by a multilayering technique it is possible to increase the amount of PAE to the fibres. Using a single addition point, about 11 mg/g of PAE is possible to adsorb on the fibres. Using three
10 layers, more than 20 mg/g PAE is possible to adsorb with a resulting increase in wet tensile strength of 50%.

Dry tensile strength index show a similar trend as the wet tensile strength index but, as expected, the increase in dry strength is not as high as the increase in wet strength.

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Trials 2-12

- In these trials different amounts of PAE/ CMC were added and the Z-potential and colloid phase charge were measured. The results from some of these measurements are shown in Figs. 4 and 5. Corresponding figures for addition in four and five layers show the same
20 trends, i e increases with PAE addition and decreases with CMC addition.

- As shown in Fig. 5 the charge in the colloidal phase is balancing around zero charge, indicating that the adsorption of PAE / CMC on the fibres is almost total, i e not much of the additives end up in the water phase. The deviation from zero charge should preferably
25 not exceed $\pm 5 \mu\text{eq/l}$, more preferably not exceed $\pm 2 \mu\text{eq/l}$.

- In Fig. 6 there is shown the dry tensile strength index versus adsorbed amount of PAE, at which e g "7/2/7-10-15" means 7 mg/g PAE, 2 mg/g CMC, then 7, 10, 15 mg/g PAE in the third layer. In the trials the dry tensile strength index reached its highest level at
30 relatively low adsorbed amounts of PAE. At an adsorbed amount of approximately 5 mg/g the strength is levelling out.

In Fig. 7 there is shown the wet tensile strength index versus adsorbed amount of PAE.

Fig. 8 shows the relative wet strength versus adsorbed amount of PAE. Fig. 7 and 8 show that wet tensile strength index and the relative wet strength level out, but it seems like the highest level is not fully reached. As mentioned above, the dry tensile index start to level out at 5 mg/g adsorbed amount of PAE. The wet tensile strength index
5 levels out but at higher levels of adsorbed amount of PAE. A maximum relative wet strength of 40% is reached.

However the absolute values are also very interesting. A wet tensile index of almost 30 Nm/g is achieved using the multilayer technique. Normally 65 g/m² lab sheets end up at
10 approximately 10 Nm/g.

When studying Fig. 6-8 it seems like three layers is enough to reach maximum strength with the concept used. It was with three layers possible to almost reach the highest strength levels. However this may differ for other types of additives and/or other types
15 of particles than cellulose fibres.

For the trials using G-PAM instead of or together with PAE basically the same effect was obtained as for PAE. The wet tensile strength index was slightly lower when using G-PAM compared to PAE, while in some cases a higher dry strength was obtained. The
20 order of addition when using both PAE and G-PAM seemed to effect the result, e g the adsorption of strength additive was higher when starting with PAE than with G-PAM.

The trials show that charge measurements using PCD and Z-potential instruments provide good control of polymer addition. The multilayering technique gives an
25 increased amount of additives that are adsorbed to the fibres, which helps to give e g an increased strength up to a certain level.

In a full scale continuous process, such as a papermaking process, the amount of polymer to be added is preferably controlled and determined by Z-potential and PCD
30 measurements after each addition of polymer in each step during the starting up of the process. These amounts are then used in the process. The Z-potential and PCD measurements are during the run of the process preferably performed only after the headbox. Addition of the first polymer is e g made in the pulper, and the other polymers are then added at different steps in the wet end of the paper machine.

35

In the examples above only the addition of strength additives to cellulose fibers for papermaking are described. It is however to be understood that the invention may be applied for consecutively adsorption of thin layers of optional types of alternating cationic and anionic polymers on the surface of fibres or other types of particles or groups of particles in order to build up thin multilayers of the interacting polymers on the particle surface.

By adding the polymers in consecutive steps and letting them form several layers on the particle surface, it is possible to adsorb higher amounts of polymer to the particle surface than is possible when adding them in one step forming only one layer. With regard to wet strength agents such as PAE and G-PAM it is possible by the method according to the invention to produce paper and nonwoven products containing at least 1.5, preferably at least 1.7, more preferably at least 2.0, even more preferably at least 2.2 and most preferably at least 2.5 % by weight or more of a wet-strength agent. These values refer to the amount of wet-strength agent adhering to the fibres and measured according to the total nitrogen method disclosed above. In some of the laboratory trials up to 3.8 % by weight wet-strength agent adhered to the fibres (Fig. 7 and 8).

This also means that it with the method according to the invention is possible to produce tissue paper based on cellulose fibres with no admixture of other types of fibres, such as synthetic reinforcing fibres, having a wet tensile index of at least 6.5, preferably at least 7.0 and more preferably at least 7.5 Nm/g. The term tissue paper in this respect does not include materials exerted to hydroentangling. These values refer to finished tissue products produced on a full-scale tissue machine. Fig. 7 shows a laboratory made products in which you normally achieve higher strength values. In finished tissue products produced on full-scale tissue machines and with subsequent treatments like creping, converting etc. the strength values are decreased.

This is shown in the results presented in Table 3 below showing the results of strength measurements on two different wet-strong tissue papers. No. 1 is a tissue paper used as wiping material sold by SCA Hygiene Products AB under the trademark "M-Tork" and having the following pulp composition: 33% by weight CTMP and 67% by weight softwood kraft pulp (TCF). It contains about 0.7% by weight PAE. No. 2 is a paper produced from the same type of pulps as No. 1 and where the cellulose fibres were treated in consecutive steps according to the invention with two layers PAE, one layer

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G-PAM and two layers CMC. It is from these results seen that tissue paper no. 2 showed improved strength properties. It is further noted that the papers tested contained a mixture of CTMP and softwood kraft pulp. For papers containing higher amounts of or only containing softwood kraft pulp even higher strength values would be expected.

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Table 3

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Sample	1 (ref.)	2 (invention)
Grammage g/m ²	24	21
Thickness 2kPa µm	154	162
Bulk 2kPa cm ³ /g	6.4	7.7
Tensile strength MD, dry N/m	242	438
Tensile strength CD, dry N/m	223	340
Tensile index √MDCD dry Nm/g	10	18
Stretch MD %	28	37
Stretch CD %	4.9	4.6
Stretch √MDCD %	11.7	13.1
Work to rupture MD J/m ²	39	78
Work to rupture CD J/m ²	7.983	13.63
Work to rupture index √MDCD J/g	0.7	1.6
Tensile strength MD, water N/m	102.9	206.8
Tensile strength CD, water N/m	60.8	125.8
Tensile index √MDCD water Nm/g	3	8
Relative strength water %	34	42

30

Table 4 shows the results of measurements for determining the amount of wet strength agent in the form of PAE in some commercially available tissue products and in a tissue paper made with the method according to the invention. Sample A is a tissue paper made according to the invention corresponding to the one tested as No. 2 in Table 3.

Sample B is a tissue paper produced by Fort James and sold under the trade name "Lotus Profes". Sample C is a tissue paper produced by Procter & Gamble and sold under the trade name "Bounty". Sample D is a tissue paper produced by Metsä Särä and sold under the trade name "Karrin Cleany".

5

The amount of PAE in the different tissue papers were measured by the ion exclusion chromatography method described above and gives the amount of PAE adsorbed to the fibres. It is to be noted that normally the amount of PAE or other wet strength agent added to the furnish is given as % of the wet strength agent solution added per weight
10 fibres. Wet strength agents are sold as solutions containing between about 6 and 25 % of the active component. When we talk about the amount of wet strength agent we refer to the amount of the active component adhered to the fibres.

Table 4

15	Sample	A (invention)	B (ref.)	C (ref.)	D (ref.)
	Amount PAE (% by weight)	2	0.45	1.2	0.7

20 As is seen from these results paper A produced according to the invention contained considerably higher amounts of PAE than the commercial wet-strong tissue products tested.

NOVAS

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Claims

1. Method of producing a particle or group of particles intended for use in paper- and/or nonwovenmaking having a coating of at least two, preferably at least three, outside each other located thin layers of alternating cationic and anionic polymers, at which the particle or group of particles is treated in consecutive steps with solutions of the alternating cationic and anionic polymers,

characterized in

that the amount of the respective polymer to be added in each step is controlled by charge measurements of the treatment solution or a liquid containing the particles or group of particles and the polymer solution, during and/or after the treatment in each step in order to determine that substantially all polymer is adsorbed to the particle surface.

2. Method as claimed in claim 1,

characterized in

measuring the Z-potential of the particles or groups of particles during and/or after the treatment in each step in order to determine the amount of cationic/anionic polymer adsorbed to the particle surface.

3. Method as claimed in claim 1 or 2,

characterized in

that the particle is a fiber.

4. Method as claimed in claim 3,

characterized in

that the fiber is a cellulosic fiber.

5. Method as claimed in claim 3,

characterized in

that the fiber is a synthetic or regenerated fiber.

Empfang AMENDED SHEET

6. Method as claimed in claim 1 or 2,
characterized in
that the particle is a filler particle, coating particle or another type of particle used in
papermaking.

7. Method as claimed in any of the preceding claims,
characterized in
that at least one of said polymer is a strength additive used in papermaking, such as a
dry-strength and/or wet-strength agent.

8. Method as claimed in any of the preceding claims,
characterized in
that in a continuous process for consecutive adsorption of thin layers of interacting
polymers on the surface of particles or groups of particles, the amount of the respective
polymer to be added in each step is determined at the starting-up of the process.

9. Paper or nonwoven product,
characterized in
that it contains fibres, filler particles or other particles produced according to the method
of any of claims 1-8.

10. Paper or nonwoven product,
characterized in
that it contains fibres, filler particles or other particles having at least three, outside each
other located thin layers of alternating cationic and anionic polymers and that it contains
at least 1.5, preferably at least 1.7, more preferably at least 2.0, even more preferably at
least 2.2 and most preferably at least 2.5 % by weight of a wet-strength agent.

11. Paper or nonwoven product as claimed in claim 10,
characterized in
that the wet-strength agent is a cationic polyelectrolyte such as polyaminoamide-
epichlorhydrin (PAE) and/or glyoxylated polyacryl amide (G-PAM).

AMENDED SHEET

Enf 20882011 11.0001 10.21

12. Tissue paper based on wood pulp cellulose with no admixture of other types of fibers, such as synthetic reinforcing fibers, characterized in that it contains at least at least three, outside each other located thin layers of alternating cationic and anionic polymers and that it has a wet tensile index of at least 6,5, preferably at least 7,0 and more preferably at least 7,5 Nm/g.

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum)

P15905PC/CA

Box No. I TITLE OF INVENTION Method of adsorption of cationic and anionic polymers on the surface of particles and paper or nonwoven product containing such particles	
Box No. II APPLICANT	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) SCA HYGIENE PRODUCTS AB S-405 03 GÖTEBORG Sweden	☐ This person is also inventor. Telephone No. Facsimile No. Teleprinter No.
State (i.e. country) of nationality: SE	State (that is, country) of residence: SE
This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.) SANDBERG, Sussan Gubbekullavägen 15 S-439 35 ONSALA Sweden	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality: SE	State (that is, country) of residence: SE
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) GÖTEBORGS PATENTBYRÅ DAHLS AB Sjöporten 4 S-417 64 GÖTEBORG Sweden	Telephone No. +46-31-507700 Facsimile No. +46-31-7790640 Teleprinter No.
☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS	
If none of the following sub-boxes is used, this sheet is not to be included in the request.	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) ANDREASSON, Bo Parkgatan 29 S-852 38 SUNDSVALL Sweden	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality: SE	State (that is, country) of residence: SE
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.	

Box No. V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes: at least one must be marked):

Regional Patent

- ☒ AP ARIPO Patent: GH Ghana, GM Gambia KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired specify on dotted line)

- | | |
|--|--|
| ☒ AE United Arab Emirates | ☒ LC Saint Lucia |
| ☒ AG Antigua and Barbuda | ☒ LK Sri Lanka |
| ☒ AL Albania | ☒ LR Liberia |
| ☒ AM Armenia | ☒ LS Lesotho |
| ☒ AT Austria and utility model | ☒ LT Lithuania |
| ☒ AU Australia | ☒ LU Luxembourg |
| ☒ AZ Azerbaijan | ☒ LV Latvia |
| ☒ BA Bosnia and Herzegovina | ☒ MA Morocco |
| ☒ BB Barbados | ☒ MD Republic of Moldova |
| ☒ BG Bulgaria | ☒ MG Madagascar |
| ☒ BR Brazil | ☒ MK The former Yugoslav Republic of Macedonia |
| ☒ BY Belarus | ☒ MN Mongolia |
| ☒ BZ Belize | ☒ MW Malawi |
| ☒ CA Canada | ☒ MX Mexico |
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| ☒ CN China | ☒ NO Norway |
| ☒ CR Costa Rica | ☒ NZ New Zealand |
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| ☒ CZ Czech Republic and utility model | ☒ PT Portugal |
| ☒ DE Germany and utility model | ☒ RO Romania |
| ☒ DK Denmark and utility model | ☒ RU Russian Federation |
| ☒ DM Dominica | ☒ SD Sudan |
| ☒ DZ Algeria | ☒ SE Sweden |
| ☒ EE Estonia and utility model | ☒ SG Singapore |
| ☒ ES Spain | ☒ SI Slovenia |
| ☒ FI Finland and utility model | ☒ SK Slovakia and utility model |
| ☒ GB United Kingdom | ☒ SL Sierra Leone |
| ☒ GD Grenada | ☒ TJ Tajikistan |
| ☒ GE Georgia | ☒ TM Turkmenistan |
| ☒ GH Ghana | ☒ TR Turkey |
| ☒ GM Gambia | ☒ TT Trinidad and Tobago |
| ☒ HR Croatia | ☒ TZ United Republic of Tanzania |
| ☒ HU Hungary | ☒ UA Ukraine |
| ☒ ID Indonesia | ☒ UG Uganda |
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| ☒ IS Iceland | ☒ VN Viet Nam |
| ☒ JP Japan | ☒ YU Yugoslavia |
| ☒ KE Kenya | ☒ ZA South Africa |
| ☒ KG Kyrgyzstan | ☒ ZW Zimbabwe |
| ☒ KP Democratic People's Republic of Korea | |
| ☒ KR Republic of Korea and utility model | |
| ☒ KZ Kazakhstan | |

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

☒ CO - Colombia

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM		☐ Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 06.04.2000	0001268-2	Sweden		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): SE 0001268-2

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (If two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):	Request to use results of earlier search; reference to that search (If an earlier search has been carried out by or requested from the International Searching Authority):		
ISA / SE	Date (day/month/year) 06.04.2000	Number SE 00/00389	Country (or regional Office) Sweden

Box No. VIII CHECK LIST; LANGUAGE OF FILING.

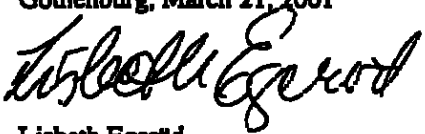
This international application contains the following number of sheets: request : 4 description (including sequencelisting part) : 16 claims : 3 abstract : 1 drawings : 4 sequence listing part of description : _____ Total number of sheets : 28	This international application is accompanied by the item(s) marked below: 1. ☒ fee calculation sheet 2. ☐ separate signed power of attorney 3. ☐ copy of general power of attorney; reference number, if any: 4. ☐ statement explaining lack of signature 5. ☐ priority document(s) identified in Box No. VI as item(s): 6. ☐ translation of international application into (language): 7. ☐ separate indications concerning deposited microorganism or other biological material 8. ☐ nucleotide and/or amino acid sequence listing in computer readable form 9. ☒ other (specify): ITS-Report
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Figure of the drawings which should accompany the abstract: Fig. 1	Language of filing of the international application: English
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Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Gothenburg, March 21, 2001



Lisbeth Egeröd
GÖTEBORGS PATENTBYRÅ DAHLS AB

For receiving Office use only		2. Drawings: ☐ received: ☐ not received:
1. Date of actual receipt of the purported international application:		
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid.	

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Date of receipt of the record copy by the International Bureau:	

Form PCT/RO/101 (last sheet) (July 1998; reprint July 2000) See Notes to the request form

METODO DE ADSORCIÓN DE POLIMEROS CATIONICOS Y ANIONICOS
SOBRE LA SUPERFICIE DE PARTICULAS Y PAPEL O PRODUCTO NO
TEJIDO QUE CONTIENE TALES PARTICULAS

CAMPO TECNICO

La presente invención se refiere a un método para producir una partícula o un grupo de partículas destinadas a uso en papel -y/o elaboración de no tejidos que tienen un recubrimiento de al menos 2, preferiblemente al menos 3, capas delgadas localizadas al exterior una de la otra de polímeros catiónicos y aniónicos, en el cual la partícula o grupo de partículas se trata en etapas consecutivas con soluciones de polímeros catiónicos y aniónicos. También se refiere a un producto de papel o no tejido que contiene tales partículas o grupos de partículas. Este además se refiere a productos de papel que contienen cantidades crecientes de agentes de refuerzo para humedad y a papel tejido que tiene resistencia a la humedad mejorada.

ANTECEDENTES DE LA INVENCION

El uso creciente de fibras recuperadas en producción de papel y el uso de componentes con propiedades de unión mas pobres, tales como llenadotes y minerales, han incrementado la necesidad de un secado más efectivo y agentes de refuerzo para la humedad en el papel. Tradicionalmente dos métodos diferentes se han utilizado para agregar químicos que mejoran la resistencia al papel, por ejemplo al agregar químicos al final húmedo del proceso de papel o mediante la aplicación en la superficie por medio de una prensa de tamaño. La adición de final húmedo es usualmente más efectiva que la aplicación de superficie contada por kilogramo de producto utilizado. Con el fin de mantener la adición hecha en el final húmedo en la lámina de papel, los químicas de final húmedo son principalmente de manera exclusiva catiónicos, y para elaborarlos menos sensibles a disolverse y materiales coloidales y la concentración creciente de electrolitos originada por el cierre creciente de los sistemas, sus cargas catiónicas usualmente se incrementan. Esto conduce a su vez a una absorción de saturación decreciente de los químicos aditivos a las fibras, que conducen a un efecto reducido

máximo de los químicos aditivos. Esto involucra que existe necesidad tanto de nuevos métodos de aplicar químicos que mejoren la resistencia al papel, como de nuevos sistemas químicos.

Además existe la necesidad creciente de mejorar la opacidad del papel acabado. En razón a que hoy los agentes para resistencia más frecuentemente utilizados contribuyen de manera negativa a la opacidad la necesidad tenemos métodos de desarrollar resistencia en el papel es adicionalmente reforzada.

Tal forma seria utilizar prensas de tamaño en una mayor proporción, pero esto sin embargo conduciría a grandes reducciones de la capacidad de manufactura y la economía de producción en razón a que el papel tiene que ser secado una vez adicionalmente dependiendo del rehumedecimiento que se ejerza sobre la prensa de tamaño.

Esto involucra que existe gran necesidad para nuevas formas de tratar fibras y otras partículas contenidas en el papei, tales como partículas llenadotas, en el final humedecido de la máquina de papel.

Es conocido construir multicapas delgadas de polímeros electro activos sobre sustratos cargados electrostáticamente para uso en óptica, tales como sensores, reducción de fricción etc. Esto se describe en, por ejemplo, Thin Solid Films, 210/211 (1992) 831-835 y en Thin Solid Films, 244 (1994) 806-809. El sustrato es inmerso con este alternativamente en soluciones diluidas de un polimerización con un enjuague intermedio con el fin de remover restos de polimerización previos que no están unidos al sustrato. El grosor de cada capa depositada se describe por estar entre 5-20 Å. No existe indicación de que los sustratos tratados puedan ser partículas, tales como fibras o partículas llenas de gotas.

Aplicación

En la US 5, 338, 407 se describe un método para mejorar las propiedades de resistencia de secado del papel, en el cual un carboxi metil guar aniónico o un carboxi metil hidroxil etil guar y u guar catiónico se agregan al proporcionado. Estos dos componentes son agregados en mezcla o separadamente. No existe indicación de que el tratamiento se haga bajo tales condiciones que se construya una doble capa sobre las fibras con un

componente en una capa y el otro componente en la otra capa.

En las patentes estadounidenses 5, 507, 914 y 5, 185, 062 se describen métodos para mejorar las propiedades de desagüamiento y la retención del papel al agregar polímeros aniónicos y catiónicos a la pulpa. No existe indicación de que el tratamiento tenga lugar bajo tales condiciones que se cree una doble multicapa sobre las fibras de pulpa con el componente aniónico en una capa y el componente catiónico en la otra capa.

El tratamiento de superficie doble de las partículas llenadoras con polímeros aniónicos y catiónicos se describe en la EP-A-0,850 879, wo 95/32335, US-A-4,495,245 y US-A-4, 925,530. No existe indicación de que el tratamiento tenga lugar bajo tales condiciones controladas que se crea una doble multicapa sobre las fibras de pulpa con el componente aniónico en una capa y el componente catiónico en la otra capa.

La solicitud de patente Internacional PCT/SE99/02149 describe un método como se estableció en la introducción anterior y de acuerdo al cual las partículas o grupos de

partículas son producidas las cuales tienen un encubrimiento de al menos 2, preferiblemente al menos 3, capas delgadas localizadas afuera una de la otra de polímeros interactuantes. Las partículas o grupos de partículas son tratadas en etapas consecutivas con soluciones de los polímeros interactuantes, y el respectivo polímero se agrega solo en tal cantidad en cada etapa que sustancialmente todos los polímeros se absorben a la superficie de la partícula. Esto se logra al remover el exceso de polímero previo entre cada etapa de tratamiento alternativamente al agregar el polímero respectivo solo en tal cantidad en cada etapa que sustancialmente todo el polímero se adsorbe a la superficie De la partícula.

El objeto y característica más importante de la invención

El objeto de la presente invención es suministrar un método de acuerdo con lo anterior y que ofrezca una vía para asegurar que cada polímero para formar la respectiva capa sobre la superficie de las partículas o grupo de partículas se agregue solo en tal cantidad en cada etapa que sustancialmente todo el polímero se adsorba a la

superficie de la partícula. Esto se ha logrado de acuerdo con la invención por el hecho de que la cantidad del respectivo polímero a ser agregada en cada etapa se controla mediante medidas de carga eléctrica de la solución de tratamiento o un líquido que contiene las partículas o grupo de partículas y la solución de polímero, después del tratamiento en cada etapa con el fin de determinar que sustancialmente todo el polímero se adsorba a la superficie de la partícula.

Con el fin de determinar la cantidad de polímero catiónico/aniónico adherido a la superficie de la partícula el potencial Z de las partículas o grupos de partículas se puede medir.

Las partículas o grupos de partículas pueden ser de tipo opcional, sin embargo fibras, por ejemplo fibras celulósicas, fibras regeneradas y diferentes tipos de fibras sintéticas, y partículas llenadotas son las principalmente de interés.

Los polímeros interactuantes son preferiblemente polielectrolitos catiónicos y aniónicos, pero ellos también pueden ser los así llamados iones zwiter.

De acuerdo con una modalidad de la invención las partículas y fibras de celulosa para la elaboración de papel y al menos uno de los polímeros es un aditivo de resistencia tal como un agente de resistencia a la humedad y/o secado.

La invención también se refiere a un producto de papel o no tejido, que contiene fibras y/o partículas llenadotas producidas por el método descrito anteriormente. El término papel utilizado aquí se refiere a todos los tipos de papel, tales como papel tejido, papel gráfico, cartón de recubrimiento interior, material de limpieza etc. El material no tejido puede ser de tipo opcional.

La invención además se refiere a productos de papel que contienen cantidades crecientes de agentes de resistencia a la humedad y a papel de tejido que tiene resistencia a la humedad mejorada.

DESCRIPCION DE LOS DIBUJOS

La figura 1 muestra los resultados de las medidas de potencial Z de las fibras de celulosa tratadas en etapas consecutivas con polímeros catiónicos y aniónicos en la forma de PAE (poliaminoamida-epiclorohidrina) y CMS (carboxi metil celulosa).

La figura 2 muestra el resultado de las mediciones de carga de la fase coloidal antes y después de lavar las fibras en el ensayo de la figura 1.

La figura 3 muestra el índice tensil de resistencia a la humectación de 30 gramos de láminas de papel hechas de las fibras tratadas contra la cantidad adsorbida de PAE.

La figura 4 muestra el potencial Z de las fibras después de la adición del PAE /CMC/PAE.

La figura 5 muestra la carga de la fase coloidal de las mediciones PCD para adición del PAE/CMC/PAE.

La figura 6 muestra el índice de resistencia tensil de secado contra la cantidad adsorbida de PAE.

La figura 7 muestra el índice de resistencia tensil al humedecimiento contra la cantidad adsorbida de PAE.

La figura 8 muestra la resistencia a la humedad de relativa contra la cantidad adsorbida de PAE.

DESCRIPCION DE LA INVENCION

De acuerdo con la presente invención las partículas o grupos de partículas, por ejemplo fibras o partículas llenadoras, son tratadas con polímeros catiónicos y aniónicos con el fin de construir multicapas delgadas de polímeros interactuantes sobre la superficie de partícula.

Las partículas son tratadas en etapas consecutivas con soluciones de polímeros catiónicos y aniónicos alternativamente, en el cual el tiempo de tratamiento para cada etapa es suficiente para formar una capa del grosor molecular deseado. Para partículas o grupos de partículas que tienen una superficie aniónica, el cual

por ejemplo es el caso de las fibras celulósicas, la primer capa debe ser un polímero catiónico, y viceversa. Al agregar el polímero en etapas consecutivas y permitirles formar varias capas sobre la superficie de partícula, es posible adsorber mas altas cantidades de polímero a la superficie de la partícula de los que es posible cuando se las agrega en una etapa inter mezcladas formando solo unas capa.

La adición se controla de tal forma que sustancialmente no excede la cantidad de polímero respectivo que se agrega en cada etapa, de tal forma que sustancialmente todo el polímero se adsorbe a la superficie de la partícula. Esto se hace al medir la carga eléctrica de la solución de tratamiento o el líquido en el cual las partículas tratadas o grupos de partículas están contenidos. Después de haberle permitido al polímero adsorber la superficie de partícula un cierto periodo de tiempo la carga eléctrica de la solución debe ser cercana a cero. Las mediciones de carga se hacen con medición de potencial de corriente, por ejemplo con un instrumento PCD (detector de carga de partícula).

Con el fin de determinar la cantidad de polímero catiónico/aniónico adherido a la superficie de partícula el potencial Z se mide de acuerdo con el método descrito adelante.

El método de acuerdo con la invención para construir las multicapas deseadas se basa en la atracción electrostática entre los polielectrolitos cargados de manera opuesta. Al tratar las partículas en etapas consecutivas con una solución que contiene polielectrolitos de carga opuesta y permitirles a estos adsorberse espontáneamente a la superficie de partícula, las multicapas de la clase establecida son construidas. En principio todos los tipos de polielectrolitos se pueden utilizar.

De acuerdo con una modalidad el método se utiliza para adsorber aditivos de resistencia a fibras celulósicas utilizadas para la elaboración de papel. En razón a que la fibra de celulosa tiene una superficie aniónica el primer polímero a ser adsorbido es un polímero catiónico. Este por ejemplo puede ser poliaminoamida-epiclorhidrina (PAE) o poliacril amida glioxilada (G-PAM). Esta capa hará la superficie de la

fibra catiónicamente cargada. En la próxima etapa un polímeroaniónico, por ejemplo, CMC (carboxi metil celulosa) se agrega. La superficie de la fibra cambiará de nuevo a aniónica. Luego la siguiente capa de polímero catiónico se puede agregar y así sucesivamente.

A través de tal tratamiento cantidades mayores de fibras de celulosa de aditivos de resistencia, por ejemplo PAE o G-PAM se pueden adsorber a la superficie de la fibra de lo que es posible con las técnicas convencionales, lo que dará como resultado unas propiedades de resistencia mejoradas del papel producido.

Por supuesto es posible también hacer nuevos tipos de modificaciones en la superficie a las partículas o grupos de partículas a través de adsorción consecutiva de capas delgadas de polímeros interactuantes de acuerdo con la invención. Al, por ejemplo, tratar fibras con capas consecutivas de polielectrolitos cargados hidrófobos sería posible por ejemplo desarrollar nuevos tipos de químicos hidrofobizantes para la hidrofobización del papel. Sería también posible construir capas de superficie "inteligentes" sobre las fibras, las cuales

alteran las propiedades con temperatura, Ph, contenido de sal etc.

Aplicaciones adicionales son las fibras de intercambio de iones donde las "membranas" con propiedades de intercambio de iones se suministran sobre la superficie de la fibra, agentes de resistencia a la humedad donde los polímeros agregados son reactivos con las fibras y con cada uno de los otros, con el fin de suministrar uniones permanentes entre las fibras y para la producción de capas de superficie altamente hinchantes, donde los químicos agregados forman estructuras de ge hinchado sobre la superficie de la fibra para uso en productos higiénicos absorbentes. Otra aplicación posible son nuevos tipos de fibras para papel de impresión, donde los polímeros adsorbidos cambian de color cuando sobre ellos se ejerce un campo eléctrico, magnético o electromagnético. Tales polímeros están disponibles hoy en día.

Las fibras que son tratadas con el método de acuerdo con la invención pueden ser de una clase opcional, fibras naturales así también como sintéticas. Principalmente la fibra celulósica es el interés. Sin embargo sería posible

tratar fibras sintéticas, por ejemplo, al darles más superficie hidrofílica.

También grupos de aglomerados de fibras o partículas pueden ser tratados de acuerdo con el método.

Ejemplos de polielectrolitos adecuados aniónicos y catiónicos que se pueden utilizar en el método de acuerdo con la invención son dadas adelante.

Polielectrolitos aniónicos: El almidón aniónico con diferentes grados de sustitución, guar aniónico, sulfonato de polistireno, carboxi metil celulosa con diferentes grados de sustitución, galactoglucomanan aniónico, ácido polifosfórico, ácido polimetacrílico, sulfato de polivinilo, alginato, copolímeros de acril amida y ácido acrílico o ácido 2-acrílico amida-2-alquilpropano sulfónico.

Polielectrolito catiónico: galactoglucomanan catiónico, guar catiónico, almidón catiónico, polivinil amina, polivinil piridina y sus derivados N-alquilo, polivinil pirrolidona, chitosan, alginato, poliacril amidas modificadas, polidialil dialquilo, aminas de amida

catiónica, productos de condensación entre diciano diamidas, formaldehído y una sal de amonio, productos de reacción entre epiclorhidrina, poliepiclorhidrina y amonio, aminas primarias y secundarias, polímeros formados por reacción entre aminas dterciarias o aminas secundarias o dihaloalcanos, polietilen iminas y polimeros formados por polimerización de monómeros de amida-(dialquilaminoalquil) acrílico.

Ejemplo 1

Los polímeros utilizados durante los ensayos se enlistan en la tabla 1 adelante.

Tabla 1

<u>Nombre</u>	<u>Polímero</u>	<u>Suministrador</u>	<u>D.S.</u>	<u>Viscosidad</u> (mPas)
Kenores 1440	Poli aminoamida- epiclorohidrina, (PAE)	Eka Chemicals		
Parez 631 NC	Poliacrilamida glioxalatada (G- PAM)	Cytec industries		
Cekol 50000G	Carboximetil celulosa, (CMC)	Metsa Speciality Fibres	0,78	7200 (1% conc)
Finnfix BW			0,4- 0,6	100-700 (4% conc.)

*D.S grado de sustitución.

El PAE y G-PAM se diluyeron en agua des ionizada hasta un contenido activo de 10 g/l antes de uso. Los diferentes CMC se disolvieron en agua des ionizada mediante dispersión utilizando un mezclador manual, hasta una concentración adecuada entre 5 y 10 g/l dependiendo de la viscosidad.

La pulpa utilizada fue un TCF, blanqueado completamente seco, Celeste 85 de SCA Östrand. La pulpa fue trillada a 25 °SR y se diluyó con agua de grifo a una concentración de 3 g/l. El pH durante los ensayos fue de 7,5 y la conductividad fue ajustada a 1200 $\mu\text{S}/\text{cm}$ utilizando NaCl.

Tres, cuatro y cinco capas de PAE y CMC alternativos fueron hechas. La adición de los aditivos fue controlada al medir la carga eléctrica con un potencial Z e instrumentos PCD. En algunos ensayos se utilizó G-PAM en lugar de o junto con PAE. La secuencia de adición se lista en la tabla 2 siguiente.

Tabla 2

Trial	Adición (mg/g)								
	PAE	CMC	PAE	CMC	PAE	G-PAM	CMC	PAE	G-PAM
1	20	20	20	20	20				
2	15	7	30	4	15				
3	15	4	15						
4	15	4	30						
5	7	2	7						
6	7	2	10						
7	7	2	15						
8	5	1	5	1	5				
9		2	7	2	7				
10						7	2	7	
11						7	2		7
12	7						2		7

El tiempo de adsorción para los aditivos fue de 10 minutos.

Preparación terminada.

En el ensayo 1 las adiciones de PAE y CMC fueron considerablemente sobre dosificadas, 20 mg/g de pulpa. La pulpa fue entonces desaguada, lavada con agua desionizada y desaguada de nuevo entre cada etapa con el fin de remover el exceso de PAE y CMC. Esto se repitió hasta que se hicieron 5 capas. Iniciando y finalizando con PAE, ver tabla 2 arriba.

En los ensayos 2-12 las adiciones de PAE y CMC fueron sucesivamente optimizadas a niveles más realistas. Fueron hechas tanto las tres, cuatro como cinco capas, ver tabla 2. La adición de los aditivos fue hecha etapa de lavado intermedia, siempre controlada al medir la carga con potencial Z e instrumentos PCD. De los tres ensayos utilizando G-PAM en lugar o junto con PAE se desarrollaron tonel fin de avaluar otro aditivo con resistencia a la humedad utilizando una técnica de multicapa.

Preparación de lámina.

Láminas de 30g/cm^2 se formaron en un formador de lámina dinámica. Las láminas fueron presionadas entre borradores y luego secadas bajo condiciones restringidas. Se formaron dos láminas de cada punto de muestra y se presionaron a dos diferentes densidades, ~ 350 Y ~ 450 kg/m^3 . Finalmente las láminas fueron curadas durante 10 minutos a 105°C . La resistencia tensil fue entonces interpolada a una densidad de 400 kg/m^2 .

Determinaciones de carga

Determinación de la carga de fibra utilizando un instrumento de potencial Z

El potencial Z de las fibras se midió con un instrumento de potencial de corriente (Magedans SZ2, suministrado por Mútek) [Penniman, J.G., Comparison of pulp pad streaming potencial measurement and mobility measurement. Tappi journal, 1992 75 111-115 and Jaycock, M. J.; Assumptions made in the measurement of zeta - potential by streaming current/potencial detectors. Paper technology, 1995 36 35-38. 19, 20; Barron, W., et al., The streaming current detector: a comparison with conventional electrokinetic techniques. Colloids and Surfaces, 1994 88 129-139; Sanders, N. D. and J. H. Schaefer, Comparing papermaking wet-end charge-measuring techniques in kraft and groundwood systems. Tappi journal, 1995 78 142-150].

El potencial se mide entre dos electrodos, un electrodo de pantalla ubicado cerca de la almohadilla de fibra, que se forma cuando esta se bombea contra una pantalla, y el segundo electrodo es un electrodo de

anillo situado sobre la parte inferior de la almohadilla de fibra. La conductividad se mide entonces entre estos dos electrodos y se presenta un valor calculado del potencial Z (ζ).

Determinación de la carga de potencial utilizando un PCD

Un PCD 03 (detector de carga de partículas) suministrado por medidas Mútek un diferencial de voltaje inducido al mover un medio de carga, por ejemplo, sustancias coloidales en un agua blanca. Polímeros de alta masa molecular y sustancias coloidales unidas a las superficies de teflón de los equipos. El pistón oscilante se mueve e indica una diferencia de potencial que se detecta [Jaycock, M. J., Assumptions made in the measurement of zeta -potential by streaming current/potencial detectors. Paper technology, 1995 36 35-38; Barron, W., et al., The streaming current detector: a comparison with conventional electrokinetic techniques. Colloids and Surfaces, 1994 88 129-139 and Sanders, N. D. and J. H. Schaefer, Comparing papermaking wet-end charge-measuring techniques in kraft and groundwood systems. Tappi journal, 1995 78 142-150.20-22].

Los resultados se presentan, como la carga en $\mu\text{eq/l}$, calculada de la cantidad de polímero de referencia necesario para titular una carga cero. Con PCD esta es la carga de fase coloidal que es medida.

Evaluación de la resistencia tensil

La evaluación de la resistencia de las láminas fue desarrollada de acuerdo con métodos estándar SCAN P 44: 81 para resistencia tensil seca. Para resistencia tensil húmeda las piezas de ensayo fueron probadas de acuerdo con el SCAN P 58: 86. Una desviación de estos métodos fue que la amplitud de las piezas de ensayo fue de 15 mm. El tiempo de empapamiento de las piezas de ensayo antes del ensayo de la resistencia tensil fue de 15s. Los resultados de la resistencia tensil se presentan como valores medios geométricos de máquina y en dirección transversal,

$$\frac{\sqrt{MD \cdot CD}}{\text{Gramage}} \quad \text{Nm/g.}$$

Análisis de aditivos de resistencia en láminas

Contenido total de nitrógeno

La adsorción de PAE y G-PAM en las láminas se analizó al medir el contenido de nitrógeno total en las láminas. El método se basa en combustión de destello y se llama análisis total de nitrógeno dumas y el instrumento de medición utilizado es el instrumento Carlo Erba NA 1500 suministrado por CE Termo Quest. Se suministra un manual junto con el instrumento.

Cromatografía de exclusión de ión.

En algunos ensayos la adsorción de PAE y G-PAM en las láminas se analizó mediante cromatografía de exclusión de ión.

Un gramo de muestra de papel se hidroliza con 1,0 M de NaOH. La hidrólisis se hace a 100°C durante 24 horas. La resina PAAE es hidrolizada entonces a DETA y Adipato (ver formula adelante).

La solución se neutraliza con intercambiador de iones y el ácido adipico resultante se analiza con cromatografía de exclusión de ión. La resina con resistencia a la humedad se trata y analiza de la misma forma para calcular la cantidad de ácido adipico en la resina actual. Este resultado es utilizado entonces para calcular la cantidad de resina PAE en el papel.

La cromatografía de exclusión de ión se utiliza principalmente para el análisis de ácidos inorgánicos y orgánicos débiles. La columna cromatográfica se empaca con una fase estacionaria que consiste de un intercambiador de catión basado en poliestireno sulfonatado/divinilbenzeno. Dependiendo del grado de reticulación de la resina de poliestireno/divinilbenzeno, se pueden difundir diferentes ácidos orgánicos en la fase estacionaria a un mayor o menos grado. Este mecanismo junto con el intercambio de ión se utiliza para separación cromatográfica de ácidos orgánicos en solución.

La conductividad suprimida se utiliza para detección. El equipo utilizado para el análisis se describe adelante:

Columna: 2 x Dionex ICE-AS1 columnas en series
Supresor: Dionex AMMS-ICE
Detector: Dionex PED (modo de conductividad)
Eluente: Acido heptafluorobutirico 1,0 Mm:
0,8ml/min

El rango de trabajo para el método es 0,01-1,0 % en papel (calculado como resina PAE seca) y la desviación estándar relativa para la muestra De papel con 0,3% PAE (resinas secas) es 3,8%.

Ensayo 1

En el ensayo 1 tanto el PAE como el CMC se agregaron en exceso de acuerdo con la secuencia de adición de la tabla 2. Esto se hizo para asegurar las fibras saturadas. Durante este ensayo mediciones del potencial Z y el PCD se desarrollaron para controlar tanto la adsorción de los polímeros como la desorción de los polímeros en la etapa de lavado intermedio.

La figura 1 muestra el potencial Z de las fibras durante el ensayo 1, antes y después de lavar las fibras. Como se puede ver el potencial Z no es mayormente influenciado por el lavado de las fibras. Una disminución pequeña en el potencial Z observado se puede detectar cuando se lavan las fibras tratadas PAE y un pequeño incremento cuando se lavan las fibras tratadas CMC, lo cual presumiblemente se debe a la desorción aditiva durante la etapa de lavado.

La figura 2 muestra los resultados de mediciones de carga de la fase coloidal (mediciones PCD) durante el ensayo 1, antes y después del lavado de las fibras. La figura 2 muestra que cuando se agrega PAE/CMC en exceso una gran cantidad del polímero agregado permanece en la fase coloidal en lugar de adsorber a las fibras. En la etapa de lavado el exceso se remueve.

La figura 3 muestra el índice tensil de humedad de las láminas contra la cantidad adsorbida de PAE. Cuando se elaboran las cinco capas el índice tensil de humedad se nivela para salir, aunque la adsorción de PAS incrementa. La explicación a esto no es clara. De cualquier forma es claro que mediante una técnica de

multi capa es posible incrementar la cantidad de PAE a las fibras. Utilizando e punto de adición simple, cerca de 11 mg/g de PAE es posible adsorber sobre las fibras. Utilizando tres capas, más de 20 mg/g de PAE es posible adsorber con un incremento resultante en la resistencia tensil húmeda de 50%.

El índice de resistencia tensil seca muestra una tendencia similar a la del índice de resistencia tensil húmeda pero, pero se esperaba, el incremento en la resistencia seca no s tan alto como el incremento en la resistencia húmeda.

Ensayos 2-12

En estos ensayos diferentes cantidades de PAE/CMC fueron agregados y se midieron en el potencial Z y la carga de fase de coloide. Los resultados de algunas de estas mediciones se muestran en las figuras 4 y 5. Las figuras correspondientes para la adición en cuatro y cinco capas muestran las mismas tendencias, es decir se incrementan con la adición de PAE y se disminuyen con la adición de CMC.

Como se muestra en la figura 5 la carga en la fase coloidal se balancea alrededor de la carga cero, indicando que la adsorción del PAE/CMC sobre las fibras es casi total, es decir no mucho de los aditivos acaban en la fase de agua. La desviación de la carga cero debe preferiblemente no exceder $\pm 5 \mu\text{eq/l}$, más preferiblemente no exceder $\pm 2 \mu\text{eq/l}$.

En la figura 6 se muestra índice de resistencia tensil seca contra la cantidad adsorbida de PAE, en la cual por ejemplo "7/2/7-10-15" significa 7 mg/g PAE, 2 mg/g CMC, luego 7,10,15 mg/g PAE en la tercera capa. En estos ensayos el índice de resistencia tensil seca alcanzó su nivel más alto a cantidades adsorbidas relativamente bajas de PAE. En una cantidad adsorbida de aproximadamente 5 mg/g la resistencia se estabiliza.

En la figura 7 se muestra el índice de resistencia tensil húmedo contra la cantidad adsorbida de PAE.

La figura 8 muestra la resistencia húmeda relativa contra la cantidad adsorbida de PAE. Las figuras 7 y 8 muestran que el índice de resistencia tensil húmeda y la resistencia húmeda relativa se estabilizan, pero parece

que el nivel mas alto no se alcanza. Como se mencionó anteriormente, el índice de resistencia tensil arranca la estabilidad a 5 mg/g de cantidad adsorbida de PAE. El índice de resistencia tensil húmeda se estabiliza pero a niveles más altos de cantidad adsorbida de PAE. La resistencia húmeda relativa máxima del 40% se alcanza.

Sin embargo los valores absolutos son también muy interesantes. Un índice de resistencia tensil de casi 30 Nm/g se logra utilizando la técnica multicapa. Normalmente láminas 65 g/m² acaban en aproximadamente 10Nm/g.

Cuando se estudian las figuras 6-8 parece que tres capas son suficientes para alcanzar el máximo de resistencia con el concepto utilizado. Fue con tres capas casi posible alcanzar los niveles de resistencia más altos. Sin embargo esto puede diferir para otros tipos de aditivos y/o otros tipos de partículas que las fibras de celulosa.

Para los ensayos utilizando G-PAM en lugar o junto con PAE básicamente se obtienen los mismos efectos que para PAE. El índice de resistencia tensil húmeda fue

ligeramente inferior cuando se utilizó G-PAM comparado con el PAE, mientras que en algunos casos se obtuvo una resistencia seca mayor. El orden de adición cuando se utilizan tanto PAE como G-PAM parece afectar el resultado, por ejemplo la adsorción del aditivo de resistencia fue mayor cuando se arrancó con PAE que con G-PAM.

Los ensayos muestran que las mediciones de carga utilizando PCD e instrumentos de potencial Z suministran buen control de la adición de polímero. La técnica multi capa da una cantidad creciente de aditivos que son adsorbidos a las fibras, lo que ayuda a dar por ejemplo una resistencia creciente hasta un cierto nivel.

En un proceso continuo de escala completa, tal como un proceso de elaboración de papel, la cantidad de polímero a ser agregada se controla preferiblemente y se determina mediante el potencial Z y las mediciones PCD después de cada adición de polímero en cada etapa durante el arranque del proceso. Estas cantidades son entonares utilizadas en e proceso. El potencial Z y las mediciones PCD son desarrollados preferiblemente durante la corrida del proceso solo después de la cabecera de caja. La

adición del primer polímero es hecha por ejemplo en el pulpeador, y los otros polímeros son entonces agregados en diferentes etapas en el extremo húmedo De la máquina de papel.

En los ejemplos anteriores solo la adición de los aditivos de resistencia a fibras de celulosa para la preparación del papel se describe. Sin embargo se debe entender que la invención se puede aplicar para adsorción consecutivamente de capas delgadas de tipos opcionales de polímeros catiónicos y aniónicos alternantes sobre la superficie de las fibras u otros tipos de partículas o grupos de partículas con el fin de construir multi capas delgadas de los polímeros interactuantes sobre la superficie de la partícula. Al agregar los polímeros en etapas consecutivas y permitirles formar varias capas sobre la superficie de la partícula, es posible adsorber mayores cantidades de polímero a la superficie de la partícula que lo que es posible cuando se agregan en una etapa que forman solo una capa. Con relación a los agentes de resistencia húmeda tal como el par Y el G-PAM es posible mediante el método de acuerdo con la invención producir papel y productos no tejidos que contienen al

menos 1,5, preferiblemente al menos 1,7, más preferiblemente al menos 2,0 aún más preferiblemente al menos 2,2 y más preferiblemente al menos 2,5% en peso o más del agente resistente a la humedad. Estos valores se refieren a la cantidad de agente resistente a la humedad que se adhiere a las fibras y se mide de acuerdo con el método de nitrógeno total descrito anteriormente. En algunos de los ensayos de laboratorio hasta el 3,8% en peso del agente resistente a la humedad se adhiere a las fibras (figura 7 y 8).

Esto también significa que con el método de acuerdo con la invención es posible producir papel tejido basado en fibras de celulosa sin mezcla de otros tipos de fibra, tales como fibras de refuerzo sintético, que tienen un índice de resistencia tensil de al menos 6,5, preferiblemente al menos 7,0 y más preferiblemente al menos 7,5 Nm/g. El término papel tejido a este respecto no incluye materiales ejercidos a hidroentramamiento. Estos valores se refieren a los productos de tejidos terminados producidos sobre una máquina de tejido a escala completa. La figura 7 muestra productos hechos en el laboratorio en los cuales usted normalmente logra valores de resistencia más altos. En los productos de

tejido acabados producidos con máquinas de tejido a escala completa y con tratamientos subsecuentes como crepeado, conversión etc. Los valores de resistencia son disminuidos.

Esto se muestra en los resultados en la tabla 3 abajo que muestran los resultados de las mediciones de resistencia sobre dos diferentes papeles de tejido fuertemente húmedo. El número 1 es un papel tejido utilizado como material relimpieza vendido por SCA Hygiene Products AB bajo la marca "M-TORK" y que tiene la siguiente composición De pulpa: 36% en peso CTMP y 64% en peso de pulpa kraft de madera blanda (TCF). Este contiene aproximadamente 0,7% en peso de PAE. El número 2 es un papel producido del mismo tipo de pulpas como el número 1 y en donde las fibras de celulosa fueron tratadas en etapas consecutivas de acuerdo con la invención con dos capas PAE, una capa G-PAM y dos capas CMC. Es de la vista de estos resultados que el papel tejido número 2 mostró propiedades de resistencia mejoradas. Se anota además que los papeles ensayados contenían una mezcla de CTMP y pulpa kraft de madera blanda. Para papeles que contienen altas cantidades o solo contienen pulpa kraft de madera blanda a un mayor valor de resistencia se esperarían.

Tabla 3

Muestra	1 (ref.)	2 (invención)
Gramaje g/m ²	24	21
Grosor 2kpa μ m	154	162
Masa 2kPa cm ³ /g	6,4	7,7
Resistencia tensil MD, N/m seco	242	438
Resistencia tensil CD, N/m seco	223	340
Índice tensil vMDCD seco Nm/g	10	18
Tensión MD %	28	37
Tensión CD %	4,9	4,6
Tensión vMDCD %	11,7	13,1
Trabajo hasta ruptura MD J/m ²	39	78
Trabajo hasta ruptura CD J/m ²	7,983	13,63
Trabajo hasta índice de ruptura v MDCD J/g	0,7	1,6
Resistencia tensil MD, agua N/m	102,9	206,8
Resistencia tensil CD, agua N/m	60,8	125,8
Indice tensil vMDCD agua Nm/g	3	8
Agua con resistencia relativa por %	34	42

La tabla 4 muestra los resultados de las mediciones para determinar la cantidad de agente de resistencia húmeda en la forma de PAE en algunos productos tejidos comercialmente disponibles y en el papel de tejido hecho con el método de acuerdo con la invención. La muestra A es un papel tejido hecho de acuerdo con la invención que corresponde a uno ensayado como No. 2 en la tabla 3.

La muestra B es un tejido de papel producido por Fort james y vendido bajo el nombre comercial "Lotus Profes". La muestra C es un tejido de papel producido por Procter & Gamble y vendido bajo el nombre comercial "Bounty". La muestra D es un papel de tejido producido por Metă Sărla y vendido bajo el nombre comercial "Katrin Cleany".

La cantidad de PAE en los diferentes papeles de tejido fueron medidas por el método de cromatografía de exclusión de ion descrito anteriormente y da la cantidad de PAE adsorbida en las fibras. Debe notarse que normalmente la cantidad de PAE u otro agente de resistencia a la humectación agregado al resultado se da en porcentaje de la solución de agente resistente a la humedad agregado por peso de fibras. Los agentes de resistencia a la humectación son vendidos como soluciones que contienen entre 6 a 25% del compuesto activo. Cuando hablamos acerca de la cantidad de agente resistente a la humedad nos referimos a la cantidad de componente activo adheridos a las fibras.

Tabla 4

Muestra	A (Invención)	B (ref.)	C (ref.)	D (ref.)
Cantidad de PAE (% en peso)	2	0,45	1,2	0,7

Como puede verse de estos resultados el papel A producido de acuerdo con la invención contenía cantidades considerablemente más altas de PAE que los productos de tejido comerciales de fuerte humectación ensayados.

REIVINDICACIONES

1. Un método para producir una partícula o grupo de partículas que tiene el propósito de ser usados en papel y/o productos no tejidos que tienen un recubrimiento de por lo menos 2, preferiblemente por lo menos 3, por fuera de cada uno de cada otro localizadas unas capas delgadas de polímeros alternantes catiónicos y aniónicos, en los cuales la partícula o grupo de partículas es tratada en pasos consecutivos con soluciones de los polímeros alternantes catiónicos y aniónicos, caracterizado en que

La cantidad del polímero respectivo para ser agregado en cada etapa es controlado por la medición de carga de la solución de tratamiento o de un líquido que contiene las o grupo de partículas y la solución del polímero, durante y/o después del tratamiento en cada etapa para poder determinar que sustancialmente todo el polímero es absorbido a la superficie de la partícula.

2. El método según la reivindicación 1, caracterizado en que la medida del potencial - Z de las partículas o grupos de partículas durante y/o después del tratamiento en cada etapa para poder determinar la cantidad de polímero catiónico/aniónico/adsorbido en la superficie de la partícula.

3. El método según las reivindicaciones 1 o 2,
✓ caracterizado en que la partícula es una fibra.

4. El método según la reivindicación 3 caracterizado
✓ en que la fibra es una fibra celulósica.

5. El método según la reivindicación 3,
✓ caracterizado en que la fibra es una fibra sintética o regenerada.

6. El método según las reivindicaciones 1 o 2,
✓ caracterizado en que la partícula es una partícula de carga, una partícula de recubrimiento u otro tipo de partícula usado en la fabricación de papel.

7. El método según una cualquiera de las reivindicaciones precedentes, caracterizado en que por lo menos uno de dichos polímeros es un aditivo de resistencia usado en la fabricación de papel, tal como un agente resistente al secado y/o resistente a la humectación.

8. El método según una cualquiera de las reivindicaciones precedentes, caracterizado en que en un proceso continuo para la adsorción consecutiva de capas delgadas de polímeros interactuantes sobre la superficie de las partículas o grupos de partículas, la cantidad del polímero respectivo a ser agregado en cada etapa es determinado en el inicio del proceso.

9. Papel o producto no tejido, caracterizado en que contiene fibras, partículas de carga o llenadoras u otras partículas producidas de acuerdo con el método de cualquiera de las reivindicaciones 1 a 8.

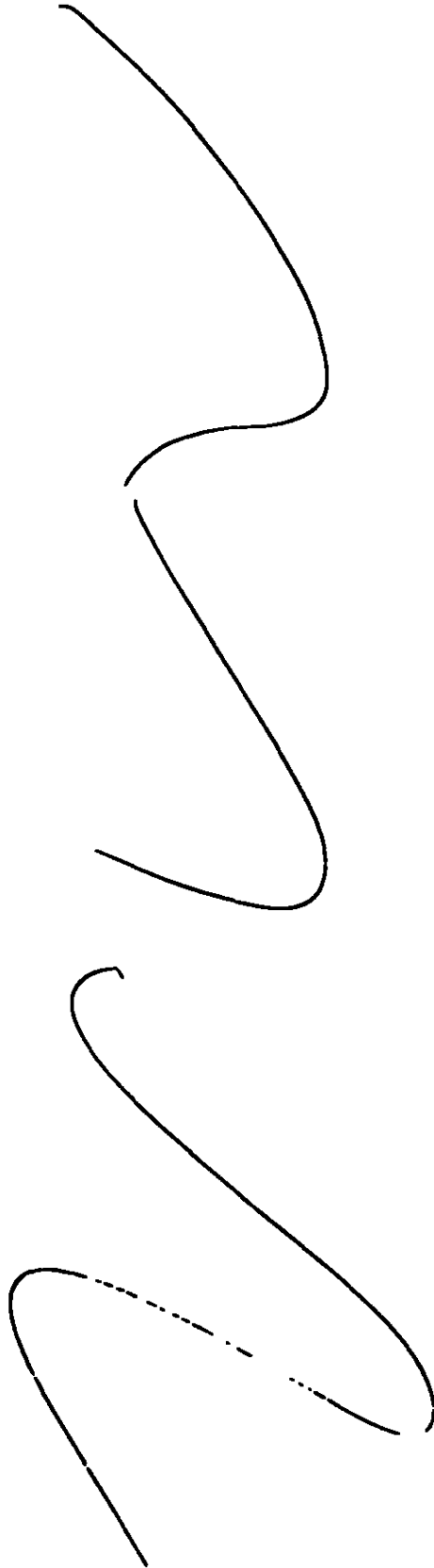
10. Papel o producto no tejido, caracterizado en que este contiene fibras, partículas de carga u otras

partículas que tienen por lo menos 3, por fuera una de cada otra localizadas unas capas delgadas de polímeros alternantes catiónicos y aniónicos y que este contiene por lo menos 1,5 preferiblemente por lo menos 1,7, y más preferiblemente por lo menos 2,0, aún más preferiblemente por lo menos 2,2 y mucho más preferible por lo menos 2,5% en peso del agente resistente a la humedad.

11. Papel o producto no tejido de acuerdo con la reivindicación 10, caracterizado en que el agente resistente a la humectación es un polielectrolito catiónico tal como poliaminoamida - epiclorhidrin (PAE) y/o glioxilato de poliacrilamida (G-PAM).

12. Un tejido de papel basado en celulosa de pulpa de madera con ninguna mezcla de otros tipos de fibra, tales como fibras reforzadas sintéticas, caracterizado en que este contiene por lo menos 3, capas delgadas localizadas una por fuera de la otra de polímeros catiónicos y aniónicos alternantes y que tiene un índice de tensión a la humedad de por lo menos 6,5, preferiblemente por

lo menos 7,0 y más preferiblemente por lo menos
7,5 Nm/g.



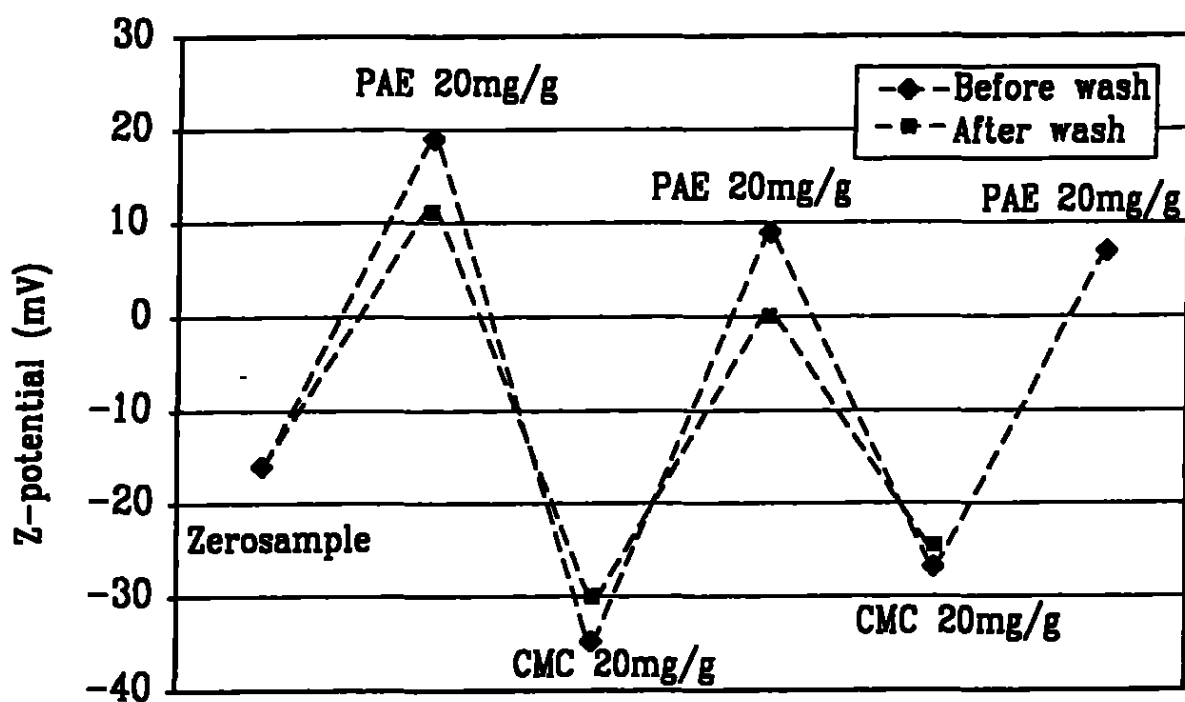


FIG.1

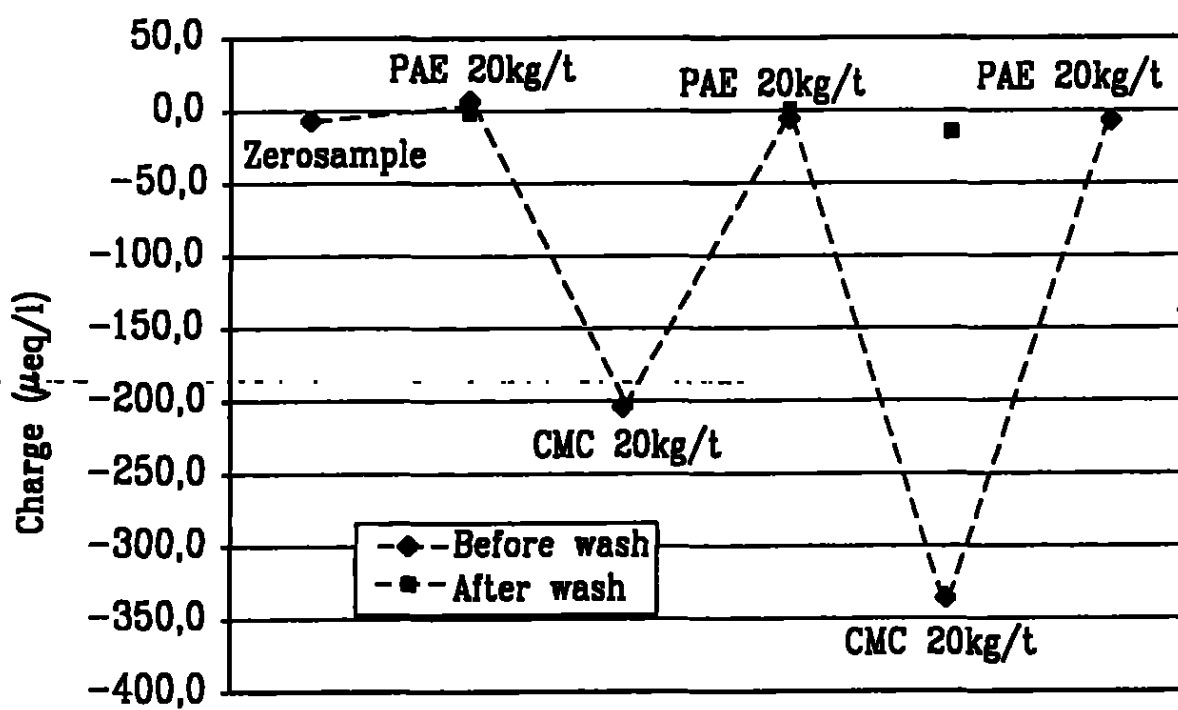


FIG.2

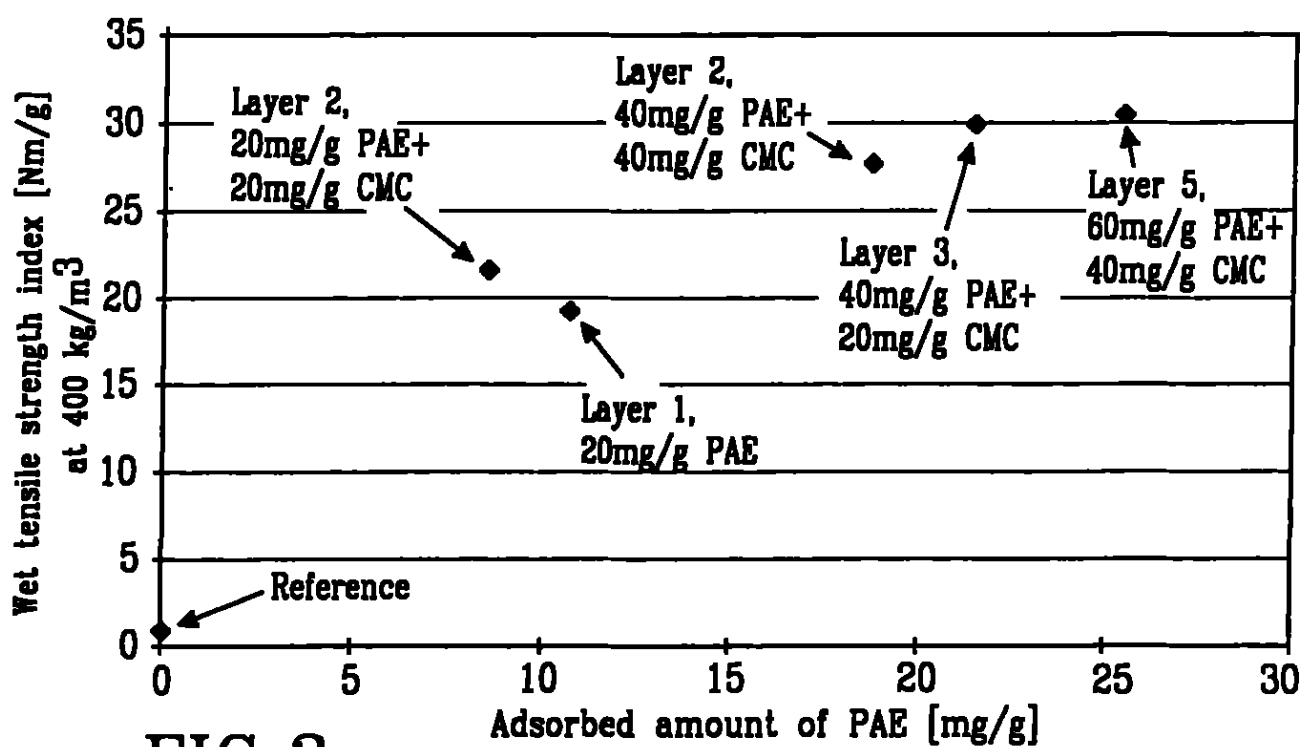


FIG.3

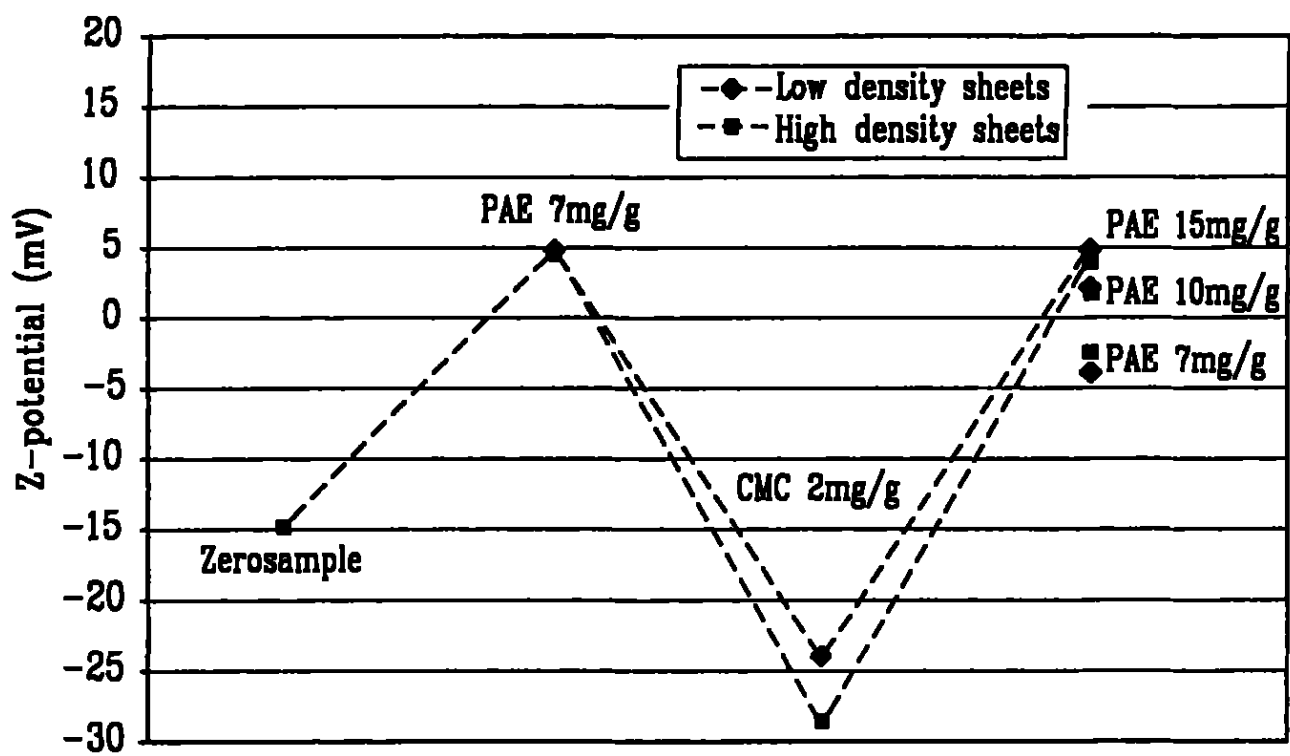


FIG.4

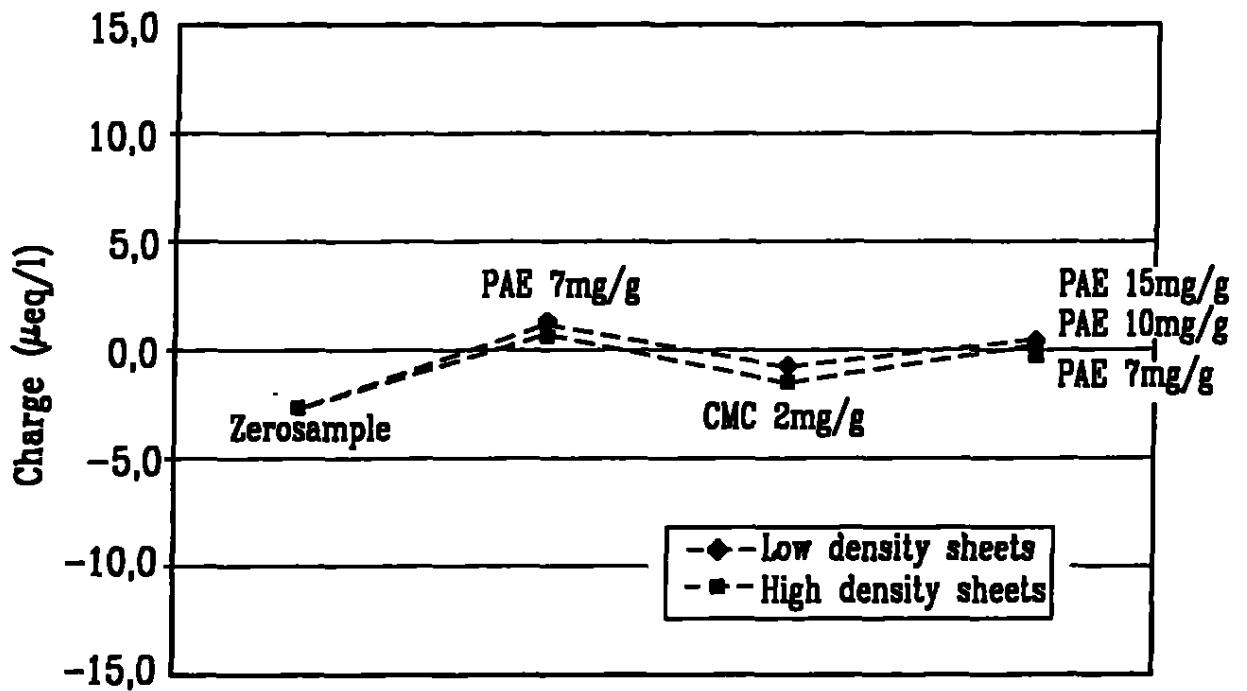


FIG. 5

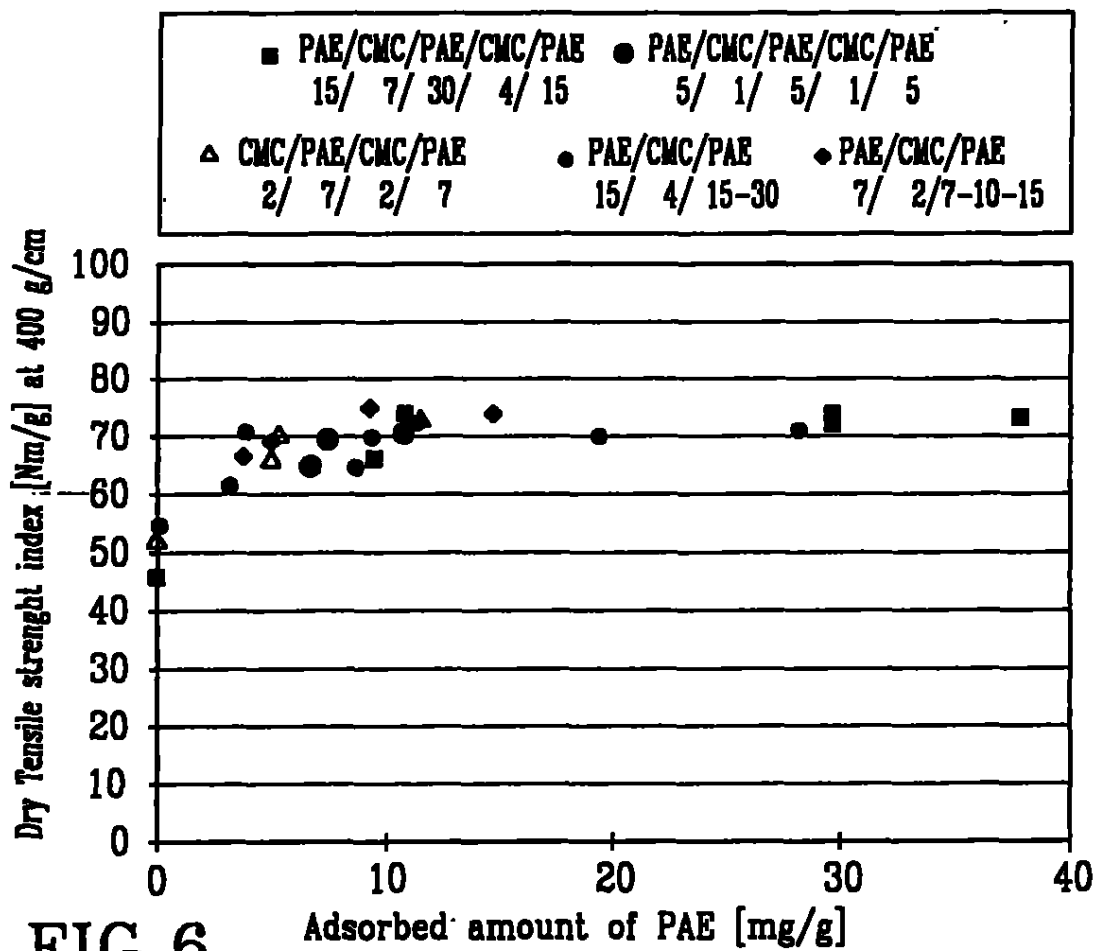
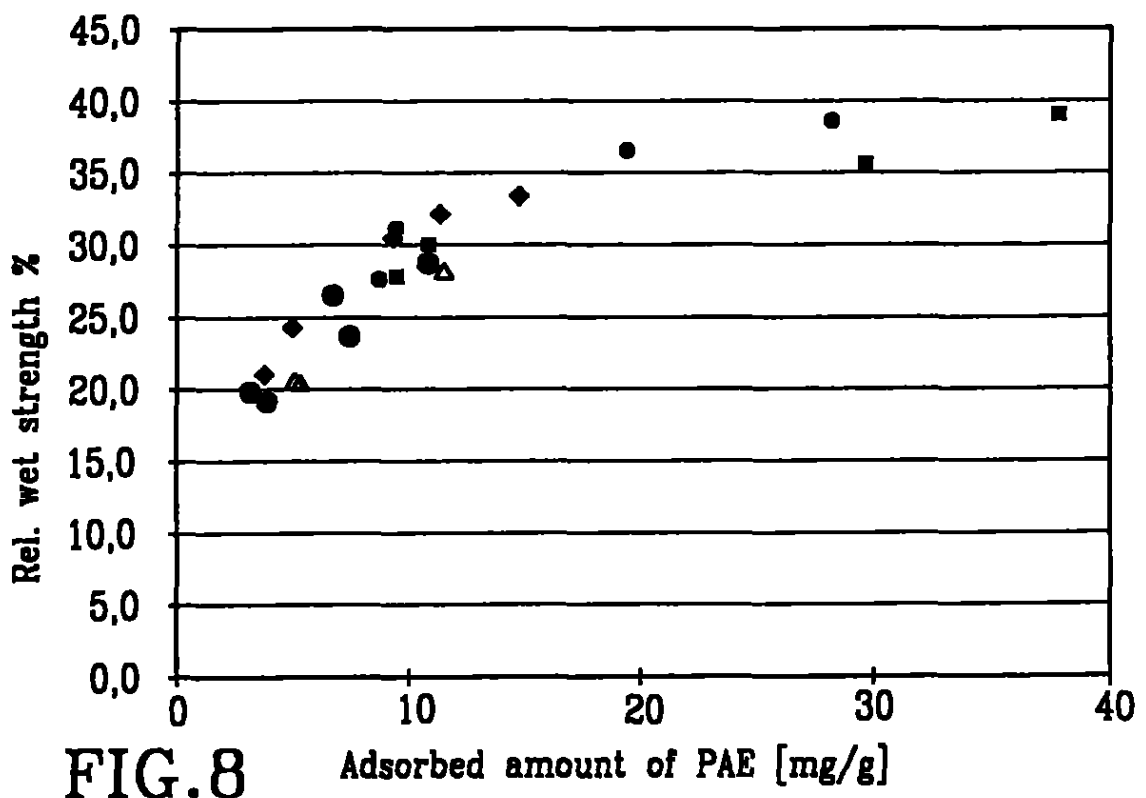
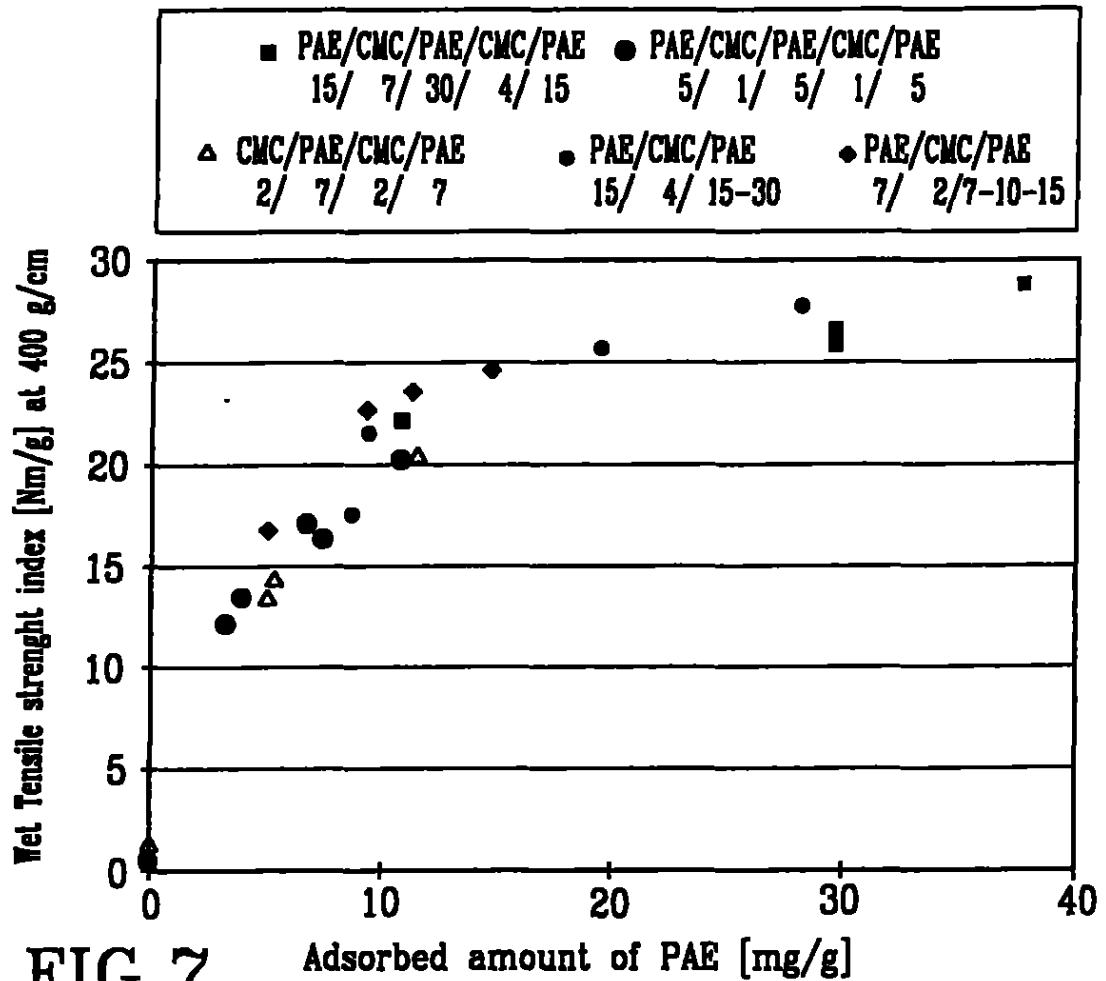


FIG. 6



87

Expediente No		02088336	No de Follo
Item		No de unidades	
1	CD		
2	DVD		
3	REVISTA		
4	LIBRO		
5	PERIODICO		
6	DISQUETES		
7	SOBRE DE MANILA	1	
8	SOBRE BLANCO TAMAÑO CARTA		
9	SOBRE BLANCO TAMAÑO OFICIO		
10	OTROS:		
Observaciones: <i>anc final</i>			



88

Industria y Comercio
SUPERINTENDENCIA

SUPERINDUSTRIA Y COMERCIO

Radicación : 02000336 00000000

Folios: 88

Fecha (AÑO): 2002-10-31 16:50:00

Trámite : 011 PCT-PATENT 379 FASE NDCI 411 PRESENTAR

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 02 - 65,102
FECHA : SEPTIEMBRE 30 DE 2002

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	7030556	30/09/2002	23,260,000.00

***** CONCEPTO *****

CANT. REGISTRADO	CONCEPTO	TOTAL CONCEPTO
1 50003-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	378,000.00
	TOTAL :	378,000.00

SON: TRESCIENTOS SETENTA Y OCHO MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

010 11256 -841-003-2

Carrera 13 No. 27-00 Pisos 5, 7 y 10
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SUPERINTENDENCIA Y COMERCIO

Radicación: 02006336 00000000

Folios

Industria y Comercio

Fecha (ACT): 2002-10-01 16:30:00

Trámite: 011 PCT-PATENT 379 FASE INCI 411 PRESENTA

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA

REQUISITOS NECESARIOS PARA PRESENTACION DE LA SOLICITUD DEL TRÁMITE

USUARIO RADICADOR

PATENTE DE INVENCION ☒MODELO DE UTILIDAD ☐☐☒

- Indicación de que se solicita la concesión de una patente ☐
- Datos de identificación del solicitante o de la persona que presenta la solicitud ☐
- Descripción de la invención ☐
- Dibujos de ser e. los pertinentes ☐
- Comprobante de Pago de las tasas establecidas ☐

☐☒☐☒☐☒☐☒☐☒COMPLETA ☒

INCOMPLETA

☐☐DISEÑO INDUSTRIAL ☐

- Indicación de que se solicita el registro de Diseño Industrial ☐
- Datos de identificación del solicitante o de la persona que presenta la solicitud ☐
- Representación gráfica y foto gráfica del Diseño Industrial o muestra del material que incorpora el diseño ☐
- Comprobante de pago de las tasas establecidas ☐

☐☐☐☐☐☐☐☐☐☐COMPLETA ☐

INCOMPLETA

☐☐ESQUEMA DE TRAZADO ☐

- Indicación de que se solicita el registro de un Esquema de trazado ☐
- Datos de identificación del solicitante o de la persona que presenta la solicitud ☐
- Representación gráfica del esquema de trazado ☐
- Comprobante de pago de las tasas establecidas ☐

☐☐☐☐☐☐☐☐COMPLETA ☐

INCOMPLETA

☐☐

Firma Responsable

Fecha

Carrera 13 No. 27-60 Piso 2m

Commutador 362 08

Fax 750 52 20 e-mail info@sergi.com

Bogotá D.C. Colombia



90

2020
Bogotá, D.C.,

Doctor:
EMILIO FERRERO
Apoderado
S C A HYGIENE PRODUCTS A B

Oficio N° **05599**

ASUNTO:	Radicación N°	02-88336
	Solicitud internacional	PCT/SE2001/000612
	Fecha inicio fase nacional	06/11/2002
	Trámite	011
	Evento	379
	Actuación	330
	Folios	001

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

- ☐ La solicitud nacional no contiene la traducción de la solicitud internacional tal como fue modificada. (Numeral 5.2.5, capítulo quinto del título décimo de la Circular Única de la SIC).
- ☐ La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante. (Art. 26-k) Decisión 486).
- ☐

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

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


ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones.

El anterior requerimiento fue notificado por fijación en lista de fecha, 19 JUL 2003.