

FORMULARIO ÚNICO 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 Zeist B.V. Dirección: NL-3700 Zeist, The Netherlands Nacionalidad o domicilio: Zeist, Holanda Lugar de constitución: Zeist, Holanda		IDENTIFICACIÓN C.C. ☐ NIT: ☐ C.E. ☐ OTRO ☐ Cual _____ NÚMERO _____
	Teléfono: _____ Fax: _____ E. Mail: _____		
3) REPRESENTANTE O APODERADO	Nombre: DILIA MARÍA RODRÍGUEZ D'ALEMAN Dirección: Carrera 11 N°. 93-43 Of. 404 Santafé de Bogotá D.C. Teléfono: 6350835 Fax: 6350824 E. Mail: clarkemodet@clarkemodet.com.co		IDENTIFICACIÓN C.C. ☒ NIT: ☐ C.E. ☐ OTRO ☐ NÚMERO: 41.654.882 TP: 20824 CSJ
4) INVENTOR (ES) (72)	Nombre: 1. THORNTON, Jeffrey, Wilson; 2. VAN BRUSSEL-VARRAEST, Dorine, Lisa; 3. BESEMER, Aris; 4. SANDBERG, Susan Dirección: 1. Jagersweg 13, NL-1272 AC Guisen, Netherland. 2. Kopeind 1, NL-2411 WG Bodegraven, The Netherland. 3. Burg-Jhr. H. v.d. Boschstraat 111, NL-3958 CE Amerongen, Netherland. 4. Gubbekullavägen 15, S-439 35 Onsala, Sweden. Nacionalidad o Domicilio: 1. American; 2. Belga; 3. Alemán; 4. Sueco		
5) PCT (88) Solicitud Internacional No. PCT/NL01/00343 Fecha: Mayo 4, 2001 Publicación Internacional No. WO 01/83887 A 1 Fecha: Noviembre 8, 2001			
6) Título (54) POLIMEROS QUE CONTIENEN ALDEHIDO COMO ADITIVOS DE RESISTENCIA A LA HUMEDAD			
7) Clasificación Internacional (51) D21H 21/20, C08B 15/00, 31/00/D21H 17:25, 17:28			
8) PRIORIDAD SI ☒ N ☐	33) País de Origen	32) Fecha	31) Número de Solicitud
	EUR PEA	04.05.2000	00201630.1
	EUROPEA	11.05.2000	00201693.9
9) Comprobante de pago N°. 02-71.629 Fecha: OCTUBRE 25, 2002			



2

Industria y Comercio

SUPERINTENDENCIA

MIT : 800176089-2

RECIBO OFICIAL DE CAJA : 02 - 71,629
FECHA : OCTUBRE 25 DE 2002

SUPERINDUSTRIA Y COMERCIO

Radicación : 82099179 00000000

Folios: 96

Fecha (MSD): 2002-10-31 16:22:36

Trámite : 011 PCT-PATENT 379 FASE NRCI 411 PRESENTAC

Resolución de 2002 DIRECCION DE INTELIGENCIA PRECATORIA

***** CONSIGNACION

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET Y CO. COLOMBIA	CONSIGNACION	BANCO POPULAR	050-00110-6	4801707	24/10/2002	2,537,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	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. _____

Carrera 13 No. 27-00 Pisos 5, 7 y 10
Conmutador 382 0840
Fax 350 5220
E-mail: info@sic.gov.co
www.sic.gov.co
Bogotá, D.C., Colombia

10)

ANEXOS

3

- ☒ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Comprobante de pago por reivindicación de prioridad
- ☒ Documento que acredite la existencia y representación legal cuando el solicitante sea persona Jurídica
- ☒ Poderes, si fuera el caso
- ☐ Documento de cesión del inventor al solicitante o a su causante
- ☐ Declaraciones
- ☐ Copia de la solicitud Internacional. (Resumen, descripción, reivindicación, Dibujos).
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicación, Dibujos)
- ☒ Copia 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 12 x 12 y 6 x 6 cm
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionados parcial o totalmente con la invención de esta solicitud.
- ☒ Otros: 1. Solicitud internacional de publicación WO 01/83887 A1
2. Notificación de transmisión del reporte del examen preliminar
3. Reporte del examen preliminar

11) FIGURA CARACTERÍSTICA:

12) Solicitud concesión de la patente,

NOMBRE: DILIA RODRÍGUEZ D'ALEMAN

FIRMA:

C.C. 41.654.882 de Bogotá TP 20824 CSJ

Instrucciones para el diligenciamiento del presente formulario. Ver reverso de esta pagina

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4

Traducción oficial No. 01/0120 del holandés al español de los sellos y autoadhesivos en holandés que aparece en el documento en el cual la compañía SCA HYGIENE PRODUCTS ZEIST B.V., con domicilio en los Países Bajos, otorga un poder a DILIA MARIA RODRIGUEZ D'ALEMAN y CLAUDIA LUCIA CARO RAMIREZ.

(Al reverso del documento):

2 veces sello: Dr. W.H.M. Fransen - notario en Zeist

sello: Visto para la legalización de la firma del Dr. W.H.M. Fransen, notario en Zeist, por el suscrito, Presidente del Juzgado del Distrito de Utrecht, el día 17-1-2001.

(Firma ilegible)

Dr. H.N. Brouwer

sello: Juzgado del Distrito en Utrecht

autoadhesivo:

Visto para la legalización de la firma del Dr. H.N. Brouwer, Presidente del Juzgado del Distrito en Utrecht, La Haya, 19 de enero de 2001.

El Ministro de Justicia, por el Ministro, el Jefe de la Dirección de Administración y Apoyo del Departamento Administrativo, por él, (Firma ilegible)

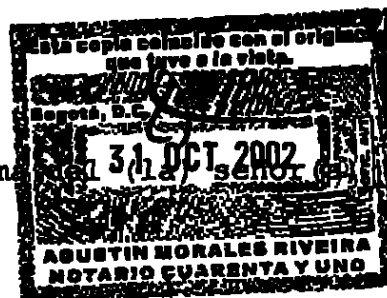
sello: Ministerio de Justicia

estampilla: Ministerio de Justicia - f2,50

sello: Visto para la legalización de la firma

P.N.A. de Raad.

La Haya, 19 de enero de 2001



MAIJA HEMPENIUS
Traductora e Intérprete Oficial
Res. 2667/89 Min. Justicia

El Ministro de Relaciones Exteriores, por él,

(Firma ilegible) - Sra. L.M. Cuelenaere

sello: Ministerio de Relaciones Exteriores - 4672 - Derechos de expedición F20,=.

Anexo al documento aparece la certificación No. 010 del Consulado de Colombia en Amsterdam, con fecha del 22 de enero de 2.001, en la cual el Cónsul certifica que el señor L.M. Cuelenaere, oficial del Ministerio de Relaciones Exteriores de los Países Bajos, ejercía en la fecha de la autenticación del documento las funciones indicadas y que la firma y el sello que aparecen son suyos.

El Cónsul certifica igualmente que la compañía **SCA HYGIENE PRODUCTS ZEIST B.V.** es una compañía debidamente constituida de acuerdo con las leyes de los Países Bajos y registrada en la Cámara de Comercio e Industria de Utrecht bajo el número 30135846. También certifica que el señor Johannes Joseph SCHEEL, director financiera de la citada compañía, está autorizado para firmar el poder adjunto.

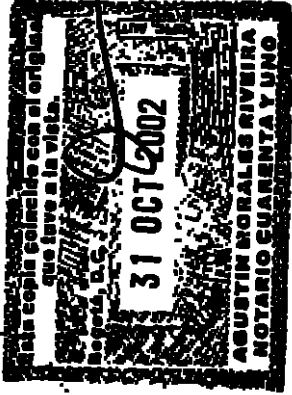
También aparece la constancia de la cancelación de los derechos consulares por un valor de US\$107,00. La firma del Cónsul a su vez está debidamente autenticada y sellada ante la Oficina de Legalizaciones del Ministerio de Relaciones Exteriores de Colombia, el día 30 de enero de 2.001 bajo el número 006423.

ES TRADUCCION FIEL Y COMPLETA.

Santafé de Bogotá, D.C., 13 de febrero de 2001.

MAIJA HEMPENIUS
Traductora e Interprete Oficial
Res. 2601/89 Min. Justicia





MINISTERIO DE RELACIONES
EXTERIORES

Macaya
109720

CUY FIRMADO APARECE EN EL
DOCUMENTO DESEMPEÑA
LAS FUNCIONES INDICADAS

NO SE ASUME
RESPONSABILIDAD DEL TEXTO

2001 FEB 21 A 11:00

Madriguera
JEFE DE LEGALIZACIÓN
SANTAFE DE BOGOTÁ

Clarke, Modet & Co. Colombia, Ltda.

Carrera 11, N° 93-53, Of. 404 - Santa Fé de Bogotá, Colombia

PODER

Yo (nosotros), abajo firmante(s)

Johannes Joseph Scheel

en mi (nuestro) carácter de representante(s) legales de

SCA Hygiene Products Zeist B.V.

una sociedad organizada y existente de acuerdo con las leyes de

Paises bajos

y en actual cumplimiento de su objeto social, con domicilio en

por el presente instrumento confiero (conferimos) poder especial a favor de DILIA MARIA RODRIGUEZ D'ALEMAN, tp. 20824 y CLAUDIA LUCIA CARO RAMIREZ, tp. 38448, con domicilio en Santa Fé de Bogotá, Colombia, para que actuando en su orden en nombre del (de la) otorgante lo (la) representen ante cualquier entidad, autoridad y/o persona, especialmente ante las del orden Administrativo, Contencioso Administrativo, Judicial, Tribunales de Arbitramento y/o cualquier otro en lo referente a los siguientes asuntos:

- 1) Solicitar, tramitar, obtener y/o registrar cualquiera de las modalidades de Propiedad Industrial, tales como: patentes de invención, modelos de utilidad; diseños industriales, variedades vegetales; marcas; lemas, nombres y enseñas comerciales y denominaciones de origen; así como sus renovaciones, prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.
- 2) Solicitar, tramitar, obtener y/o registrar derechos de autor, en cualquiera de sus presentaciones así como la protección de secretos industriales y know-how.
- 3) Solicitar, tramitar, obtener y/o registrar registros sanitarios, permisos y/o licencias de funcionamiento; así como sus renovaciones o prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.
- 4) Ejercer acciones de oposición, observación, reclamos, reconsideración, reposición, apelación, cancelación administrativa o judicial, nulidad, protección al consumidor, concesión de licencias, protección de secretos industriales y demás acciones y recursos relacionados con derechos derivados de los asuntos arriba indicados y en contra de la competencia estatal, acciones derivadas de la obtención o explotación de licencias, acciones de indemnización de perjuicios. También podrá(n) intervenir en juicios civiles, comerciales, penales, contencioso-administrativos, tutelares y de policía; en acciones o juicios promovidos por el (la) mandante o en contra el (ella).
- 5) En el ejercicio de este mandato los mandatarios arriba mencionados quedan facultados para: conciliar, cancelar, transigir, comprometer en árbitros, desistír, recibir y tomar posesión de la cosa objeto de litigio y renunciar o desistír a derechos concedidos o en curso de concesión, admitir los hechos del proceso.
- 6) Ratificar o no la agencia oficiosa.
- 7) Así mismo faculto (facultamos) a los mencionados apoderados para recibir notificaciones y designar apoderados judiciales o extrajudiciales, sustituir el presente poder y revocar las sustituciones que hicieran.

Dado y firmado en

a los días de

de

Granted and signed at

on this day of



POWER OF ATTORNEY

I (we), the undersigned

Johannes Joseph Scheel

legal representative(s) of

SCA Hygiene Products Zeist B.V.

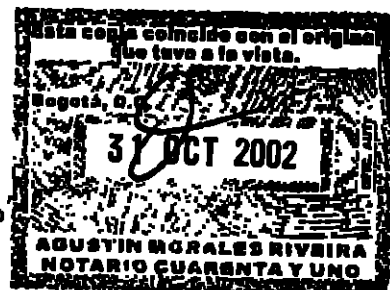
an organization existing under the laws of

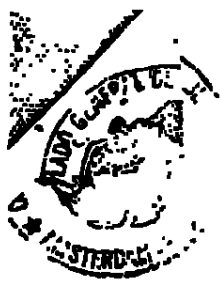
Netherlands

and in present execution of its business activity, domiciled at

do hereby grant POWER OF ATTORNEY to DILIA MARIA RODRIGUEZ D'ALEMAN, tp. 20824 and CLAUDIA LUCIA CARO RAMIREZ, tp. 38448, residing in Santa Fé de Bogotá, Colombia, to act in the order of their appointment in behalf of grantor before any entity, authority and/or natural or juridical person, especially before those Administrative, Administrative-Contentious, Judicial, arbitration courts, and/or any other, in all matters concerning the following:

- 1) To apply, process, obtain and/or register any of the modalities of Industrial Property, such as: Patents of Invention, Utility Models; Designs, vegetal varieties; Marks, Slogans, Trade Names and emblems and appellations of Origin; as well as their renewals, extensions, assignments, changes of name and/or domicile, agreements and licenses.
- 2) To apply, process, obtain and/or register copyrights of any kind as well as protection of industrial secrets or know-how.
- 3) To apply, process, obtain and/or register sanitary registrations, operating authorizations and/or licenses; as well as their renewals or extensions, assignments, changes of name and/or domicile, agreements and licenses.
- 4) To bring actions of opposition, observations, claims, reconsideration, appeal or legal remedies, cancellations, nullity, protection to the consumer, granting of licenses, protection of trade secrets and other actions related with rights derived from the above-mentioned matters and against the unfair competition, actions resulting from the obtaining or exploitation of licenses, recovering damages actions. They can also intervene or participate in Civil, Commercial, Criminal or Contentious-Administrative Trials; the actions for writ mandamus, police actions; in actions, lawsuits or litigations instituted by the grantor or against him.
- 5) To the effect of this mandate the above-named proxy are empowered to: conciliate, cancel, settle, submit to arbitration, withdraw and to receive and take possession of the litigation related object and waive or renounce the rights granted or in process of granting, admit the facts of the case.
- 6) To ratify or not the officious agency.
- 7) I (we) hereby appoint the afore mentioned attorneys with powers to receive notifications and to designate judicial and extrajudicial attorneys, substitute this Power of Attorney and to revoke such substitutions.





9
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Consulado General de Colombia

Amsterdam, Países Bajos
Teléfono: 31 20 3050111 - Fax 31 20 3050110

No. 010

El suscrito Cónsul General de Colombia en Amsterdam, Países Bajos, visto los documentos presentados por el interesado.

CERTIFICA:

- 1.- Que el señor **L.M. CUELENAERE**, quien como Oficial del Ministerio de Relaciones Exteriores en la Haya- Países Bajos, autenticó el documento precedente, ejercía en la fecha las funciones indicadas y su firma y sello corresponden a los registrados en este Consulado General.
- 2.- Que la compañía **SCA HYGIENE PRODUCTS ZEIST B.V.** es una compañía debidamente constituida de acuerdo con las leyes de los Países Bajos y cumple su objeto conforme a las mismas según registro de la Cámara de Comercio y Fabricas de Utrecht No.30135846.
- 3.- Que el señor **Johannes Joseph SCHEEL** en su carácter de Director Financiero de la citada compañía, está facultado para firmar el documento precedente de acuerdo con el Registro de la Cámara de Comercio que se tuvo a la vista.

En constancia se firma en Amsterdam, Países Bajos a los veintidós (22) días del mes de enero del año dos mil uno (2001).-

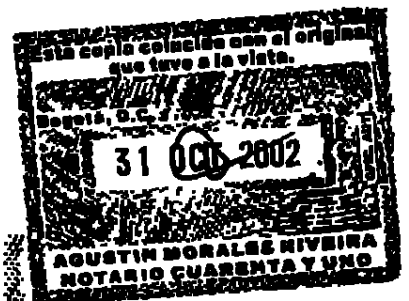
LUIS IGNACIO ANDRADE BLANCO
Cónsul General

DERECHOS PAGADOS: CIENTO SIETE DOLARES

US\$ 100,00 Fondo Rotatorio

US\$ 7,00 Impuesto de Timbre

"Se pagaran en Colombia los impuestos de timbre que se ocasionen al ejecutarse las obligaciones del presente documento, de conformidad con el Art. 519 del Estatuto Tributario".-



51 OCT 2002

521

006423
J. Cárdenas
CÚA FIRMA APARECE EN EL
FOLIO DESEMPEÑA
LAS FUNCIONES INDICADAS

2002 JUN 30 ~~ATK 30~~

**LEGALIZACIONES
FEDEBOGOTA D.C.**

CERTIFICADO NOTARIAL (SOCIEDADES)

(Powers of attorney granted in: El Salvador, Estados Unidos, México y Venezuela)

En este día del mes de ENERO del año 2001
 el Notario que suscribe DA FE de que:
Johannes Joseph Sched
 (nombre de la persona que firma el poder)

mayor de edad y domiciliado en Huizen
The Netherlinds firmó de su puño
 y letra el documento que antecede.

2. Conoce al (a la) otorgante y que este (a) está legalmente capacitado para el otorgamiento.
3. El otorgante ha firmado el referido documento en su carácter de financiel director

de la persona jurídica SC2 Hygiene
Products Zist B.V.

4. La citada persona jurídica con sede en Zist, The Netherlinds está legalmente constituida, que tiene actualmente existencia legal y que el acto para el cual se ha otorgado este poder está comprendido entre los que constituyen su objeto social.
5. El otorgante tiene directamente la representación que ostenta, que es de legítima y que está facultado para otorgar este poder.
6. las anteriores certificaciones de Mr. W. H. M. Fransen constan porque he tenido a Mr. W. H. M. Fransen documentos auténticos.

Mr. W. H. M. Fransen
 Hendrik Maria
 Fransen



Notario Público

NOTA: A continuación de lo anterior, el Consol de Colombia debe autenticar la firma del Notario Público.

CERTIFICADO NOTARIAL (INDIVIDUOS)

A las ... días del mes de ...
 de ..., el Notario que suscribe DA FE de que:

1. ...
 (nombre de la persona que firma el poder)

mayor de edad y domiciliado en ...
... firmó en su presencia
 el documento que antecede, conoce al otorgante y que
 este está legalmente capacitado para el otorgamiento.

Notario Público

NOTA: A continuación de lo anterior, el Consol de Colombia debe autenticar la firma del Notario Público.

Para todos los demás países el Señor Consol de Colombia debe expedir una certificación consular dejando constancia 1) de la existencia legal de la sociedad, 2) de que esta ejerce actualmente su objeto social, y 3) de que la persona o personas que otorgan el poder están facultadas para hacerlo, dejando constancia así mismo de que tuvo a la vista las pruebas que acreditan tales circunstancias.

NOTARIAL CERTIFICATE (CORPORATIONS)

(Powers of attorney granted in: El Salvador, Mexico, U.S.A. and Venezuela)

On this 9th day of January 2001
 the undersigned Notary CERTIFIES that:
 1. Johannes Joseph Sched
 (name of the person who signs the power of attorney)

of legal age and domiciled in Huizen,
The Netherlinds set his hand on the
 foregoing document.

2. The grantor is to him personally known and that he/she has legal capacity to execute the document.
3. The grantor has executed the foregoing document in his capacity of financiel director

of the juridical person SC2 Hygiene
Products Zist B.V.

4. The mentioned juridical person with place of business in Zist, The Netherlinds is duly organized, has actual legal existence and that the purposes for which the power of attorney is granted are within the scope of its corporate purposes.
5. The grantor has in fact the referred quality and that his/her representation is legal and that he/she is empowered to grant this power of attorney.
6. I have based the above certifications 3, 4 and 5, on the following authentic documents which for such purpose were exhibited to me:

Mr. W. H. M. Fransen
 Hendrik Maria
 Fransen



Notary Public

NOTA: Then the Colombian Consol must legalize the signature of the Notary Public.

NOTARIAL CERTIFICATE (INDIVIDUALS)

On this ... day of ...
 the undersigned Notary CERTIFIES that:

1. ...
 (name of the person who signs the Power of Attorney)

of legal age and domiciled at ...
... signed in his presence the
 foregoing document, the grantor is to him personally known and
 that he/she has legal capacity to execute the document.

Notary Public

NOTA: Then the Colombian Consol must legalize the signature of the Notary Public.

For all other countries the Colombian Consol must issue a consular certification stating 1) the legal existence of the corporation, 2) that the corporate purposes are actually being accomplished, 3) that the person or persons who grant this Power of Attorney are empowered to do it. The Consol will certify also that the documents evidencing these circumstances were exhibited to him.

Gezien voor legalisatie de handtekening
 van Mr. W. H. M. Fransen
 Notaris te Zist door mij
 President der Arrondissementsrechtbank
 te Utrecht, de 17-1-2001

Gezien voor legalisatie van de handtekening
 van Mr. W. H. M. Fransen
 President van de Arrondissementsrechtbank te Utrecht
 te Utrecht, de 17-1-2001
 De Minister van Justitie,
 namens de minister,
 hoofd van de directie Bedrijfsvoering en Onderzoeken
 Bestuursdepartement,
 voor deze,

19 11



Gezien voor legalisatie van de handtekening
 van Mr. W. H. M. Fransen

te Utrecht, de 17-1-2001



Leges 120,-

De Minister van
 Buitenlandse Zaken
 voor deze,
 Mr. J. M. C. de Krom

Ned

Octrooi

PATENT COOPERATION TREATY

INGEK. 27 SEP 2002

Exchange of IPER dated
29.08.02From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

Paraaf Bewer

To:

JORRITSMA, Ruurd et al
Nederlandsch Octrooibureau
Postbus 29720
Scheveningseweg 82
NL-2502 LS The Hague
PAYS-BAS

preliminary examination report.

opponeren aan client:

? 25-10-02

termijn omzetting in: reg./nat. fase:

4-11-2002

PCT

8

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

25.09.2002

Applicant's or agent's file reference
BO 43821 RJ /MM

IMPORTANT NOTIFICATION

International application No.
PCT/NL01/00343International filing date (day/month/year)
04/05/2001Priority date (day/month/year)
04/05/2000

Applicant

SCA HYGIENE PRODUCTS ZEIST B.V. et al

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.

For the purpose of deciding whether the claimed invention is patentable or not, the elected Offices may apply criteria additional to or different from the criteria on which the international preliminary examination report is based (see Articles 27(5), 33(5)). Additional criteria may include e.g. exemptions from patentability and the requirements of enabling disclosure and of clarity and support of claims.

Name and mailing address of the IPEA/



European Patent Office
D-80289 Munich
Tel. +49 89 2399-0 Tlx 523856 apmu d
Fax: +49 89 2399-4485

Authorized officer

Lázaro Ortiz, A

Tel. +49 89 2399-8011



Re Item V

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

Reference is made to the following documents:

D1: WO-A- 00 11046
D2: US-A-4 675 394
D3: EP-A-0 283 951
D4: EP-A-0 232 851
D5: US-A-5 958 187

1. Document D1 (see claims 1,6,14,25,56; examples) discloses use of a water-soluble polymer containing aldehyde groups per recurring unit in the range 0.25-2.25 of the polymer and/or at least 5 aldehyde groups per molecule and containing at least 1 anionic group per molecule, the ratio of aldehyde groups to anionic groups being higher than 0.75:1, as a wet strength additive. (Moreover, for paper - should be clarified in applicant's claim.) If the highest value (50%) given in claim 6 is combined with the disclosure in claim 14 and claim 25, it results in a ratio of aldehyde functionality to anionic moiety of 1:1. The molecular weight is not specified in the description, but in view of the products cited, it is assumed that it is higher than 800. It should further be noted that claim 1, contrary to what would appear to be the opinion of the applicant, is not restricted by the way the aldehyde functions have been introduced into the molecules. Furthermore, it is questionable whether it would be possible to assess on the polymer according to use claim 1 in which way the aldehyde groups have been introduced. And anyhow, it is not (yet) made clear that the monosaccharide units refers to the (bio)polymer itself. As to the expression "biopolymer" it is furthermore considered as vague and can not provide any restriction of the subject-matter in view of D1.

Therefore claim 1 would appear to lack novelty; Art. 33(2) PCT. This finding is extended to at least claims 4, 10,11 and 13.

2. In view of document D1 most of the features of the dependent claims would

appear to be either explicitly or implicitly already known and when not they would seem of a trivial nature, in particular when the contents of documents D2 (see abstract), D3 (see page 4, line 47-page 5, line 24; claims 1,2,5,15 and 16), D4(see page 4, line 5- page 7, line 15; claims 1,2,5-8) and D5 (see col. 5, line 32-col. 7, line 50) cited in the search report are considered (Art. 33(2)/Art. 33(3) PCT).

3. For the assessment of the present claims on the question whether they are industrially applicable, no particular reasoning would appear necessary to give. The industrial application would appear to be evident (Art. 33(4) PCT).

Upon entering the national/regional phase the independent claim should be drafted in the two-part form, cited documents acknowledged in the description and the description adapted to any amended claims, if national/regional regulations requires so.

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PCT/NL01/00343

Claims

(94)

1. Use of a water-soluble or water-dispersible biopolymer having a molecular weight of at least 800, containing 0.25-2.25 aldehyde groups per recurring unit of the biopolymer and/or at least 5 aldehyde groups per molecule, the aldehyde groups being present as a result of oxidation of dihydroxyethylene and/or hydroxymethyl moieties of recurring monosaccharide units, and containing at least 1 anionic group per molecule, the ratio of aldehyde groups to anionic groups being higher than 0.75:1, as a wet strength additive.
2. Use according to claim 1, in which the degree of substitution for aldehyde groups is 0.1-2.95 per recurring unit of the biopolymer, and the degree of substitution for anionic groups is 0.03-1.0 per recurring unit of the biopolymer.
3. Use according to claim 1, in which the degree of substitution for aldehyde groups is 0.25-2.25 per recurring unit of the biopolymer, and the degree of substitution for anionic groups is 0.05-0.4 per recurring unit of the biopolymer.
4. Use according to any one of claims 1-3, in which the anionic groups comprise carboxylic groups.
5. Use according to any one of claims 1-4, in which the biopolymer is a polysaccharide.
6. Use according to claim 5, in which the biopolymer is starch or cellulose or a starch- or cellulose-derived polymer.
7. Use according to claim 5 or 6, in which the aldehyde groups and the anionic groups are present as a result of oxidation of dihydroxyethylene moieties of recurring monosaccharide units.
8. Use according to claim 5 or 6, in which the aldehyde groups and the anionic groups are present as a result of oxidation of hydroxymethyl moieties of monosaccharide units.
9. Use according to any one of the preceding claims, in which anionic groups are present as a result of carboxymethylation.

10. Use according to any one of the preceding claims, in which the biopolymer further contains cationic groups with a degree of substitution of 0.01-0.50.
11. Carbohydrate derivative containing 0.10-2.95 aldehyde groups, and 0.03-1.0 anionic groups and 0.01-0.50 cationic groups per recurring unit.
12. A wet strength composition containing 10-90% of a carbohydrate derivative containing 0.10-2.95 aldehyde groups, and 0.03-1.0 anionic groups per recurring unit, and 90-10% of a cationic polymer, the percentages being based on the total of carbohydrate derivative and cationic polymer.
13. A cellulosic fibre treated with a biopolymer as defined in any one of claims 1-11, or with a mixture according to claim 12.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NL 01/00343

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D21H21/20 C08B15/00 C08B31/00 //D21H17:25,D21H17:28

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)

IPC 7 D21H C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data bases consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 11046 A (HERCULES INC) 2 March 2000 (2000-03-02) claims 1,6,14,25,59; examples	1,4,10, 13
A	US 4 675 394 A (JOBE PATRICK G ET AL) 23 June 1987 (1987-06-23) the whole document	1,5,6, 11-13
A	EP 0 283 951 A (NAT STARCH CHEM CORP) 28 September 1988 (1988-09-28) page 4, line 47 -page 5, line 24; claims 1,2,5,15,16	1,5,6, 11-13
A	EP 0 232 851 A (NAT STARCH CHEM CORP) 19 August 1987 (1987-08-19) page 4, line 5 -page 7, line 15; claims 1,2,5-8	1,5,6, 11-13
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *Z* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 958 187 A (MARINACK ROBERT J ET AL) 28 September 1999 (1999-09-28) column 5, line 32 -column 7, line 50	11-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

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(54) Title: ALDEHYDE-CONTAINING POLYMERS AS WET STRENGTH ADDITIVES

(57) Abstract: The invention concerns the use of a water-soluble or water-dispersible polymer having a molecular weight of at least 800, containing at least 5 aldehyde groups per molecule and at least 1 carboxyl group per molecule, the ratio of aldehyde groups to carboxyl groups being higher than 0.75:1, as a wet strength additive. The invention also discloses novel cationic derivatives thereof.

WO 01/83887 A1

Aldehyde-containing polymers as wet strength additives.

[0001] The present invention relates to the use of multifunctional aldehyde-containing polymers as temporary wet strength agents for paper and tissue applications, as well as non-wovens.

[0002] Wet strength is an important characteristic of paper and tissue products, and in non-woven products. Wet strength of such products can be increased by using wet strength additives. The most widely used wet strength additives for the paper industry are melamine-formaldehyde and urea-formaldehyde. There is a tendency, however, to move away from such oil-based chemicals, because they are not renewable and have a poor biodegradability. Carboxymethyl cellulose (CMC) is currently used in combination with PAE (polyamino-amide epichlorohydrin) as a wet strength agent (see Espy, TAPPI Journal, 78, 90 (1995)). However, CMC is also partly dependent on oil-based materials (monochloroacetic acid) and, moreover, is a rather expensive material.

[0003] Oxidised celluloses have the advantage of being accessible from renewable raw materials only and possibly of being less expensive than CMC, while they may have comparable properties to CMC. However, the oxidation of cellulose is hampered by the poor solubility of cellulose, making it insufficiently accessible to oxidising agents.

[0004] Aldehyde functions have been recognised as being useful in binding cellulose fibers, to improve wet strength of the fibers. Thus, dialdehyde starch (TAPPI, 57, 81 (1974); and TAPPI 45, 750 (1962)) and dialdehyde guar and the like (WO 97/36054) have been proposed as paper wet strength additives. US 3,087,852 and US 4,001,032 disclose cationic dialdehyde starch, obtained by reacting dialdehyde starch with betaine hydrazide, to be used as a paper strengthening additive.

[0005] US 5,935,383 discloses the use of anionic compounds, such as sulphato-ethyl-amino-halotriazines, for providing the cellulose surface with additional anionic sites suitable for retaining a high proportion of cationic wet strength additives such as PAE resin on the cellulose.

[0006] WO 99/23117 and WO 99/23240 describe the oxidation of cellulose and starch, respectively, with TEMPO and an oxidative enzyme (laccase) and oxygen at pH 4-9 resulting in products containing low levels of carbaldehyde and carboxyl groups.

[0007] US 3,553,193 describes the oxidation of starch with bromite or hypobromite, which results in varying levels of carbonyl (ketonic) and carboxyl groups depending on the oxidation conditions, with a carbonyl/carboxyl ratio of between 2:1 and 8:1. The oxidation products are stated to be suitable as paper strength additives. The oxidation of starch with sodium hypochlorite is believed first to yield keto groups. In a later stage of oxidation

aldehyde groups may be formed. The mechanism postulated by Whistler (J. Am. Chem. Soc., 79, 6460 (1957), see also PhD thesis of Floor, Delft University of Technology, 1989) however states that a diketo group is formed, which decomposes with OH⁻ and is oxidised. One has to assume that hypobromite reacts in an analogous way. A recent publication of
5 Deary and Davies in Carbohydr. Research 309, 17-29 (1998) reviews the bromine oxidation and confirms that keto groups are the primary products from bromine oxidation. From their experiments with α -cyclodextrins they conclude also that the keto product is formed. They present no evidence for the formation of aldehydes. Also, Torneport et al (Starch 42, 413-417 (1990)) and Salomonsson et al (Carbohydrate Res. 217 (1991)) state that oxidation of
10 starch with bromine species ($\text{Br}_2:\text{CH} = 1/40$ to $1/1$) at pH 7 results in keto groups and carboxylic acids. It is known that higher pH's lead to higher carboxylate contents.

[0008] It was found that multifunctional polymers, especially biopolymers, having both aldehyde functions and carboxylic acid and/or other anionic functions, the ratio between aldehyde functions and anionic functions (hereafter referred to as A/C ratio) being at least
15 0.75:1, preferably at least 2:1, up to about 15:1, preferably up to 10:1, are very useful as wet strength additives. These polymers are excellent substitutes for known wet strength agents such as carboxymethyl cellulose (CMC) and dialdehyde starch because of their better ecological acceptability (degradability) and their improved water-solubility and thus better accessibility to further reagents, and an improved functionality.

20 [0009] The polymers to be used can be of a synthetic type, such as a copolymer of acrylic acid and acrolein, a copolymer of maleic acid and maleic (mono)aldehyde, appropriately modified polyvinyl alcohol or appropriately (aldehyde-)substituted polyacrylic acid or the like, having the desired level of aldehyde groups and the desired A/C ratio.

[0010] It is preferred, however, that the polymer is a biopolymer. Suitable biopolymers
25 include (modified) peptides and proteins, proteoglycans and in particular polysaccharide-types of polymer. Examples of polysaccharides include α -1,4-glucans (the "starch family", including amylose, amylopectin, dextrans and cyclodextrins), α -1,6-glucans (dextran) and mixed α -glucans such as pullulan, β -1,4-glucans (cellulose), β -1,3-glucans such as scleroglucan and curdlan, xyloglucans, glucomannans and galactomannans (guar and locust
30 bean gum), other gums including heterogeneous gums like xanthan, ghatti, carrageenans, alginates, pectin, (arabino)xylans (hemicellulose), β -2,1- and β -2,6-fructans (inulin and levan), etc. The biopolymers may also be synthetically modified.

[0011] The simultaneous presence of aldehyde and anionic, such as carboxyl ($-\text{CO}_2\text{H}$), sulpho ($-\text{SO}_3\text{H}$) and phosphono ($-\text{PO}_3\text{H}_2$) groups, can be achieved by various methods.

35 These methods comprise:

- (1) introduction of anionic groups by addition, followed by introduction of aldehyde functions, e.g. by oxidation; here, the anionic groups such as carboxyl groups or other acid groups may be introduced e.g. by carboxyalkylation, sulphatation, sulphonylation, phosphatation, or the like, or they may be present in polymers which already have added acid groups by biosynthesis such as sulphate groups in carrageenans; the aldehyde functions can be introduced e.g. by oxidation of 1,2-dihydroxyethylene groups (such as those at the 2,3-position of 1,4-linked or 1,6-linked glucans) using periodate-type oxidising agents, or by partial oxidation of hydroxymethyl groups (such as those at the 6-position of 1,4-linked or 1,3-linked glucans) using nitric oxide (NOx) types of oxidising agents;
- (2) introduction of carboxyl groups by oxidation of hydroxymethyl groups followed by introduction of aldehyde functions by oxidation as under (1); here, the carboxyl (anionic) groups are introduced by oxidation of the hydroxymethyl groups, such as those at the 6-position of 1,4-linked or 1,3-linked glucans, using NOx-type of oxidising agents, or they may be present in polymers already containing 6-carboxyl groups by biosynthesis, if necessary after hydrolysis of ester groups, such as pectins, xanthans and alginates; the aldehyde groups can again be introduced e.g. by oxidation of 1,2-dihydroxyethylene groups, or by partial oxidation of further hydroxymethyl groups;
- (3) controlled oxidation of hydroxymethyl groups (such as those at the 6-position of 1,4-linked or 1,3-linked glucans) so as to partly convert them to aldehyde functions and to convert only a (minor) part of the aldehyde functions so obtained to carboxyl functions;
- (4) introduction of aldehyde groups, e.g. by oxidation of 1,2-dihydroxyethylene groups (such as those at the 2,3-position of 1,4-linked or 1,6-linked glucans) using periodate-type oxidising agents, followed by partial further oxidation thereof to carboxyl groups using different oxidising agents such as chlorite or bromine;
- (5) introduction of (protected) aldehyde groups (e.g. furan acetals) by etherification, e.g. as described in US 4,731,162 and US 4,741,804, followed by introduction of carboxymethyl groups.
- Further combinations of partial reaction steps as described above are also contemplated.
- [0012] The individual reaction steps referred to above are known in the art. Carboxymethylation of polysaccharides is also widely used in the art, and is commonly performed using sodium monochloroacetate in alkaline medium or by hydroxyalkylation (e.g. with ethylene oxide) followed by catalytic oxidation. Other carboxyalkylation, such as carboxyethylation, can be accomplished by base-catalysed addition of acrylamide followed by hydrolysis, or by addition of succinic or maleic or other anhydride, etc. Sulphate and sulphonylation

groups can be introduced by reaction with sulphuric acid derivatives such as chloro-sulphonic acid or with vinylsulphonic acid or taurine analogues. Phosphorylation can be achieved by reaction with phosphoric acid or its derivatives or with haloalkyl-phosphonic acids.

- 5 [0013] Also, oxidation of 1,2-dihydroxyethylene groups in the recurring units of polysaccharides is extensively known, and can be performed with periodate or similar polyoxy-anions, resulting in C-C bond scission according to the equation:



- 10 and thus to opening of the cyclic anhydromonosaccharide unit. These products are usually referred to as "dialdehyde carbohydrates" such as dialdehyde starch (DAS) and dialdehyde inulin (DAI).

- [0014] The partial further oxidation of these dialdehyde carbohydrates can be accomplished, e.g. with sodium chlorite with or without hydrogen peroxide, the molar amount of chlorite, with respect to the dialdehyde product, determining the carboxyl content of the
15 final product.

- [0015] A particularly advantageous method of further oxidising dialdehyde carbohydrates in a partial and controlled manner is described in PCT/NL99/00673 (WO00/26257, published 11 May 2000) and proceeds by reacting the dialdehyde product with a catalytic amount of halogen, such as chlorine, iodine and especially bromine. Halogen is regenerated
20 in situ by oxidation with an oxidising agent. Sodium hypochlorite can be used for the (re)generation of the molecular halogen, but preference is given to peracids. The catalytic amount of molecular halogen may be 0.2-40, preferably from 1 to 10 mole%, with respect to the amount of peracid. The peracid may be any peralkanoic acid such as peracetic acid, perpropionic acid, perlauric acid etc., a substituted peralkanoic acid such as peroxy-trifluoroacetic acid, an optionally substituted aromatic peracid such as perbenzoic acid or
25 m-chloroperbenzoic acid, or an inorganic peracid such as perboric or persulphuric acid. The molar amount of oxidising agent (e.g. peracid) with respect to the dialdehyde product, determines the carboxyl content of the final product.

- [0016] This method, besides reducing the amount of halide produced, is also beneficial to
30 the properties of the partially oxidised products, in particular as to a more regular distribution of carboxyl and aldehyde groups. In addition, this method is cheaper than the oxidation with sodium chlorite in the presence of hydrogen peroxide and produces less halide waste.

- [0017] The selective oxidation of hydroxymethyl groups (i.e. primary hydroxyl functions)
35 to aldehyde and/or carboxyl functions has been known for several years. Nitric oxides, i.e. nitrogen dioxide and dinitrogen tetroxide or nitrite/nitrate are known in the art as suitable

oxidising agents for these oxidations, as described e.g. in US Patent 3,364,200 and NL patent application 93.01172 and by Painter, Carbohydrate Research 55, 950193 (1977) and *ibid.* 140, 61-68 (1985). This oxidation may be performed in an apolar, e.g. halogenated, solvent, or in an aqueous solvents, such as phosphoric acid.

- 5 [0018] A preferred reagent for the selective oxidation of hydroxymethyl groups is constituted by nitroxyl compounds, such as TEMPO (2,2,6,6-tetramethyl-piperidine-N-oxide) and related compounds such as 2,2,5,5-tetramethylpyrrolidine-N-oxyl, 2,2,5,5-tetramethylimidazoline-N-oxyl, and 4-hydroxy TEMPO and derivatives thereof such as the 4-phosphonooxy, 4-acetoxy, 4-benzoyloxy, 4-oxo, 4-amino, 4-acetamino, 4-maleimido, 4-
10 isothiocyanato, 4-cyano and 4-carboxy TEMPO. TEMPO is used in these reactions as a catalyst (e.g. using 0.1-25 mol% with respect to final oxidising agent) in the presence of a final oxidising agent such as hypochlorite or hydrogen peroxide. TEMPO oxidation has been described e.g. in WO 95/07303. Further intermediate oxidants such as metal complexes (see PCT/NL00/00118 = WO 00/50388), enzymes such as laccase or per-
15 oxidases (see WO 99/23240 and WO 99/23117 and PCT/NL00/00117 = WO 00/50621) can be used. Examples of metal complexes are complexes of a transition metal such as manganese, iron, cobalt, nickel, copper, vanadium or ruthenium, with a complexing agent, especially nitrogen-containing compound such as a bipyridyl, a trimethyl-triazonane or other poly(tertiary amine) or a (poly)histidine; such metal complexes can be used in an
20 amount of 1-25 mol% with respect to the number a aldehyde or carboxyl groups desired. The actual oxidising species in the TEMPO-mediated oxidations is believed to be the nitrosonium ion. The A/C ratio can be controlled by selecting appropriate conditions: aldehyde formation is favoured at low temperatures (0-20 °C) and at relatively low pH (3-7) and by controlled addition and/or low levels of oxidising agent.
- 25 [0019] The anionic groups in the products thus obtained may be free carboxyl, sulpho or phosphono groups (acid form) or may be in the salt form, e.g. with sodium, potassium, ammonium or substituted ammonium as the counter cation. The aldehyde- and acid-containing products have at least 5 aldehyde groups, especially at least 10 aldehyde groups, and at least 1 anionic group, especially at least 3 anionic groups, such as carboxyl groups,
30 per molecule, also depending on the molecular weight (degree of polymerisation, DP). Thus, for smaller molecules, e.g. having a molecular weight below 3,000, the number of aldehyde groups per molecule may be lower, e.g. at least one per 600 Da, with a minimum of 2. The degree of substitution (DS) for aldehyde groups is preferably between 5 and 98 % of the maximum value, more preferably between 25 and 75%. As the maximum number of
35 aldehyde groups in most oxidised polysaccharides is 3 per recurring (monosaccharide) unit, the DS expressed in number of substituent groups per recurring unit is at least 0.10,

preferably between 0.15 and 2.95, more preferably between 0.25 and 2.25). The DS for anionic groups, especially carboxylic groups, is preferably between 0.03 and 1.0, more preferably between 0.05 and 0.4 per recurring unit.

5 [0020] If desired for the purpose of enhancing wet strength, the multifunctional product can be further chemically modified. A particularly suitable derivative is a product also containing cationic groups. Such cationic groups can be introduced by reacting a part of the aldehyde groups with an amine, hydrazine, hydrazide or the like, optionally under reductive conditions, or by reacting, at some stage during the production, saccharidic hydroxyl groups with ammonium-containing reagents such as trimethylammonio-alkyl halides or
10 epoxides. These multifunctional cationic compounds contain at least 0.01 up to about 0.50 cationic groups per recurring unit, preferably from 0.02 to 0.25 cationic groups per recurring unit; they are also part of the invention.

[0021] Alternatively, the aldehyde-anionic polymers can be combined with separate cationic compounds such as, for example, cationic polysaccharides, in particular cationic
15 DAS, or with other conventional cationic wet strength agents such as PEI (polyethyleneimine) or PAE, to produce a composite wet-strength agent. The weight ratio between the aldehyde/anionic polymer and the cationic compound can be e.g. from 90:10 to 10:90, especially from 75:25 to 15:85. Such composite wet strength agents are a distinct embodiment of the invention.

20 [0022] The aldehyde-containing anionic polymers can be combined, usually as aqueous solutions or dispersions with cellulosic fibres in a manner known for the application of wet strength agents. The amount of agent is preferably between 0.1 and 4 % by weight, especially between 0.2 and 2 % by weight, with respect to the cellulosic fibre. If desired, cationic wet strength agents can be applied subsequently followed by drying the fibre web.
25 Addition of a cationic polymer is usually necessary for multifunctional derivatives that do not themselves contain cationic groups, because otherwise there would insufficient absorption of the derivative to the fibre. Further alternate layering with aldehyde-containing anionic polymer and cationic polymer can also be advantageous.

30 Examples

Abbreviations:

6-AS: 6-aldehyde starch

DAS: dialdehyde starch

MACC: monoaldehyde-carboxy cellulose

35 MACS: monoaldehyde-carboxy starch

PAE: polyamide-amide epichlorohydrin
PCD: particle charge determination
PEI: polyethyleneimine

5 **Example 1**

a) Preparation of MACS with peracetic acid/bromide to different degrees of oxidation

Dialdehyde starch (oxidation degree 100%) was prepared by adding 6.6 g sodium periodate (31 mmole) to a slurry of 5.0 g (dry weight) starch (31 mmole) in 100 ml water which was brought to pH 5 with diluted acetic acid and cooled to 4°C. The mixture was stirred for 24
10 hours at 4°C in the absence of light. The obtained product was isolated by filtration and washed with water until iodate could no longer be detected by reaction with potassium iodide.

To obtain MACS, the dialdehyde starch was reslurried in 100 ml water and part of the aldehydes were further oxidised to carboxylates. To achieve this, sodium bromide (0.5 g)
15 was added and then peracetic acid (0.6 M) was added portion-wise (see Table 1). The pH was kept constant at pH 5 using 0.5 M NaOH (pH-stat). After reaction, the aldehyde carboxy starch was purified by membrane filtration (molecular cut-off 5000 MW) and freeze-dried.

Table 1: Conversion of DAS to MACS

Sample	Totally added peracetic acid solution (ml of 0.6 M solution)	% aldehydes oxidised to carboxylates
A5	5	5
A10	10	10
A30	31	30
A50	52	50

20

b) Application as wet strength additive

The addition levels were 10 mg/g MACS and 10 mg/g PAE.

Sheets were prepared as in example 8. The results are presented in Figure 1.

The highest relative wet strength was obtained in the sheets treated with MACS with an
25 oxidation degree of 10% and PAE. The performance of this combination is better than the combination of CMC and PAE, which is commonly used nowadays. It may be noted that when no additives are used, essentially no wet strength is obtained (compare Figure 6).

Example 2

MACS with an oxidation degree of 50% was prepared as described in Example 1. This polymer was added to pulp together with PEI (3mg/g and 7mg/g, respectively).

5 Sheets were prepared as in example 8. The results are presented in Figure 2. It may be noted that PEI does not give wet strength by itself (like PAE does). The wet strength shown in the case of MACS + PEI can be completely ascribed to MACS.

Example 3*a) Preparation of MACS with chlorite/hydrogen peroxide to different degrees of oxidation*

10 Dialdehyde starch (oxidation degree 100%) was prepared as described in example 1.

To obtain MACS, 5 g of the dialdehyde starch (30 mmole AGU) was reslurried in 100 ml water and cooled to 4°C. In order to oxidise part of the aldehydes to carboxylates, hydrogen peroxide (640 µl of a 30 % solution, 6 mmole) and 700 mg sodium chlorite (80% grade, 7.5 mmole) were added (see Table 2). The pH was kept constant at pH 5 using 0.5 M NaOH (pH stat.). After reaction, the aldehyde carboxy starch was purified by filtration and washing with water and the product was subsequently freeze-dried.

15

Table 2: Conversion of DAS to MACS

Sample	Added hydrogen peroxide solution (30%) (µl)	Added sodium chlorite (80%) (mg)	% aldehydes oxidised to carboxylates
Ac5	320	350	5
Ac10	640	700	10
Ac15	960	1050	15

b) Application as wet strength additive

20 Sheets were prepared as in example 8.

The addition levels were 10 mg/g MACS and 10 mg/g PAE. The results are presented in Figure 3.

Example 4

25 Dialdehyde cellulose (oxidation degree 100%) was prepared by adding 6.6 g sodium periodate (31 mmole) to a slurry of 5.0 g (dry weight) cellulose (31 mmole) in 100 ml water which was brought to pH 5 with diluted acetic acid and cooled to 4°C. The mixture was stirred for 1 week at 4°C in the absence of light. The obtained product was isolated by filtration and washed with water until iodate could no longer be detected by reaction with

30 potassium iodide.

To obtain MACC, the dialdehyde cellulose was reslurried in 100 ml water and half of the aldehydes were further oxidised to carboxylates. To achieve this, sodium bromide (0.5 g) was added and then peracetic acid (0.6 M) was added portion-wise (52 ml of a 0.6 M solution). The pH was kept constant at pH 5 using 0.5 M NaOH (pH-stat). After reaction, the aldehyde carboxy cellulose was purified by membrane filtration (molecular cut-off 5000 MW) and freeze-dried.

Sheets were prepared as in example 8. The results are presented in Figure 3.

Example 5

MACS with an oxidation degree of 10 % was prepared as described in example 1. This material was added to pulp (10 mg/g) together with cationic dialdehyde starch (10 mg/g). Sheets were prepared as in example 8. The results are presented in Figure 3.

Example 6

MACS with an oxidation degree of 10 % was prepared as described in example 1. 1 g of this material was suspended in water and Girard's reagent ($\text{NH}_2\text{NHCOCH}_2\text{N}^+(\text{CH}_3)_3$, betaine hydrazide, 100 mg for 10% cationisation) was added. The solution was stirred for 2 hours at 40°C and was subsequently freeze dried. A cationic MACS derivative was obtained. This sample was added to pulp (addition level 10 mg/g), and sheets were prepared as in example 8. The cationic MACS derivative adsorbs onto the fibres and gives wet strength. When added together with PAE (10 mg/g), the performance increased with lowering of the content of cationic groups (see Figure 4).

Example 7

6-Aldehyde starch was prepared by a TEMPO-mediated oxidation of starch. 5.0 g (dry weight) starch (31 mmol) was gelatinised in 250 ml water. TEMPO (65 mg) and horseradish peroxidase (100 mg) were added. The pH of the solution was adjusted to 5.0 using diluted acetic acid. Hydrogen peroxide (3.75 ml of a 30 % solution, 33 mmole) was diluted to a volume of 125 ml and was added gradually at a rate of 5 ml/hour. The reaction time was 25 hours at room temperature. Adjustment of the pH during reaction was not necessary. The product was purified by membrane filtration (molecular cut-off 5000 MW) and freeze-dried.

1 g of this material was redissolved in water and Girard's reagent (100 mg for 10% cationisation) was added. The solution was stirred for 2 hours at 40°C and was subsequently freeze dried again. A cationic 6-aldehyde starch was obtained. This sample

was added to pulp (addition level 10 mg/g) together with PAE (10 mg/g). Sheets were prepared as in example 8. The results are shown in Figure 5.

Example 8

5 Sheet making with derivatives of the invention

1. Refining

500-530 grams of Östrand TCF pulp is diluted to 12 litres and refined to 25 SR° by a Laboratory refiner RIL, Escher Wyss. The pulp, when refined, is about 40 g/L so it is diluted to the concentration of 3 g/L.

10 2. Dynamic sheet former, Formette

A wire of 0,4 m² is used and we want the Grammage to be 30 g/m².

The pulp is poured into the beater and the wet strength additive is added during stirring for 5 minutes. If PAE is added, it is added after five minutes and the pulp is stirred again for two minutes. Drum speed 1400 rotations/min, dewatering 30 sec.

15 3. Press

An absorbent paper is put over the sheet and the wire is taken off. Before pressing another absorbent paper is put over the sheet, so the sheet is between the two absorbent papers. The sheet is pressed at 0,5 bar once. To be able to compare sheets with each other, two sheets of the same composition are made but pressed at two different pressures, 0,5 bar and 5 bar. In
20 this way we can compare them at the same density 400 g/cm³.

4. Drying

The sheet is cut into four pieces and dried two and two with a fixed point for three minutes at a temperature of 140 °C.

5. Cutting

25 The sheet is cut into 15 mm strips for testing of dry and wet strength.
100*100mm is also cut out for measuring the thickness and Grammage.

6. Conditioning

The strips which wet strength is going to be tested are placed in a heating chamber, 105° C for 10 minutes. Then both the strips for wet and dry strength are placed in a climate room,
30 temperature 23°C, moisture 50% for four hours.

7. Grammage and thickness

100*100 mm pieces of the sheet is used for measuring the Grammage and thickness.

Grammage is measured on a regular balance on 4 layers to get an average.

Thickness is also measured on four layers and on five different spots to get a good average.

8. Tensile strength measurement

The strength both wet and dry is measured in an Instron SCAN-P58:86.

Five 15-mm strips are measured to get an average.

When measuring the wet strength the strip is soaked for 15 sec in tap water.

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Example 9:***Large-scale preparation of MACS and application in a full scale tissue paper machine***

The preparation of MACS with 15% of the aldehydes oxidised to carboxylic acids, as described in Example 1, was scaled up to 40 kg scale.

10 In the first step, 100% dialdehyde starch (DAS) was prepared. Sodium periodate (27 kg) was dissolved in 200 L water in a double-walled 300 L vessel equipped with a mechanical stirrer. The solution was cooled to 5°C. To this solution, potato starch (25 kg, 20.5 kg dry matter) was added portion-wise, keeping the temperature below 10°C. The slurry was stirred for 24 hours at 5°C. Then, the sodium iodate salts were removed by decantation after
15 settling of the DAS. The granules were washed with deionised water until no sodium iodate could be detected with potassium iodide and sulphuric acid. This procedure was repeated once and one more time using 21 kg sodium periodate and 20 kg starch. The overall yield of dialdehyde starch was 47 kg of DAS (82 % of theory, due to some losses during the washing procedure).

20 In the second oxidation step, MACS was prepared. DAS (11.75 kg) was slurried in about 150 L deionised water in a 300 L double-walled vessel. Sodium bromide (1.41 kg) was added and subsequently peracetic acid (7.07 kg, 39% activity) was added slowly using a pump running at 20 mL/min. The pH maintained between 4.7 and 5.3 by a pH controller adding 4 M NaOH. The temperature was kept between 15°C and 20°C. After all chemicals
25 were added, the solution was stirred overnight to ensure complete reaction. After reaction, the volume was reduced and part of the sodium acetate salts formed during reaction were removed using a membrane filtration unit (exclusion limit of 10000 D) to obtain a solution containing about 10 % MACS. This procedure was executed 4 times, and the products were mixed. The reaction yield of MACS in the second oxidation step was 42 kg (87 % of
30 theoretical).

A solution (490 kg) containing 8.6 % MACS was obtained. The polymer obtained in this way had similar characteristics regarding molecular weight and charge density as the material described in Example 1.

A tissue paper containing MACS was produced at a paper machine. See Example 10.

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Example 10: Application in a full scale tissue paper machine

With the MACS thus prepared (see Example 9), tissue paper was made on an industrial scale (continuous process) and the properties of the tissue were compared to those obtained with conventional wet strength agents.

5 Three kinds of tissues were made using the following composition of pulp: 65% TCF pulp (total chlorine free pulp) and 33% HTCTM pulp (high temperature chemi-thermo-mechanical pulp).

The first run was the reference, in which only PAE (9 kg/ton pulp) was applied. The second run was prepared using PAE (9 kg/ton pulp) and CMC, Hercobond C129 with a degree of
10 substitution of 0.65-0.9, (1.7 kg/ton pulp). In the third run, PAE (9 kg/ton) and 1.7 kg MACS per ton were used. The results with regard to the dry strength, wet strength, and wet tensile index are summarised in Table 3.

15 *Table 3. Wet and dry strength properties of tissue paper with PAE, PAE/CMC and PAE/MACS, respectively.*

Run	Tissue samples	Dry strength (Nm/g)	Wet strength (Nm/g)	Tensile strength index (%)
1	PAE(ref.)	8.9	2.5	28.1
2	PAE/CMC	11.6	3.2	27.3
3	PAE/MACS	10.8	3.2	29.6

As can be seen from Table 3, both MACS and CMC improve the properties of the tissue with regard to wet and dry strength and CMC and MACS exhibit the same properties.

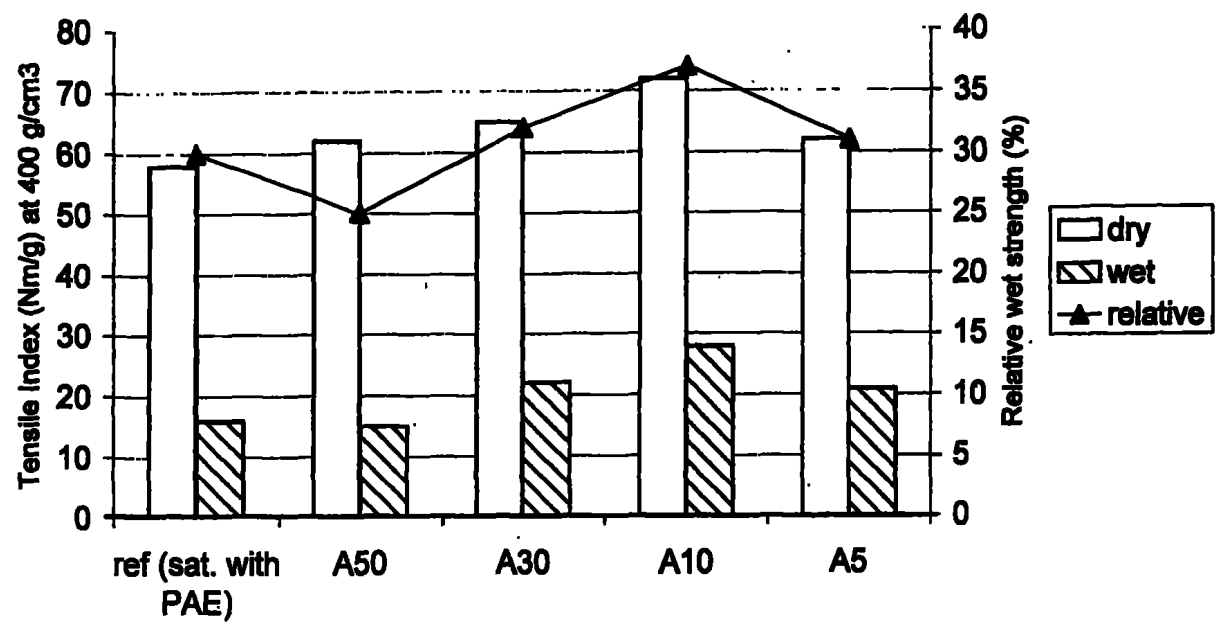
Claims

1. Use of a water-soluble or water-dispersible polymer having a molecular weight of at least 800, containing 0.25-2.25 aldehyde groups per recurring unit of the polymer and/or at least 5 aldehyde groups per molecule and containing at least 1 anionic group per molecule, the ratio of aldehyde groups to anionic groups being higher than 0.75:1, as a wet strength additive.
2. Use according to claim 1, in which the degree of substitution for aldehyde groups is 0.1-2.95 per recurring unit of the polymer, and the degree of substitution for anionic groups is 0.03-1.0 per recurring unit of the polymer.
3. Use according to claim 1, in which the degree of substitution for aldehyde groups is 0.25-2.25 per recurring unit of the polymer, and the degree of substitution for anionic groups is 0.05-0.4 per recurring unit of the polymer.
4. Use according to any one of claims 1-3, in which the anionic groups comprise carboxylic groups.
5. Use according to any one of claims 1-4, in which the polymer is a polysaccharide.
6. Use according to claim 5, in which the polymer is starch or cellulose or a starch- or cellulose-derived polymer.
7. Use according to claim 5 or 6, in which the aldehyde groups and the anionic groups are present as a result of oxidation of dihydroxyethylene moieties of recurring monosaccharide units.
8. Use according to claim 5 or 6, in which the aldehyde groups and the anionic groups are present as a result of oxidation of hydroxymethyl moieties of monosaccharide units.
9. Use according to any one of the preceding claims, in which anionic groups are present as a result of carboxymethylation.
10. Use according to any one of the preceding claims, in which the polymer further contains cationic groups with a degree of substitution of 0.01-0.50.

11. Carbohydrate derivative containing 0.10-2.95 aldehyde groups, and 0.03-1.0 anionic groups and 0.01-0.50 cationic groups per recurring unit.
12. A wet strength composition containing 10-90% of a carbohydrate derivative containing 0.10-2.95 aldehyde groups, and 0.03-1.0 anionic groups per recurring unit, and 90-10% of a cationic polymer, the percentages being based on the total of carbohydrate derivative and cationic polymer.
13. A cellulosic fibre treated with a polymer as defined in any one of claims 1-11, or with a mixture according to claim 12.

Fig 1

MACS with varying carboxylic acid content
(10kg/ton; in the presence of 10kg/ton PAE)

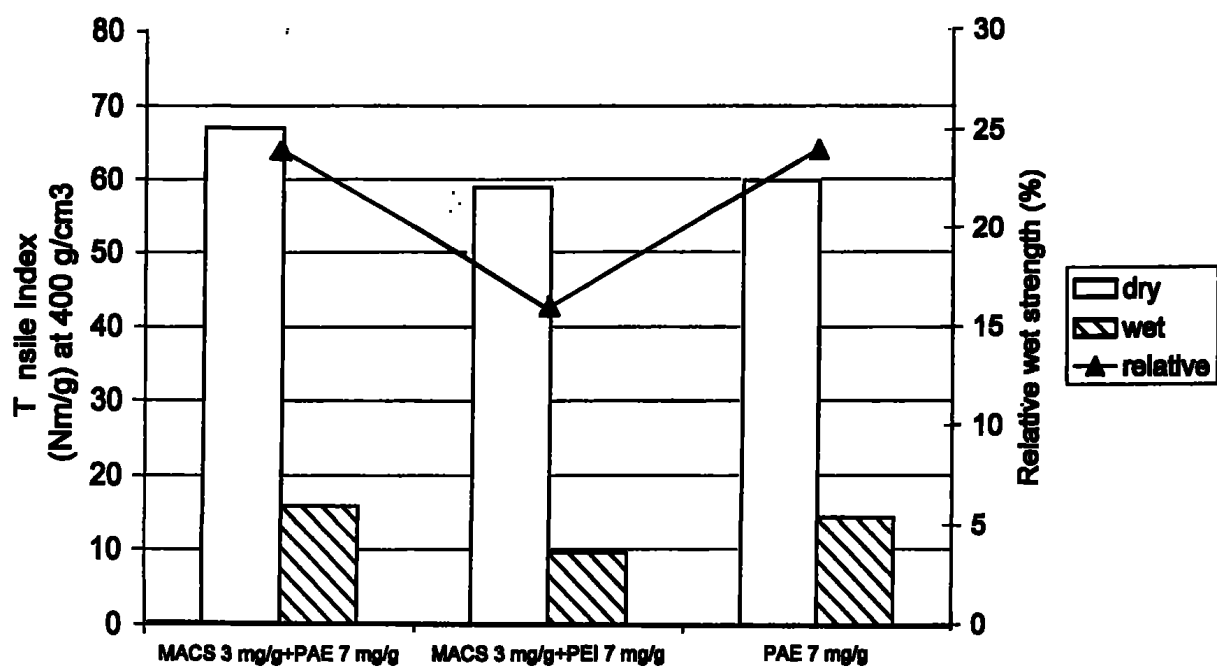


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Fig 2

MACS together with cationic polymers

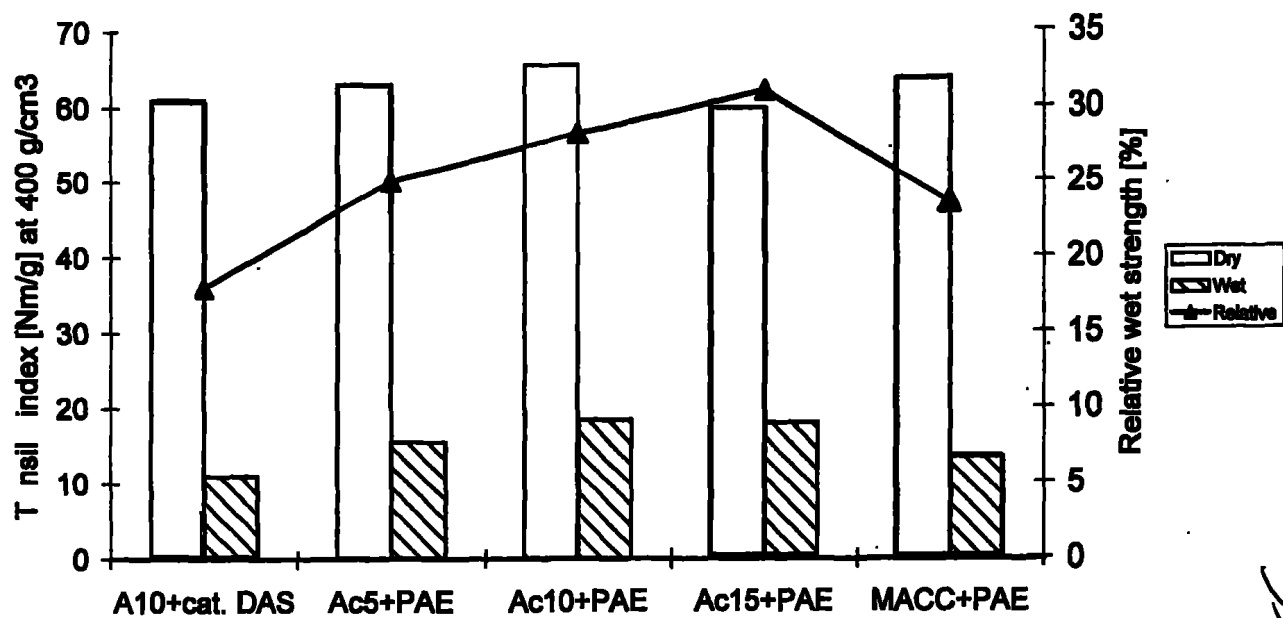


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Fig 3

MACS, MACC
(10 kg/ton; in the presence of 10 kg/ton cationic polymer)



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3A

POLIMEROS QUE CONTIENEN ALDEHIDO COMO ADITIVOS DE RESISTENCIA A LA HUMEDAD.

La presente invención se relaciona con el uso de polímeros multifuncionales que contienen aldehído como agentes temporales resistentes a la humedad para aplicaciones en papel y tejido, así como también no tejidos.

La resistencia a la humedad es una característica importante de los productos de papel y tejido y en productos no tejidos. La resistencia a la humedad de tales productos se puede incrementar al utilizar aditivos resistentes a la humedad. Los aditivos resistentes a la humedad más ampliamente utilizados para la industria del papel son melamina-formaldehído urea-formaldehído. Existe una tendencia, sin embargo, a apartarse de tales químicos basados en aceite, por que ellos no son renovables y tienen una pobre biodegradabilidad. La carboximetilcelulosa (CMC) es habitualmente utilizada en combinación con la PAE (poliamino-amida epiclorohidrina) como un agente resistente a la humedad (ver Espy, TAPPI

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Journal, 78, 90 (1995)). Sin embargo, el CMC es también parcialmente dependiente de materiales basados en aceite (ácido monocloroacético) y, más aún es un material un poco costoso.

Las celulosas oxidadas tienen la ventaja de ser accesibles de la materia prima renovable solamente y posiblemente de ser menos costosa que el CMC, mientras que ellas pueden tener propiedades comparables con el CMC. Sin embargo, la oxidación de la celulosa se impide por la pobre solubilidad de la celulosa, haciéndola insuficientemente accesible a los agentes de oxidación.

Las funciones aldehído se han reconocido por ser útiles en las fibras de celulosa ligantes, para mejorar la resistencia a la humedad de las fibras. De esta manera, el almidón dialdehído (TAPPI, 57, 81 (1974); y el TAPPI 45, 750 (1962)) y el guar de aldehído y los similares (WO 97/36054) se han propuesto como aditivos para resistencia a la humedad en el papel. La US 3,087,852 y la US 4,001,032 describen almidón de aldehído catiónico, obtenido al hacer reaccionar almidón de

aldehído con botaina hidrazida, para ser utilizada como un aditivo de fortalecimiento del papel.

La US 5,935,383 describe el uso de compuestos aniónicos, tales como sulfato-etil-amino-halotriazinas, para suministrarle a la superficie de la celulosa sitios aniónicos adicionales adecuados para retener una alta proporción de aditivos cationicos resistentes a la humedad tales como la resina PAE sobre la celulosa.

La WO 99/23117 y la WO 99/23240 describen la oxidación de celulosa y almidón, respectivamente, con TEMPO y una enzima oxidativa (la casa) y oxígeno a un pH 4-9 que da como resultado productos que contienen bajos niveles de grupos carbaldehído y carboxilo.

La US 3, 553,193 describe la oxidación de almidón con bromito o hipodromito, que da como resultado varios niveles de grupo carbonilo (cetónico) y carboxilo dependiendo de las condiciones de oxidación, con una proporción de carbonilo/carboxilo de de entre 2:1 y 8:1. Los productos de oxidación se establecen por ser

adecuados como aditivos que dan resistencia al papel. La oxidación del almidón con hipoclorito de sodio se cree que primero produce grupos zeto. En una etapa posterior de oxidación se pueden formar grupos aldehído. El mecanismo postulado por Whistler (J. Am. Chem. Soc., 79,6460 (1957), ver también tesis de PhD de Floor, Delft University of Technology, (1989) in embargo establece que se forma un grupo dizeto, que se descompone con OH-y se oxida. Uno tiene que asumir que el hipobromito reacciona de una manera análoga. Una reciente publicación de Deary y Davies en carbohidr. Research 309, 17-29 (1998) revisa la oxidación del bromo y confirma que los grupos zeto son productos primarios provenientes de la oxidación del bromo. De tales experimentos con α -ciclodextrinas ellos concluyen también que se forma el producto zeto. Ellos no presentan evidencia de la formación de aldehídos. También, Torneport et al (Starch 42,413-417 (1990) y Salomonsson et al (carbohydrate Res. 217 (1991)) establecen que la oxidación del almidón con especies de bromo (Br_2 : CH = 1/40 a 1/1) a un pH 7 da como resultado grupos zeto y ácidos carboxílico. Es conocido que el pH mayor conduce a contenidos de carboxilato mayor.

SA

Se ha encontrado que los polímeros multifuncionales, espacialmente los biopolímeros, tienen tanto funciones aldehído como funciones de ácido carboxílico y/o funciones aniónicas, la proporción entre las funciones aldehído y las funciones aniónicas (en lo sucesivo denominadas como proporción A/C) son al menos 0,75:1, preferiblemente al menos 2:1, hasta aproximadamente 15:1, preferiblemente hasta 10:1, son muy útiles como aditivos resistentes a la humedad. Estos polímeros son substitutos excelentes para agentes resistentes a la humedad conocidos tales como carboximetil celulosa (CMC) y almidón dialdehído en razón a su mejor aceptabilidad de ecológica (degradabilidad) y su solubilidad mejorada al agua y así una mejor accesibilidad a reactivos adicionales y una funcionalidad mejorada.

Los polímeros al ser utilizados pueden ser de un tipo sintético, tal como un copolímero o un ácido acrílico y acroleína, un copolímero de ácido maleico y (mono) aldehído maleico, alcohol de polivinilo apropiadamente modificado o ácido poliacrílico sustituido

(aldehído) apropiadamente o similares, que tienen el nivel deseado de grupos aldehído y la proporción deseada A/C.

Se prefiere, sin embargo, que el polímero sea un biopolímero. Los biopolímeros adecuados incluyen péptidos (modificados) y proteínas, proteoglicanos y en particular tipos de polisacárido de polímero. Ejemplo de polisacáridos incluyen α -1,4-glucanos (la "familia del almidón", que incluye amilosa, amilopectina, dextrinas y ciclodextrinas), α -1,6-glucanos (dextranos) y α -glucanos mezclados tales como puluano, β -1,4-glucanos (celulosa), β -1,3-glucanos tales como escleroglucano y curdlan, xiloglucanos, glucomananos y galactomananos (guar y goma de frijol de acacia falsa) otras gomas que incluyen gomas heterogéneas como xantano, ghatti, carrageninas, alginatos, pectina, (arabino) xilanos (hemicelulosa), β -2,1- y -2,6-fructanos (inulina y levan), etc. Los biopolímeros también se pueden modificar sintéticamente.

La presencia simultánea de aldehído y aniónicos tales como carboxil ($-\text{CO}_2\text{H}$), sulfo ($-\text{SO}_3\text{H}$) y grupos

fosfono (PO_3H_2), se pueden lograr mediante varios métodos.

Estos métodos comprenden:

(1) introducción De grupos aniónicos mediante adición, seguida por la introducción de funciones aldehído, por ejemplo mediante oxidación; aquí, los grupos aniónicos tales como los grupos carboxilo u otros grupos ácidos se pueden introducir por ejemplo mediante carboxialquilación, sulfatación, sulfoalquilación, fosfatación, o similar, o ellos se pueden presentar en polímeros que ya han agregado grupos ácido mediante biosíntesis tal como grupo sulfato en carrageninas; las funciones aldehído se pueden introducir por ejemplo mediante oxidación de grupos 1,2-dihidroxietileno (tales como aquellas en la posición 2,3-de los glucanos 1,4-ligado o 1,6-ligado) utilizando agentes de oxidación tipo periodato, o mediante oxidación parcial de grupos hidroximetilo (tales como aquellos en la posición 6 de glucanos 1,4-ligados o 1,3-ligados) utilizando tipos de óxido nítrico (NO_x) de agentes oxidantes;

(2) La introducción de grupos carboxilo mediante la oxidación de grupos hidroximetilo seguido por la

introducción de funciones aldehído mediante la oxidación como adelante (1); aquí, los grupos (aniónicos) carboxilo se introduce mediante la oxidación de grupos hidroximetilo, tales como aquellos en la posición 6 de glucanos 1,4-ligados o 1,3-ligados, utilizando tipo NOx de agentes de oxidación, o ellos se pueden presentar en polímeros que ya contienen grupos 6-carboxilo mediante la biosíntesis, si es necesario después de la hidrólisis de grupos ester, tales como pectinas, xantanos y aginatos; los grupos aldehído pueden ser introducidos de nuevo por ejemplo mediante oxidación de grupos 1,2-dihidroxietileno, o mediante la oxidación parcial de grupos hidroximetil o adicionales;

(3) La oxidación controlada de grupo de hidroximetilo (tales como aquellos en la posición 6 de glucanos 1,4-ligados o 1,3-ligados) con el fin de convertirlos parcialmente a funciones aldehído y de convertir solo una parte (menor) de las funciones aldehído así obtenidas a funciones carboxilo;

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(4) La introducción de grupos aldehído, por ejemplo mediante la oxidación de grupos 1,2-dihidroxietileno (tales como aquellos en la posición 2,3 de los glucanos 1,4-ligados o 1,6-ligados) utilizando agentes de oxidación tipo periodato, seguido por la oxidación parcial de estos a grupos carboxilo utilizando diferentes agentes de oxidación tales como clorito o bromo;

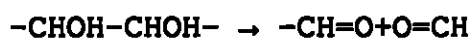
(5) La introducción de grupos aldehído (protegidos) (por ejemplo acetales furanos) mediante la eterificación, por ejemplo como se describió en la US 4, 731,162 y US 4,741, 804, seguida por la introducción de grupos carboximetilo.

Las combinaciones adicionales de etapas de reacción parcial como se describió anteriormente también se contemplan.

Las etapas de reacción individuales a las que nos referimos anteriormente son conocidas en la técnica. La carboximetilación de polisacáridos también es ampliamente utilizada en la técnica, y es desarrollada comúnmente utilizando monoclороacetato de sodio en medio alcalino o

mediante hidroxialquilación (por ejemplo con óxido de etileno) seguido por oxidación catalítica. Otra carboxialquilación, tal como carboxietilación, se puede lograr mediante la adición de pase catalizada de archilamida seguida por la hidrólisis, o mediante la adición de anhídrido succínico o maleico u otro anhídrido, etc. Los grupos sulfato o los grupos sulfa se pueden introducir mediante la reacción con derivados de ácido sulfúrico tales como ácido cloro sulfónico o con ácido vinilsulfónico análogos de taurina. La fosforilación se puede lograr mediante la reacción con ácido fosfórico o sus derivados o con ácidos haloalquilfosfónico.

También, la oxidación de grupos 1,2-dihidroxietileno en las unidades requirentes de polisacaridos son extensivamente conocidos, y se pueden desarrollar con periodato o aniones polioxi similares, que dan como resultado una escisión de enlace C-C de acuerdo con la ecuación:



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Y así la abertura de la unidad anhidro monosacárida cíclica. Estos productos son usualmente denominados como "carbohidratos de dialdehído" tales como almidón dialdehído (DAS) e inulina dialdehído (DAI).

La oxidación adicional parcial de estos carbohidratos dialdehído se puede lograr, por ejemplo, con clorito de sodio con o sin peróxido de hidrógeno, la cantidad molar de clorito, con respecto al producto dialdehído, que determina el contenido de carboxilo del producto final.

Un método particularmente ventajoso de oxidar carbohidratos dialdehído de una manera parcial y controlada se describe en la PCT/NL99/00673 (WO00/26257, publicada el 11 de mayo del 2000) y procede al hacer reaccionar el producto dialdehído con una cantidad catalítica de halógeno, tal como cloro, yodo y Especialmente bromo. El halógeno se regenera in situ mediante oxidación con un agente oxidante. El hipoclorito de sodio se puede utilizar para la (re)generación de

Halógeno molecular, pero se le da preferencia a los peróxidos. La cantidad catalítica de halógeno molecular puede ser 0,2-40, preferiblemente desde 1 a 10 moles % con respecto a la cantidad de peróxido. El peróxido puede ser un ácido peralcanóico tal como ácido peracético, ácido perpropiónico, ácido peralúrico etc., un ácido peralcanoico sustituido tal como ácido peroxi-trifluoroacético, un perácido aromático opcionalmente sustituido tal como ácido perbenzoico o ácido m-cloroperbenzoico, o un perácido inorgánico tal como ácido perborico o persulfúrico. La cantidad molar de agente oxidante (por ejemplo perácido) con respecto al producto dialdehído, determina el contenido de carboxilo del producto final.

Este método, que reduce además la cantidad de haluro producida también es benéfica para las propiedades de los productos parcialmente oxidados, en particular con una distribución más regular de grupos carboxilo y aldehído. Adicionalmente, este método es más barato que la oxidación con clorito de sodio en la presencia de

peróxido de hidrogeno y produce menos desperdicio de haluro.

La oxidación selectiva de los grupos hidroximetilo (es decir funciones hidroxilo primarias) a aldehído y/o funciones carboxilo se han conocido durante varios años. Los óxidos nítricos, es decir dióxido de nitrógeno y tetróxido de tinitrógeno o nitrito/nitrato son conocidas en la técnica como agentes de oxidación adecuados para estas oxidaciones, como se describió por ejemplo en la patente US 3,364,200 y la solicitud de patente NL 93.01172 y por Painter, Carbohydrate Research 55,950193 (1977) y ibid. 140, 61-68 (1985). La oxidación se puede desarrollar en un solvente apolar, por ejemplo halogenado, o en unos solventes acuosos, tales como ácido fosfórico.

Un reactivo preferido para la oxidación selectiva de grupos hidroximetilo se constituye de compuestos nitroxilo, tales como TEMPO (2,2,6,6-tetrametil-piperidina, N-óxido) y compuestos relacionados tales como 2,2,5,5-tetrametil pirrolidina-N-oxil, 2,2,5,5-

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tetrametilimidazolina-N-oxil, y 4-hidroxi TEMPO y derivados de estos tales como el 4-fosfonooxi, 4-acetoxi, 4-benzoiloxi, 4-oxo, 4-amino, 4-acetamino, 4-maleimido, 4-isotiocianato, 4-ciano, y 4-carboxi(TEMPO. El TEMPO se utiliza en estas reacciones como un catalizador (por ejemplo utilizando 0,1-25 moles % con respecto al agente de oxidación final) en la presencia de un agente de oxidación final tal como hipoclorito o hipoclorito de hidrogeno. La oxidación tempo se ha descrito por ejemplo en la WO 95/07303. Los oxidantes intermedios adicionales tales como los complejos metálicos (ver PCT/NL00/00118 = WO 00/50388), enzimas tales como lacasa o peroxidasa (ver WO 99/23240 Y WO 99/23117 y PCT/NL00117 = WO 00/50621 se pueden utilizar. Ejemplos de tales complejos metálico son complejos de n metal de transición como manganeso, hierro, cobalto, níquel, cobre, vanadio o rutemio, con un agente de acomplejamiento, especialmente un compuesto que contienen nitrógeno tal como bupiridilo, una trimetil-triazonano u otro poli (amina terciaria) o una (poli) histidina; tales como complejos de metal que se pueden utiliza en una cantidad de 1-25 moles % con respecto al número de grupos aldehído o carboxilo deseados. Las

actuales especies de oxidación en las oxidaciones mediadas por TEMPO se creen que son el ión nitrosonio. La proporción A/C se puede controlar al seleccionar condiciones apropiadas: la formación aldehído se favorece a temperaturas bajas (0-20°C) y aun relativo bajo pH (3-7) y mediante la adición controlada y/o bajo niveles de agentes de oxidación.

Los grupos aniónicos en los productos así obtenidos pueden ser carboxilo libre, grupos sulfa o fosfono (forma ácida) o puede ser en forma de sal, por ejemplo, con sodio, potasio, amonio o amonio sustituido como el contra catión. Los productos que contienen aldehído un ácido tienen al menos 5 grupos aldehído, especialmente al menos 10 grupos aldehído, y al menos un grupo aniónico, especialmente al menos 3 grupos aniónicos, tales como grupos carboxilo por molécula, también dependiendo del peso molecular (grado de polimerización, DP). De esta manera, para moléculas más pequeñas, por ejemplo que tienen un peso molecular inferior a 3000, el numero de grupos aldehídos por molécula puede ser inferior, por ejemplo, al menos uno por 600 Da, con un mínimo de 2. El

grado de sustitución (DS) para los grupos aldehído esta preferiblemente entre 5 y 98% del valor máximo más preferiblemente entre 25 y 75%. Como el número máximo de grupos aldehído en la mayoría de los polisacáridos oxidados es 3 por unidad recurrente (monosacárido), el DS expresado en número de grupos sustituyentes por unidad recurrente es al menos 0,10, preferiblemente entre 0,15 y 2,95, más preferiblemente entre 0,25 y 2, 25). El DS para los grupos aniónicos, especialmente grupos carboxílico, está preferiblemente entre 0,03 y 1,0, más preferiblemente entre 0,05 y 0,4 por unidad recurrente.

Si se desea para el propósito de mejorar la resistencia a la humedad, el producto multifuncional puede ser modificado químicamente de manera adicional. Un derivado particularmente adecuado es un producto que también contienen grupos cationicos. Tales grupos catiónicos se pueden introducir al hacer reaccionar una parte del grupos aldehído con una amina, hidracina, hidrazido o similar, opcionalmente bajo condiciones reductoras o al reaccionar, en alguna etapa durante la producción, grupos hidroxilo sacarídico con reactivos que

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contienen amonio tales como haluros de trimetil amonio-alquilo o epoxidos. Estos compuestos multifuncionales catiónicos contienen al menos 0,1 hasta aproximadamente 0,50 grupos cationicos por unidad recurrente, preferiblemente de 0,02 a 0,25 grupos catiónico por unidad recurrente; ellos también son parte de la invención.

Alternativamente, los polímeros aldehído-aniónico se pueden combinar con compuestos catiónicos separados tales como, por ejemplo, polisacáridos catiónicos, en particular DAS catiónico, o con otros agentes resistentes a la humedad catiónicos convencionales tales como PEI (polietileno-imina) o PAE, para producir un agente compuesto resistente a la humedad. La proporción en peso entre el aldehído/polímero aniónico y el compuesto catiónico puede ser por ejemplo de 90:10 a 10:90, especialmente de 75:25 a 15:85. Tales agentes compuestos resistentes a la humedad son una modalidad distinta a la invención.

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Los polímeros aniónicos que contienen aldehído se pueden combinar, usualmente como soluciones acuosas o dispersiones con fibras celulósicas de una manera conocida para la aplicación de agentes resistentes a la humedad. La cantidad del agente esta preferiblemente entre 0,1 y 4% en peso, especialmente entre 0,2 y 2% en peso, con respecto a la fibra celulósica. Si se desea, los agentes cationicos resistentes a la humedad se pueden aplicar subsecuentemente seguidos por el secado de red de fibra. La adición de un polímero catiónico es usualmente necesaria para los derivados multifuncionales que no contienen ellos mismos grupos catiónicos, por que de otra manera había insuficiente absorción de derivado a la fibra. Un tendido de capa alternativo adicional con polímero aniónico que contienen aldehído y polímero catiónico también puede ser ventajosa.

EJEMPLOS

Abreviaturas:

6-AS: almidón -6 aldehído.

DAS: almidón dialdehído

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MACC: monoaldehído-carboxi celulosa

MACS: monoaldehído-carboxi almidón

PAE: poliamida-amida epiclorohidrina

PCD: determinación de carga de partícula

PEI: polietilenoimina

EJEMPLO 1

a) Preparación de MACS con ácido peracético/bromuro a diferentes grados de oxidación.

Almidón dialdehído (grado de oxidación 100%) se preparó al agregar 6,6 g de periodato de sodio (31 mmoles) a una lechada de 5,0 g (pesos secos) almidón (31 mmol) en 100 ml de agua la cual fue traída a un pH 5 con ácido acético diluido y enfriada a 4°C. La mezcla se agitó durante 24 horas a 4°C en ausencia de luz. El producto obtenido se aisló mediante filtración y se lavó con agua hasta que el yodato ya no pudo ser detectado mediante la reacción con yoduro de potasio.

Para obtener MACS, el almidón de aldehído fue relechado en 100 ml de agua y parte de los aldehídos fueron adicionalmente oxidados hasta carboxilatos. Para

lograr esto, se agregó bromuro de sodio (0,5 g) y luego ácido peracético (0,6 M) se agregó en porciones (ver tabla 1). El pH se mantuvo constante a un pH 5 utilizando 0,5 M de NaOH (pH-stat.). Después de la reacción, el almidón de carboxialdehído se purificó mediante filtración con membrana (corte molecular 5000 MW) y se seco por congelamiento.

Tabla 1: conversión de DAS a MACS

muestra	Solución de ácido peracético totalmente agregado (ml de solución 0,6 M)	% de aldehídos oxidados a carboxilatos
A5	5	5
A10	10	10
A30	31	30
A50	52	50

b) Aplicación como aditivo resistente a la humedad.

SA

Los niveles e adición fueron 10 mg/g de MACS y 10 mg/g de PAE.

Las láminas se prepararon como en el ejemplo 8. Los resultados se presentan en la figura 1.

La mayor resistencia relativa a la humedad se obtuvo en las láminas tratadas con MACS con un grado de oxidación del 10% y PAE. El desempeño de esta combinación es mejor que la combinación de CMC y PAE, que es comúnmente utilizada actualmente. Se puede notar que cuando no se utilizan aditivos, esencialmente no se obtiene resistencia a la humedad (compare figura 6).

EJEMPLO 2

Los MACS con un grado de oxidación del 50% se prepararon como se describió en el ejemplo 1. Este polímero se agregó a pulpa junto con PEI (3 mg/g y 7 mg/g, respectivamente). Las láminas se prepararon como en el ejemplo 8. Los resultados se presentaron en la figura 2. Se puede notar que el PEI no da resistencia a la humedad en si mismo (como lo hace el PAE). La resistencia



a la humedad mostrada en el caso de los MACS más PEI puede ser completamente atribuida a los MACS.

Ejemplo 3

a) preparación de MACS con ~~clorito~~/peróxido de hidrogeno a diferentes grados de oxidación.

Almidón dialdehído (grado de oxidación 100%) se preparó como se describió en el ejemplo 1. Para obtener MACS, se relucharon 5 g de almidón dialdehído (30 mmol AGU) en 100 ml de agua y se enfriaron a 4°C. Con el fin de oxidar parte de los aldehídos a carboxilatos, se agregaron peroxido de hidrógeno (640 µl de solución al 30%, 6 mmol) y 700 mg de clorito de sodio (grado 80%, 7,5 mmol) (ver tabla 2). El pH se mantuvo constante a un PH 5 utilizando NaOH 0,5 m (pH stat). Después de reacción, el almidón de carboxialdehído se purificó mediante filtración y se lavó con agua y el producto se seco en seco subsecuentemente.

Tabla 2: conversión de DAS a MACS

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muestra	Solución de peróxido de hidrógeno agregado (30%) (μl)	Clorito de sodio agregado (80%) (mg)	% de aldehídos oxidados a carboxilatos
Ac5	320	350	5
Ac10	640	700	10
Ac15	960	1050	15

b) aplicación como aditivo resistente a la humedad.

Las láminas se prepararon como en el ejemplo 8.

Los niveles de adición fueron 10 mg/g MACS y 10 mg/g de PAE. Los resultados se presentan en la figura 3.

EJEMPLO 4

La celulosa de aldehído (grado de oxidación 100%) se preparó al agregar 6,6 g de periodato de sodio (31 mmol) a una lechada de 5,0 g (peso seco) celulosa (31 mmol) en 100 ml de agua que se trajo a un pH 5 con ácido acético diluido y se enfrió a 4°C. La mezcla se agitó durante una

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semana a 4°C en ausencia de luz. El producto obtenido se aisló por filtración y se lavó on agua hasta que el yodato no pudo ser detectado mediante la reacción con yoduro de potasio.

Para obtener MACC, la celulosa de aldehído se relecho en 100 ml de agua y la mitad de los aldehídos se oxidaron adicionalmente hasta carboxilatos. Para lograr esto, se agregó bromuro de sodio (0,5 g) luego se agregó ácido peracético (0,6 M) en porciones (52 ml de una solución 0,6 M). El pH se mantuvo constante a un pH 5 utilizando NaOH 0,5 M (Ph-stat.). Después de la reacción, se purificó la aldehído carboxi celulosa mediante filtración con membrana (corte molecular 5000MW) y secada por congelamiento.

Las láminas se prepararon como el ejemplo 8. Los resultados se presentan en la figura 3.

EJEMPLO 5

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Los MACS con un grado de oxidación del 10% se prepararon como se describió en el ejemplo 1. Este material se agregó a la pulpa (10 mg/g). Junto con almidón de aldehído catiónico (10 mg/g). Las láminas se prepararon como en el ejemplo 8. Los resultados se presentan en la figura 3.

EJEMPLO 6

Los MACS con un grado de oxidación del 10% se prepararon como se describió en el ejemplo 1. Un g de este material fue suspendido en agua y un reactivo de Girard ($\text{NH}_2\text{NHCOCH}_2\text{N}^+(\text{CH}_3)_3$, hidrazido de betaina, 100 mg para cationización al 10%) se agregaron. La solución se agitó durante 2 horas a 40°C y seco por congelamiento subsecuentemente. Un derivado catiónico de MACS se obtuvo. Esta muestra se agregó a pulpa (nivel de adición 10 mg/g), y se prepararon las láminas como en el ejemplo 8. Los derivados de MACS cationicos se adsorbieron sobre las fibras y le dieron resistencia a la humedad. Cuando se agregaron junto con PAE (10 mg/g) el desempeño se

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incrementó con la disminución del contenido de los grupos cationicos (ver figura 4).

EJEMPLO 7

Almidón de 6-aldehído se preparó mediante una oxidación mediada por TEMPO de almidón 5,0 g (peso seco) el almidón (61 mmol) se gelatinizó en 250 ml de agua. Se agregó TEMPO (65 mg) hiperoxidasa de rábano picante (100 mg). El pH e la solución se ajustó a 5,0 utilizando ácido acético diluido. El peróxido de hidrogeno (3,75 ml e una solución al 30%, 33 mmol) se diluyó a un volumen de 125 ml y se agregó gradualmente a una proporción de 5 ml/hora. El tiempo de reacción fue de 25 horas a temperatura ambiente. El ajuste del pH durante la reacción no fue necesario. El producto se purificó mediante filtración con membrana (corte molecular 5000 MW) y secada por congelamiento.

Un g de este material se predisolvió en agua y se agregó reactivo de Girard (100 mg para cationización del 10%). La solución se agitó durante 2 horas a 40°C y se

seco por congelamiento subsecuentemente de nuevo. Se obtuvo un almidón catiónico de 6-aldehído. Esta muestra se agregó a pulpa (nivel de adición 10 mg/g) junto con PAE (10 mg/g). Las láminas se prepararon como en el ejemplo 8. Los resultados se muestran en la figura 5.

EJEMPLO 8

Lamina hecha con derivados de la invención

1. Refinación

500-530 gramos de pulpa Ostrand TCF se diluyó hasta 12 litros y se refinaron a 25 SR° mediante un refinador laboratory R1L Escher Wyss. La pulpa, cuando se refinó, es de aproximadamente 40 g/L de tal forma que esta se diluye a la concentración de 3 g/L.

2. Formadora de lámina dinámica, Formette

Un alambre de 0,4 m² se utilizó y queríamos que el gramaje fuera 30 g/m².

La pulpa se vertió en una batidora y se agregó el aditivo de resistencia a la humedad durante la agitación durante 5 minutos. Si se agrega el PAE este se agrega después de 5 minutos y la pulpa se agita de nuevo durante 2 minutos. La velocidad del tambor 1400 rotaciones/min, desaguado 30 segundos.

3. Prensa

Un papel absorbente se pone sobre la lámina y el alambre es retirado. Antes de presionar otro papel absorbente este se pone sobre la lámina, así la lamina esta entre dos papeles absorbentes. La lámina se presiona a 0,5 bar de una vez. Para ser capaz de comparar la láminas una con la otra se hacen dos láminas de la misma composición pero presionadas a dos diferentes presiones 0,5 bar y 5 bar. De esta manera podemos compararlas a la misma densidad 400 g/cm³.

4. Secado

La lámina se corta en cuatro piezas y se secan dos y dos con un punto fijo durante 3 minutos a una temperatura de 140°C.

5. Corte

La lámina se corta en tiras de 15 mm para ensayos de secado y resistencia a la humedad.

100*100 mm también se corta para medir el grosor y el gramaje.

6. Acondicionamiento

Las tiras cuya resistencia a la humedad va hacer ensayada se ubican en una cámara de calentamiento, 105°C durante 10 minutos. Luego ambas tiras para resistencia a la humedad y al secado se ubican en un cuarto climatizado, temperatura 23°C, humedad 50% durante 4 horas.

7. Gramaje y grosor

Piezas de 100*100 mm de lámina se utilizan para medir el gramaje y el grosor.

El gramaje se mide sobre un balance regular de 4 capas para lograr un promedio.

El grosor también se mide sobre 4 capas y sobre dos diferentes manchas para conseguir un buen promedio.

8. Medición de resistencia tensil

La resistencia tanto en húmedo como en seco se mide en un Instron SCAN-P58:86.

Cinco tiras de 15-mm se miden para conseguir un promedio.

Cuando se mide la resistencia a la humedad la tira es embebida durante 15 segundos en agua de grifo.

EJEMPLO 9:

Preparación a gran escala de MACS y aplicación en una máquina de papel de tejido a escala completa.

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La reparación del MASC con 15% de aldehídos oxidados a ácidos carboxílicos, como se describen en el ejemplo 1 se escaló hasta una escala de 40 kg.

En la primera etapa se preparó almidón dialdehído al 100% (DAS). Periodato de sodio (27 kg) se disolvió en 200 L de agua en un vaso de doble pared de 300 l equipado con agitador mecánico. La solución se enfrió hasta 5°C. A esta solución se agregó almidón de papa (25 kg, 20,5 kg de materias secas) en porciones, manteniendo la temperatura por debajo de 10°C. La lechada se agitó durante 24 horas a 5°C. Luego, las sales de yodato de sodio se removieron mediante decantación después de el decantamiento del DAS. Los granos no se lavaron con agua desionizada hasta que no se pudo detectar el yodato de sodio con yoduro de potasio y ácido sulfúrico. Este procedimiento se repitió una vez y una vez más utilizando 21 kg de periodato de sodio y 20 kg de almidón. La producción total de almidón dialdehído fue de 47kg de DAS (82% del teórico, debido a algunas pérdidas durante el procedimiento de lavado).

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En la segunda etapa de oxidación, se prepararon los MACS. El DAS (11,75 kg) fue lechado en aproximadamente 150 L de agua desionizada en un vaso de doble pared de 300 L. Se agregó bromuro de sodio (1,41 kg) y subsecuentemente ácido peracético se agregó (7,07 kg, 39% de actividad) lentamente utilizando una bomba que corre a 20 mL/min. El pH se mantuvo entre 4,7 y 5,3 mediante un controlador de pH agregando NaOH 4M. La temperatura se mantuvo entre 15°C y 20°C. Después se agregaron todos los químicos, la solución se agitó durante toda la noche para asegurar que se completara la reacción. Después de reacción, el volumen se redujo y parte de las áreas de acetato de sodio que se formaron durante la reacción se removieron utilizando una unidad de filtración de membrana (exclusión límite de 10000 D) para obtener una solución que contenía aproximadamente 10% de MACS. Este procedimiento se ejecutó 4 veces, y los productos se mezclaron. El rendimiento de la reacción de MACS en la segunda etapa de oxidación fue de 42 kg (87 % del teórico).

Una solución (490 kg) que contenía 8,6% de MACS se obtuvo. El polímero obtenido de esta manera tuvo

características similares con relación al peso molecular y la densidad de carga que el material descrito en el ejemplo 1.

El papel de tejido que contenía MACS se produjo en una máquina de papel. Ver ejemplo 10.

EJEMPLO 10: aplicación en una máquina de papel de tejido a escala completa.

Con los MACS así preparados (ver ejemplo 9), el papel tejido se hizo a escala industrial (proceso continuo) y las propiedades del tejido se compararon con aquellas obtenidas con agentes convencionales resistentes a la humedad.

Tres clases de tejido se hicieron utilizando la siguiente composición de pulpa: 65% de pulpa TCF (pulpa total libre de cloro) y 33% de Pulpa HTCTM (pulpa quicio-termo-mecánica a alta temperatura).

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La primer corrida fue la referencia, en la cual solo se aplicó PAE (9 kg/ton de pulpa). La segunda corrida se preparó utilizando PAE (9, kg/ton de pulpa) y CMC, hercobond C129 con un grado de sustitución de 0,65-0,9, (1,7 kg/ton de pulpa). La tercer corrida, PAE (9 kg/ton) y 1,7 kg de MACS por toneladas se utilizó- Los resultados con relación a la resistencia a la humedad, e índice tensil húmedo se resumen en la tabla 3.

Tabla 3. Propiedades de resistencia en húmedo y en seco con papel tejido con PAE, PAE/CMC y PAE/MACS, respectivamente.

Corrida	Muestras de tejido	Resistencia en seco (Nm/g)	Resistencia en húmedo (Nm/g)	índice de resistencia tensil (%)
1	PAE(ref.)	8,9	2,5	28,1
2	PAE/CMC	11,6	3,2	27,3
3	PAE/MACS	3,2	3,2	29,6

Como se puede ver de la tabla 3, tanto los MACS como los CMC mejoraron las propiedades del tejido con respecto a la resistencia en húmedo y en seco y los CMC y los MACS exhibieron las mismas propiedades.

REIVINDICACIONES

1. Uso de un polímero soluble en agua o dispersable en agua que tiene un peso molecular de al menos 800 que contienen 0,25-2,25 grupos aldehído por unidad recurrente de polímero y/o al menos 5 grupos aldehído por molécula y que contienen al menos un grupo aniónico por molécula, la proporción de los grupos aldehído a los grupos aniónico es mayor de 0,75:1, como un aditivo resistente a la humedad.

2. Uso de acuerdo a la reivindicación 1, en el cual el grado de sustitución para los grupos aldehído es 0,1-2,95 por unidad recurrente del polímero, y el grado de sustitución para los grupos aniónicos es 0,03-1,0 por unidad recurrente de polímero.

3. Uso de acuerdo a la reivindicación 1, en la cual el grado de sustitución para los grupos aldehídos es 0,25-2,25 por unidad recurrente de polímero, y el grado de sustitución para los grupos aniónicos es 0,05-0,4 por unidad recurrente de polímero.



4. Uso de acuerdo a cualquiera de las reivindicaciones 1-3, en la cual los grupos aniónicos comprenden grupos carboxílicos.

5. Uso de acuerdo a cualquiera de las reivindicaciones 1-4, en la cual el polímero es un polisacárido.

6. Uso de acuerdo a la reivindicación 5, en la cual el polímero es almidón o celulosa o un polímero derivado de almidón o celulosa.

7. Uso de acuerdo a la reivindicación 5 o 6, en la cual los grupos aldehídos y los grupos aniónicos están presentes como un resultado de oxidación de unidades estructurales de hidroxietileno de unidades monosacárido.

8. Uso de acuerdo a las reivindicación 5 o 6, en la cual los grupos aldehídos y los grupos aniónicos están presentes como un resultado de oxidación de unidades estructurales de hidroximetilo de unidades monosacárido.

9. Uso de acuerdo a cualquiera de las reivindicaciones precedentes, en las cuales los grupos aniónicos están presentes como un resultado de carboximetilación.

10. Uso de acuerdo a cualquiera de las reivindicaciones precedentes, en las cuales el polímero contienen adicionalmente grupos cationicos con un grado de sustitución de 0,01-0,50.

11. Derivado de carbohidrato que contienen 0,10-2,95 grupos aldehído y 0,03-1,0 grupos aniónicos y 0,01-0,50 grupos cationicos por unidad recurrente.

12. Una composición resistente a la humedad que contiene 10-90% de un derivado de carbohidrato que contienen 0,10-2,95 grupos aldehído, y 0,03-1,0 grupos aniónicos por unidad recurrente y 90-10% de un polímero catiónico, el porcentaje esta basado sobre el total del derivado carbohidrato y del polímero catiónico.

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13. Una fibra celulósica tratada con un polímero como se definió en cualquiera de las reivindicaciones 1-11, o con una mezcla de acuerdo a la reivindicación 12.

RESUMEN

La invención se relaciona con el uso de un polímero soluble en agua o dispersable en agua que tienen un peso molecular de al menos 800, que contiene al menos cinco grupos aldehído por molécula y al menos un grupo carboxílico por molécula, la proporción de los grupos aldehído a los grupos carboxilo es mayor de 0,75:1, como un aditivo resistente a la humedad. La invención también describe derivados cationicos novedosos de estos.

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(ULTIMAS REIVINDICACIONES PRESENTADAS)

REIVINDICACIONES

1. Uso de un biopolímero soluble en agua o dispersable en agua que tiene un peso molecular de al menos 800 que contienen 0,25-2,25 grupos aldehído por unidad recurrente de biopolímero y/o al menos 5 grupos aldehído por molécula, los grupos aldehído están presentes como un resultado de oxidación de unidades estructurales dihidroxietileno y/o hidroximetilo de unidades de monosacáridos recurrentes, y que contienen al menos un grupo aniónico por molécula, la proporción de los grupos aldehído a los grupos aniónico es mayor de 0,75:1, como un aditivo resistente a la humedad.

2. Uso de acuerdo a la reivindicación 1, en el cual el grado de sustitución para los grupos aldehído es 0,1-2,95 por unidad recurrente del biopolímero, y el grado de sustitución para los grupos aniónicos es 0,03-1,0 por unidad recurrente del biopolímero.

96₇₅

3. Uso de acuerdo a la reivindicación 1, en la cual el grado de sustitución para los grupos aldehídos es 0,25-2,25 por unidad recurrente del biopolímero, y el grado de sustitución para los grupos aniónicos es 0,05-0,4 por unidad recurrente del biopolímero.

4. Uso de acuerdo a cualquiera de las reivindicaciones 1-3, en la cual los grupos aniónicos comprenden grupos carboxílicos.

5. Uso de acuerdo a cualquiera de las reivindicaciones 1-4, en la cual el biopolímero es un polisacárido.

6. Uso de acuerdo a la reivindicación 5, en la cual el biopolímero es almidón o celulosa o un polímero derivado de almidón o celulosa.

7. Uso de acuerdo a la reivindicación 5 o 6, en la cual los grupos aldehídos y los grupos aniónicos están presentes como un resultado de oxidación de unidades estructurales de hidroxietileno de unidades de monosacárido recurrentes.

AF
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8. Uso de acuerdo a las reivindicación 5 o 6, en la cual los grupos aldehídos y los grupos aniónicos están presentes como un resultado de oxidación de unidades estructurales de hidroximetilo de unidades monosacárido.

9. Uso de acuerdo a cualquiera de las reivindicaciones precedentes, en las cuales los grupos aniónicos están presentes como un resultado de carboximetilación.

10. Uso de acuerdo a cualquiera de las reivindicaciones precedentes, en las cuales el biopolímero contiene adicionalmente grupos cationicos con un grado de sustitución de 0,01-0,50.

11. Derivado de carbohidrato que contienen 0,10-2,95 grupos aldehído y 0,03-1,0 grupos aniónicos y 0,01-0,50 grupos cationicos por unidad recurrente.

12. Una composición resistente a la humedad que contiene 10-90% de un derivado de carbohidrato que contienen 0,10-2,95 grupos aldehído, y 0,03-1,0 grupos aniónicos por

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unidad recurrente, y 90-10% de un polímero catiónico, el porcentaje esta basado sobre el total del derivado carbohidratos y del polímero catiónico.

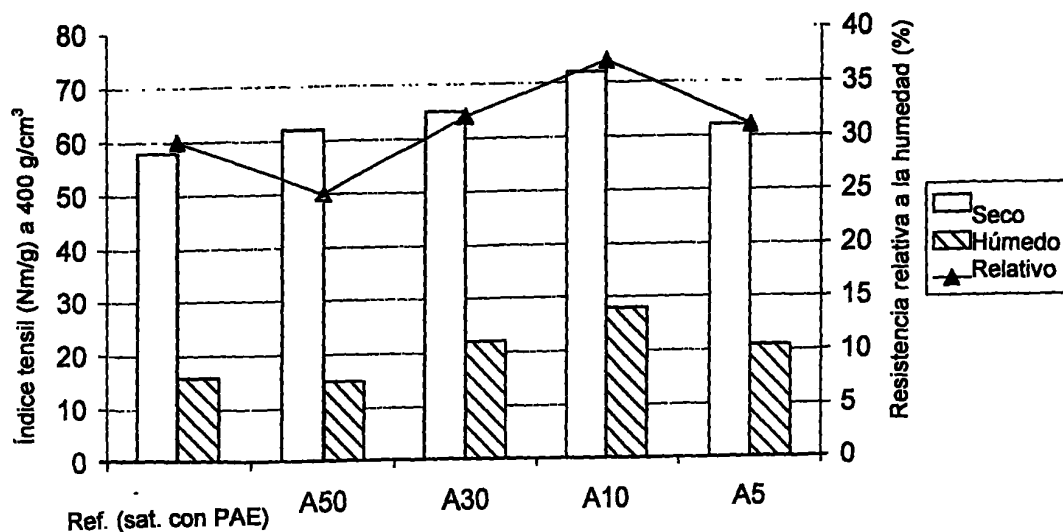
13. Una fibra celulósica tratada con un biopolímero como se definió en cualquiera de las reivindicaciones 1-11, o con una mezcla de acuerdo a la reivindicación 12.

P- 457

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Fig 1

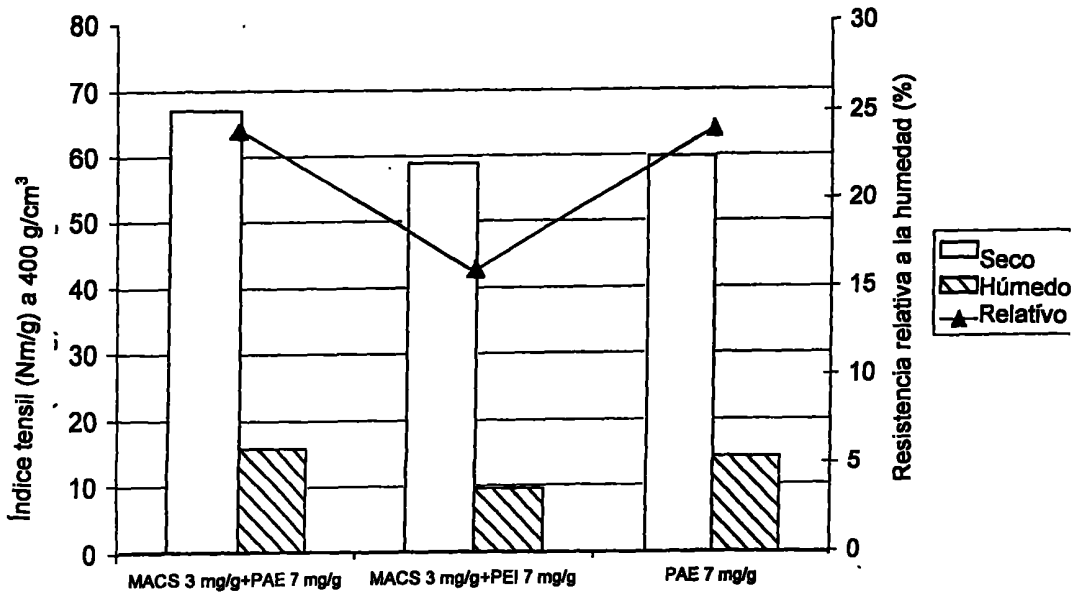
MACS con contenido de ácido
carboxílico variante
(10 kg/ton en la presencia de 10 Kg/ton PAE)



WO 01/03587

Fig 2

MACS junto con polímeros catiónicos



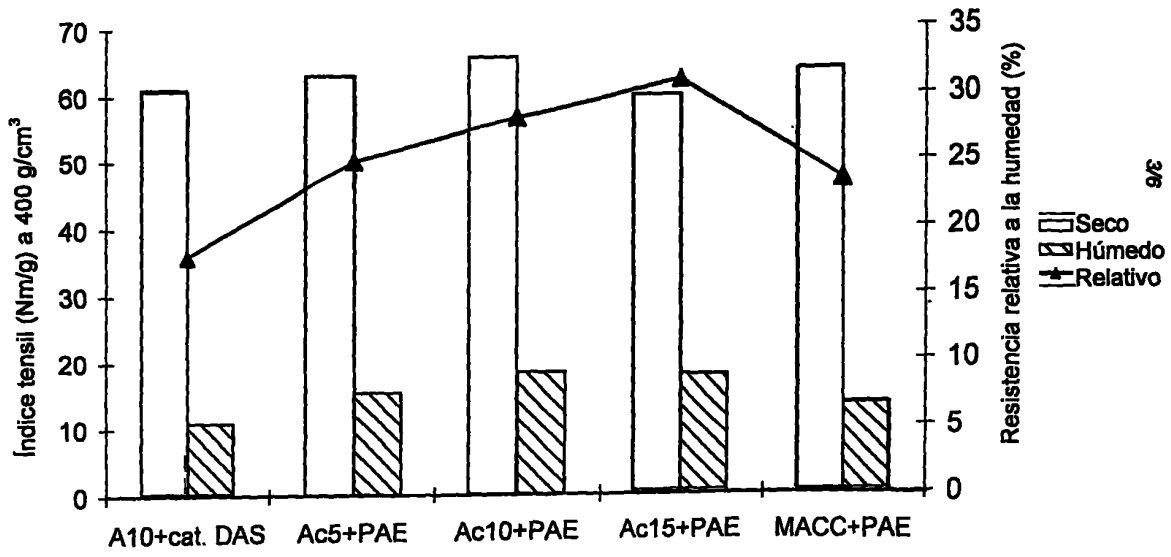
2/6

PCT/NL01/00343

7/6

Fig 3

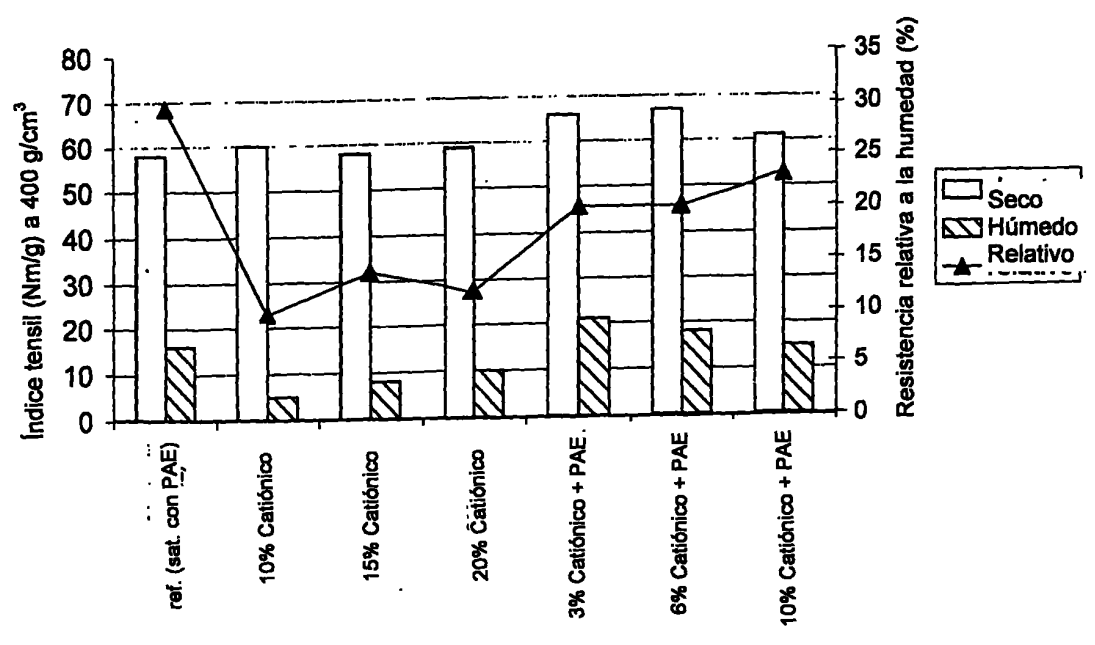
MACS, MACC
(10 kg/ton; en la presencia de 10 kg/ton de polímero catiónico)



[Handwritten signature]

Fig 4

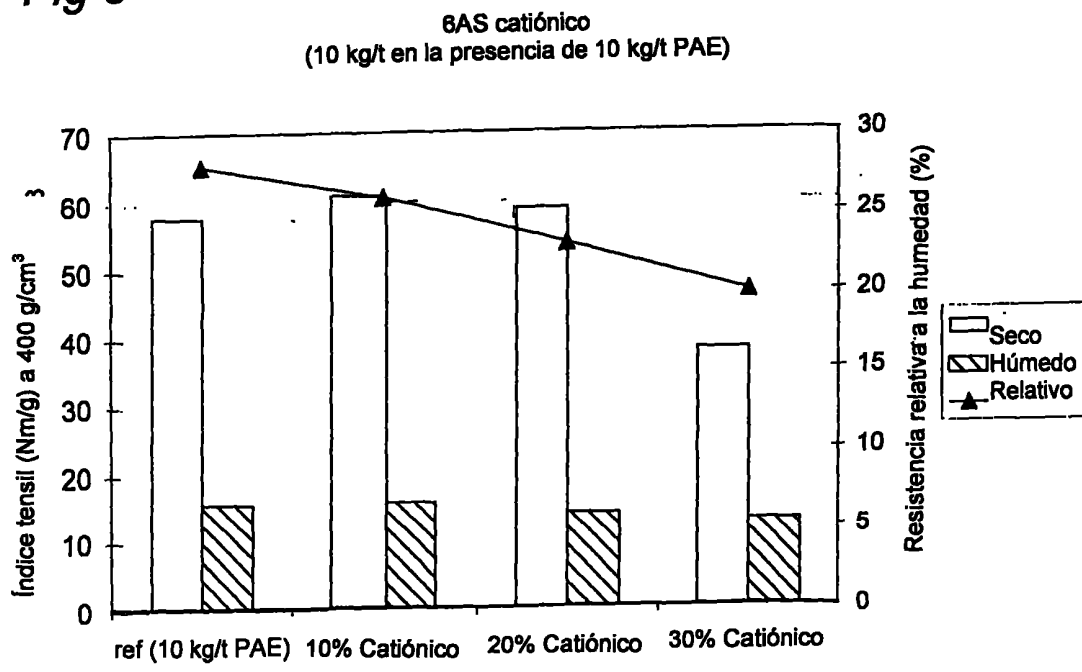
MACS catiónico (A 10 con contenido catiónico variante)
Nivel de adición: 10 kg/ton)



4/6

7/8

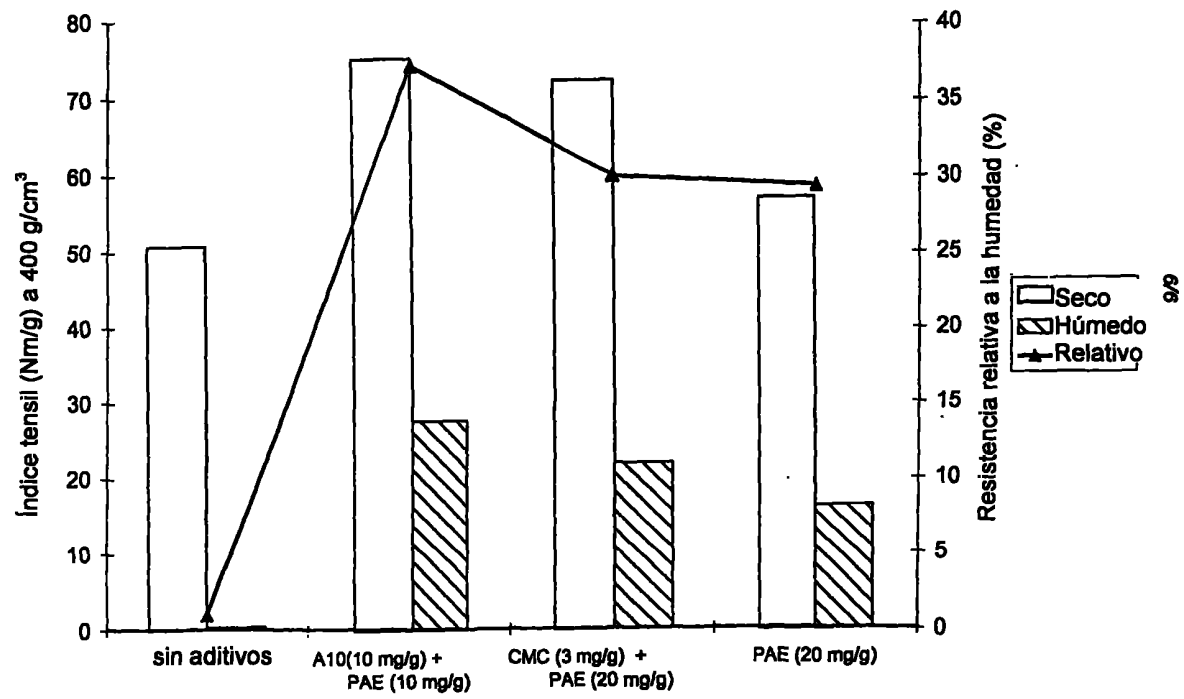
Fig 5



29.2

80

Fig 6



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WO 01/83887 A1

(54) Title: ALDEHYDE-CONTAINING POLYMERS AS WET STRENGTH ADDITIVES

(57) Abstract: The invention concerns the use of a water-soluble or water-dispersible polymer having a molecular weight of at least 800, containing at least 5 aldehyde groups per molecule and at least 1 carboxyl group per molecule, the ratio of aldehyde groups to carboxyl groups being higher than 0.75:1, as a wet strength additive. The invention also discloses novel cationic derivatives thereof.

Aldehyde-containing polymers as wet strength additives.

5 [0001] The present invention relates to the use of multifunctional aldehyde-containing polymers as temporary wet strength agents for paper and tissue applications, as well as non-wovens.

[0002] Wet strength is an important characteristic of paper and tissue products, and in non-woven products. Wet strength of such products can be increased by using wet strength additives. The most widely used wet strength additives for the paper industry are melamine-formaldehyde and urea-formaldehyde. There is a tendency, however, to move away from
10 such oil-based chemicals, because they are not renewable and have a poor biodegradability. Carboxymethyl cellulose (CMC) is currently used in combination with PAE (polyamino-amide epichlorohydrin) as a wet strength agent (see Espy, TAPPI Journal, 78, 90 (1995)). However, CMC is also partly dependent on oil-based materials (monochloroacetic acid) and, moreover, is a rather expensive material.

15 [0003] Oxidised celluloses have the advantage of being accessible from renewable raw materials only and possibly of being less expensive than CMC, while they may have comparable properties to CMC. However, the oxidation of cellulose is hampered by the poor solubility of cellulose, making it insufficiently accessible to oxidising agents.

[0004] Aldehyde functions have been recognised as being useful in binding cellulose
20 fibers, to improve wet strength of the fibers. Thus, dialdehyde starch (TAPPI, 57, 81 (1974); and TAPPI 45, 750 (1962)) and dialdehyde guar and the like (WO 97/36054) have been proposed as paper wet strength additives. US 3,087,852 and US 4,001,032 disclose cationic dialdehyde starch, obtained by reacting dialdehyde starch with betaine hydrazide, to be used as a paper strengthening additive.

25 [0005] US 5,935,383 discloses the use of anionic compounds, such as sulphato-ethyl-amino-halotriazines, for providing the cellulose surface with additional anionic sites suitable for retaining a high proportion of cationic wet strength additives such as PAE resin on the cellulose.

30 [0006] WO 99/23117 and WO 99/23240 describe the oxidation of cellulose and starch, respectively, with TEMPO and an oxidative enzyme (laccase) and oxygen at pH 4-9 resulting in products containing low levels of carbaldehyde and carboxyl groups.

[0007] US 3,553,193 describes the oxidation of starch with bromite or hypobromite, which results in varying levels of carbonyl (ketonic) and carboxyl groups depending on the oxidation conditions, with a carbonyl/carboxyl ratio of between 2:1 and 8:1. The oxidation
35 products are stated to be suitable as paper strength additives. The oxidation of starch with sodium hypochlorite is believed first to yield keto groups. In a later stage of oxidation

- aldehyde groups may be formed. The mechanism postulated by Whistler (J. Am. Chem. Soc., 79, 6460 (1957), see also PhD thesis of Floor, Delft University of Technology, 1989) however states that a diketo group is formed, which decomposes with OH⁻ and is oxidised. One has to assume that hypobromite reacts in an analogous way. A recent publication of
- 5 Deary and Davies in Carbohydr. Research 309, 17-29 (1998) reviews the bromine oxidation and confirms that keto groups are the primary products from bromine oxidation. From their experiments with α -cyclodextrins they conclude also that the keto product is formed. They present no evidence for the formation of aldehydes. Also, Torneport et al (Starch 42, 413-417 (1990)) and Salomonsson et al (Carbohydrate Res. 217 (1991)) state that oxidation of
- 10 starch with bromine species ($\text{Br}_2:\text{CH} = 1/40$ to $1/1$) at pH 7 results in keto groups and carboxylic acids. It is known that higher pH's lead to higher carboxylate contents.
- [0008] It was found that multifunctional polymers, especially biopolymers, having both aldehyde functions and carboxylic acid and/or other anionic functions, the ratio between aldehyde functions and anionic functions (hereafter referred to as A/C ratio) being at least
- 15 0.75:1, preferably at least 2:1, up to about 15:1, preferably up to 10:1, are very useful as wet strength additives. These polymers are excellent substitutes for known wet strength agents such as carboxymethyl cellulose (CMC) and dialdehyde starch because of their better ecological acceptability (degradability) and their improved water-solubility and thus better accessibility to further reagents, and an improved functionality.
- 20 [0009] The polymers to be used can be of a synthetic type, such as a copolymer of acrylic acid and acrolein, a copolymer of maleic acid and maleic (mono)aldehyde, appropriately modified polyvinyl alcohol or appropriately (aldehyde-)substituted polyacrylic acid or the like, having the desired level of aldehyde groups and the desired A/C ratio.
- [0010] It is preferred, however, that the polymer is a biopolymer. Suitable biopolymers
- 25 include (modified) peptides and proteins, proteoglycans and in particular polysaccharide-types of polymer. Examples of polysaccharides include α -1,4-glucans (the "starch family", including amylose, amylopectin, dextrans and cyclodextrins), α -1,6-glucans (dextran) and mixed α -glucans such as pullulan, β -1,4-glucans (cellulose), β -1,3-glucans such as scleroglucan and curdlan, xyloglucans, glucomannans and galactomannans (guar and locust
- 30 bean gum), other gums including heterogeneous gums like xanthan, ghatti, carrageenans, alginates, pectin, (arabino)xylans (hemicellulose), β -2,1- and β -2,6-fructans (inulin and levan), etc. The biopolymers may also be synthetically modified.
- [0011] The simultaneous presence of aldehyde and anionic, such as carboxyl ($-\text{CO}_2\text{H}$), sulpho ($-\text{SO}_3\text{H}$) and phosphono ($-\text{PO}_3\text{H}_2$) groups, can be achieved by various methods.
- 35 These methods comprise:

- (1) introduction of anionic groups by addition, followed by introduction of aldehyde functions, e.g. by oxidation; here, the anionic groups such as carboxyl groups or other acid groups may be introduced e.g. by carboxyalkylation, sulphonation, sulphoalkylation, phosphatation, or the like, or they may be present in polymers which already have added acid groups by biosynthesis such as sulphate groups in carrageenans; the aldehyde functions can be introduced e.g. by oxidation of 1,2-dihydroxyethylene groups (such as those at the 2,3-position of 1,4-linked or 1,6-linked glucans) using periodate-type oxidising agents, or by partial oxidation of hydroxymethyl groups (such as those at the 6-position of 1,4-linked or 1,3-linked glucans) using nitric oxide (NOx) types of oxidising agents;
- (2) introduction of carboxyl groups by oxidation of hydroxymethyl groups followed by introduction of aldehyde functions by oxidation as under (1); here, the carboxyl (anionic) groups are introduced by oxidation of the hydroxymethyl groups, such as those at the 6-position of 1,4-linked or 1,3-linked glucans, using NOx-type of oxidising agents, or they may be present in polymers already containing 6-carboxyl groups by biosynthesis, if necessary after hydrolysis of ester groups, such as pectins, xanthans and alginates; the aldehyde groups can again be introduced e.g. by oxidation of 1,2-dihydroxyethylene groups, or by partial oxidation of further hydroxymethyl groups;
- (3) controlled oxidation of hydroxymethyl groups (such as those at the 6-position of 1,4-linked or 1,3-linked glucans) so as to partly convert them to aldehyde functions and to convert only a (minor) part of the aldehyde functions so obtained to carboxyl functions;
- (4) introduction of aldehyde groups, e.g. by oxidation of 1,2-dihydroxyethylene groups (such as those at the 2,3-position of 1,4-linked or 1,6-linked glucans) using periodate-type oxidising agents, followed by partial further oxidation thereof to carboxyl groups using different oxidising agents such as chlorite or bromine;
- (5) introduction of (protected) aldehyde groups (e.g. furan acetals) by etherification, e.g. as described in US 4,731,162 and US 4,741,804, followed by introduction of carboxymethyl groups.
- Further combinations of partial reaction steps as described above are also contemplated.
- [0012] The individual reaction steps referred to above are known in the art. Carboxymethylation of polysaccharides is also widely used in the art, and is commonly performed using sodium monochloroacetate in alkaline medium or by hydroxyalkylation (e.g. with ethylene oxide) followed by catalytic oxidation. Other carboxyalkylation, such as carboxyethylation, can be accomplished by base-catalysed addition of acrylamide followed by hydrolysis, or by addition of succinic or maleic or other anhydride, etc. Sulphate and sulpho

groups can be introduced by reaction with sulphuric acid derivatives such as chloro-sulphonic acid or with vinylsulphonic acid or taurine analogues. Phosphorylation can be achieved by reaction with phosphoric acid or its derivatives or with haloalkyl-phosphonic acids.

- 5 [0013] Also, oxidation of 1,2-dihydroxyethylene groups in the recurring units of polysaccharides is extensively known, and can be performed with periodate or similar polyoxyanions, resulting in C-C bond scission according to the equation:



and thus to opening of the cyclic anhydromonosaccharide unit. These products are usually referred to as "dialdehyde carbohydrates" such as dialdehyde starch (DAS) and dialdehyde inulin (DAI).

- 10 [0014] The partial further oxidation of these dialdehyde carbohydrates can be accomplished, e.g. with sodium chlorite with or without hydrogen peroxide, the molar amount of chlorite, with respect to the dialdehyde product, determining the carboxyl content of the final product.

15 [0015] A particularly advantageous method of further oxidising dialdehyde carbohydrates in a partial and controlled manner is described in PCT/NL99/00673 (WO00/26257, published 11 May 2000) and proceeds by reacting the dialdehyde product with a catalytic amount of halogen, such as chlorine, iodine and especially bromine. Halogen is regenerated in situ by oxidation with an oxidising agent. Sodium hypochlorite can be used for the (re)generation of the molecular halogen, but preference is given to peracids. The catalytic amount of molecular halogen may be 0.2-40, preferably from 1 to 10 mole%, with respect to the amount of peracid. The peracid may be any peralkanoic acid such as peracetic acid, perpropionic acid, perlauric acid etc., a substituted peralkanoic acid such as peroxy-trifluoroacetic acid, an optionally substituted aromatic peracid such as perbenzoic acid or m-chloroperbenzoic acid, or an inorganic peracid such as perboric or persulphuric acid. The molar amount of oxidising agent (e.g. peracid) with respect to the dialdehyde product, determines the carboxyl content of the final product.

20 [0016] This method, besides reducing the amount of halide produced, is also beneficial to the properties of the partially oxidised products, in particular as to a more regular distribution of carboxyl and aldehyde groups. In addition, this method is cheaper than the oxidation with sodium chlorite in the presence of hydrogen peroxide and produces less halide waste.

25 [0017] The selective oxidation of hydroxymethyl groups (i.e. primary hydroxyl functions) to aldehyde and/or carboxyl functions has been known for several years. Nitric oxides, i.e. nitrogen dioxide and dinitrogen tetroxide or nitrite/nitrate are known in the art as suitable

oxidising agents for these oxidations, as described e.g. in US Patent 3,364,200 and NL patent application 93.01172 and by Painter, Carbohydrate Research 55, 950193 (1977) and ibid. 140, 61-68 (1985). This oxidation may be performed in an apolar, e.g. halogenated, solvent, or in an aqueous solvents, such as phosphoric acid.

- 5 [0018] A preferred reagent for the selective oxidation of hydroxymethyl groups is constituted by nitroxyl compounds, such as TEMPO (2,2,6,6-tetramethyl-piperidine-N-oxide) and related compounds such as 2,2,5,5-tetramethylpyrrolidine-N-oxyl, 2,2,5,5-tetramethylimidazoline-N-oxyl, and 4-hydroxy TEMPO and derivatives thereof such as the 4-phosphonooxy, 4-acetoxy, 4-benzoyloxy, 4-oxo, 4-amino, 4-acetamino, 4-maleimido, 4-
10 isothiocyanato, 4-cyano and 4-carboxy TEMPO. TEMPO is used in these reactions as a catalyst (e.g. using 0.1-25 mol% with respect to final oxidising agent) in the presence of a final oxidising agent such as hypochlorite or hydrogen peroxide. TEMPO oxidation has been described e.g. in WO 95/07303. Further intermediate oxidants such as metal complexes (see PCT/NL00/00118 = WO 00/50388), enzymes such as laccase or per-
15 oxidases (see WO 99/23240 and WO 99/23117 and PCT/NL00/00117 = WO 00/50621) can be used. Examples of metal complexes are complexes of a transition metal such as manganese, iron, cobalt, nickel, copper, vanadium or ruthenium, with a complexing agent, especially nitrogen-containing compound such as a bipyridyl, a trimethyl-triazonane or other poly(tertiary amine) or a (poly)histidine; such metal complexes can be used in an
20 amount of 1-25 mol% with respect to the number a aldehyde or carboxyl groups desired. The actual oxidising species in the TEMPO-mediated oxidations is believed to be the nitrosonium ion. The A/C ratio can be controlled by selecting appropriate conditions: aldehyde formation is favoured at low temperatures (0-20 °C) and at relatively low pH (3-7) and by controlled addition and/or low levels of oxidising agent.
- 25 [0019] The anionic groups in the products thus obtained may be free carboxyl, sulpho or phosphono groups (acid form) or may be in the salt form, e.g. with sodium, potassium, ammonium or substituted ammonium as the counter cation. The aldehyde- and acid-containing products have at least 5 aldehyde groups, especially at least 10 aldehyde groups, and at least 1 anionic group, especially at least 3 anionic groups, such as carboxyl groups,
30 per molecule, also depending on the molecular weight (degree of polymerisation, DP). Thus, for smaller molecules, e.g. having a molecular weight below 3,000, the number of aldehyde groups per molecule may be lower, e.g. at least one per 600 Da, with a minimum of 2. The degree of substitution (DS) for aldehyde groups is preferably between 5 and 98 % of the maximum value, more preferably between 25 and 75%. As the maximum number of
35 aldehyde groups in most oxidised polysaccharides is 3 per recurring (monosaccharide) unit, the DS expressed in number of substituent groups per recurring unit is at least 0.10,

preferably between 0.15 and 2.95, more preferably between 0.25 and 2.25). The DS for anionic groups, especially carboxylic groups, is preferably between 0.03 and 1.0, more preferably between 0.05 and 0.4 per recurring unit.

[0020] If desired for the purpose of enhancing wet strength, the multifunctional product
5 can be further chemically modified. A particularly suitable derivative is a product also containing cationic groups. Such cationic groups can be introduced by reacting a part of the aldehyde groups with an amine, hydrazine, hydrazide or the like, optionally under reductive conditions, or by reacting, at some stage during the production, saccharidic hydroxyl groups with ammonium-containing reagents such as trimethylammonio-alkyl halides or
10 epoxides. These multifunctional cationic compounds contain at least 0.01 up to about 0.50 cationic groups per recurring unit, preferably from 0.02 to 0.25 cationic groups per recurring unit; they are also part of the invention.

[0021] Alternatively, the aldehyde-anionic polymers can be combined with separate cationic compounds such as, for example, cationic polysaccharides, in particular cationic
15 DAS, or with other conventional cationic wet strength agents such as PEI (polyethyleneimine) or PAE, to produce a composite wet-strength agent. The weight ratio between the aldehyde/anionic polymer and the cationic compound can be e.g. from 90:10 to 10:90, especially from 75:25 to 15:85. Such composite wet strength agents are a distinct embodiment of the invention.

[0022] The aldehyde-containing anionic polymers can be combined, usually as aqueous
20 solutions or dispersions with cellulosic fibres in a manner known for the application of wet strength agents. The amount of agent is preferably between 0.1 and 4 % by weight, especially between 0.2 and 2 % by weight, with respect to the cellulosic fibre. If desired, cationic wet strength agents can be applied subsequently followed by drying the fibre web.
25 Addition of a cationic polymer is usually necessary for multifunctional derivatives that do not themselves contain cationic groups, because otherwise there would insufficient absorption of the derivative to the fibre. Further alternate layering with aldehyde-containing anionic polymer and cationic polymer can also be advantageous.

30 Examples

Abbreviations:

6-AS: 6-aldehyde starch

DAS: dialdehyde starch

MACC: monoaldehyde-carboxy cellulose

35 MACS: monoaldehyde-carboxy starch

88-91

PAE: polyamide-amide epichlorohydrin

PCD: particle charge determination

PEI: polyethyleneimine

5 Example 1

a) Preparation of MACS with peracetic acid/bromide to different degrees of oxidation

Dialdehyde starch (oxidation degree 100%) was prepared by adding 6.6 g sodium periodate (31 mmole) to a slurry of 5.0 g (dry weight) starch (31 mmole) in 100 ml water which was brought to pH 5 with diluted acetic acid and cooled to 4°C. The mixture was stirred for 24 hours at 4°C in the absence of light. The obtained product was isolated by filtration and washed with water until iodate could no longer be detected by reaction with potassium iodide.

To obtain MACS, the dialdehyde starch was reslurried in 100 ml water and part of the aldehydes were further oxidised to carboxylates. To achieve this, sodium bromide (0.5 g) was added and then peracetic acid (0.6 M) was added portion-wise (see Table 1). The pH was kept constant at pH 5 using 0.5 M NaOH (pH-stat.). After reaction, the aldehyde carboxy starch was purified by membrane filtration (molecular cut-off 5000 MW) and freeze-dried.

Table 1: Conversion of DAS to MACS

Sample	Totally added peracetic acid solution (ml of 0.6 M solution)	% aldehydes oxidised to carboxylates
A5	5	5
A10	10	10
A30	31	30
A50	52	50

20

b) Application as wet strength additive

The addition levels were 10 mg/g MACS and 10 mg/g PAE.

Sheets were prepared as in example 8. The results are presented in Figure 1.

The highest relative wet strength was obtained in the sheets treated with MACS with an oxidation degree of 10% and PAE. The performance of this combination is better than the combination of CMC and PAE, which is commonly used nowadays. It may be noted that when no additives are used, essentially no wet strength is obtained (compare Figure 6).

25

Example 2

MACS with an oxidation degree of 50% was prepared as described in Example 1. This polymer was added to pulp together with PEI (3mg/g and 7mg/g, respectively).

5 Sheets were prepared as in example 8. The results are presented in Figure 2. It may be noted that PEI does not give wet strength by itself (like PAE does). The wet strength shown in the case of MACS + PEI can be completely ascribed to MACS.

Example 3

a) Preparation of MACS with chlorite/hydrogen peroxide to different degrees of oxidation

10 Dialdehyde starch (oxidation degree 100%) was prepared as described in example 1.

To obtain MACS, 5 g of the dialdehyde starch (30 mmole AGU) was reslurried in 100 ml water and cooled to 4°C. In order to oxidise part of the aldehydes to carboxylates, hydrogen peroxide (640 µl of a 30 % solution, 6 mmole) and 700 mg sodium chlorite (80% grade, 7.5 mmole) were added (see Table 2). The pH was kept constant at pH 5 using 0.5 M NaOH (pH stat.). After reaction, the aldehyde carboxy starch was purified by filtration and washing with water and the product was subsequently freeze-dried.

Table 2: Conversion of DAS to MACS

Sample	Added hydrogen peroxide solution (30%) (µl)	Added sodium chlorite (80%) (mg)	% aldehydes oxidised to carboxylates
Ac5	320	350	5
Ac10	640	700	10
Ac15	960	1050	15

b) Application as wet strength additive

20 Sheets were prepared as in example 8.

The addition levels were 10 mg/g MACS and 10 mg/g PAE. The results are presented in Figure 3.

Example 4

25 Dialdehyde cellulose (oxidation degree 100%) was prepared by adding 6.6 g sodium periodate (31 mmole) to a slurry of 5.0 g (dry weight) cellulose (31 mmole) in 100 ml water which was brought to pH 5 with diluted acetic acid and cooled to 4°C. The mixture was stirred for 1 week at 4°C in the absence of light. The obtained product was isolated by filtration and washed with water until iodate could no longer be detected by reaction with
30 potassium iodide.

40 93

To obtain MACC, the dialdehyde cellulose was reslurried in 100 ml water and half of the aldehydes were further oxidised to carboxylates. To achieve this, sodium bromide (0.5 g) was added and then peracetic acid (0.6 M) was added portion-wise (52 ml of a 0.6 M solution). The pH was kept constant at pH 5 using 0.5 M NaOH (pH-stat.). After reaction,
5 the aldehyde carboxy cellulose was purified by membrane filtration (molecular cut-off 5000 MW) and freeze-dried.

Sheets were prepared as in example 8. The results are presented in Figure 3.

Example 5

10 MACS with an oxidation degree of 10 % was prepared as described in example 1. This material was added to pulp (10 mg/g) together with cationic dialdehyde starch (10 mg/g). Sheets were prepared as in example 8. The results are presented in Figure 3.

Example 6

15 MACS with an oxidation degree of 10 % was prepared as described in example 1. 1 g of this material was suspended in water and Girard's reagent ($\text{NH}_2\text{NHCOCH}_2\text{N}^+(\text{CH}_3)_3$, betaine hydrazide, 100 mg for 10% cationisation) was added. The solution was stirred for 2 hours at 40°C and was subsequently freeze dried. A cationic MACS derivative was obtained. This sample was added to pulp (addition level 10 mg/g), and sheets were prepared
20 as in example 8. The cationic MACS derivative adsorbs onto the fibres and gives wet strength. When added together with PAE (10 mg/g), the performance increased with lowering of the content of cationic groups (see Figure 4).

Example 7

25 6-Aldehyde starch was prepared by a TEMPO-mediated oxidation of starch. 5.0 g (dry weight) starch (31 mmol) was gelatinised in 250 ml water. TEMPO (65 mg) and horseradish peroxidase (100 mg) were added. The pH of the solution was adjusted to 5.0 using diluted acetic acid. Hydrogen peroxide (3.75 ml of a 30 % solution, 33 mmole) was diluted to a volume of 125 ml and was added gradually at a rate of 5 ml/hour. The reaction time
30 was 25 hours at room temperature. Adjustment of the pH during reaction was not necessary. The product was purified by membrane filtration (molecular cut-off 5000 MW) and freeze-dried.

1 g of this material was redissolved in water and Girard's reagent (100 mg for 10% cationisation) was added. The solution was stirred for 2 hours at 40°C and was
35 subsequently freeze dried again. A cationic 6-aldehyde starch was obtained. This sample

was added to pulp (addition level 10 mg/g) together with PAE (10 mg/g). Sheets were prepared as in example 8. The results are shown in Figure 5.

Example 8

5 Sheet making with derivatives of the invention

1. Refining

500-530 grams of Östrand TCF pulp is diluted to 12 litres and refined to 25 SR° by a Laboratory refiner R1L, Escher Wyss. The pulp, when refined, is about 40 g/L so it is diluted to the concentration of 3 g/L.

10 2. Dynamic sheet former, Formette

A wire of 0,4 m² is used and we want the Grammage to be 30 g/m².

The pulp is poured into the beater and the wet strength additive is added during stirring for 5 minutes. If PAE is added, it is added after five minutes and the pulp is stirred again for two minutes. Drum speed 1400 rotations/min, dewatering 30 sec.

15 3. Press

An absorbent paper is put over the sheet and the wire is taken off. Before pressing another absorbent paper is put over the sheet, so the sheet is between the two absorbent papers. The sheet is pressed at 0,5 bar once. To be able to compare sheets with each other, two sheets of the same composition are made but pressed at two different pressures, 0,5 bar and 5 bar. In this way we can compare them at the same density 400 g/cm³.

4. Drying

The sheet is cut into four pieces and dried two and two with a fixed point for three minutes at a temperature of 140 °C.

5. Cutting

25 The sheet is cut into 15 mm strips for testing of dry and wet strength.
100*100mm is also cut out for measuring the thickness and Grammage.

6. Conditioning

The strips which wet strength is going to be tested are placed in a heating chamber, 105° C for 10 minutes. Then both the strips for wet and dry strength are placed in a climate room, 30 temperature 23°C, moisture 50% for four hours.

7. Grammage and thickness

100*100 mm pieces of the sheet is used for measuring the Grammage and thickness.

Grammage is measured on a regular balance on 4 layers to get an average.

Thickness is also measured on four layers and on five different spots to get a good average.

8. Tensile strength measurement

The strength both wet and dry is measured in an Instron SCAN-P58:86.

Five 15-mm strips are measured to get an average.

When measuring the wet strength the strip is soaked for 15 sec in tap water.

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Example 9:

Large-scale preparation of MACS and application in a full scale tissue paper machine

The preparation of MACS with 15% of the aldehydes oxidised to carboxylic acids, as described in Example 1, was scaled up to 40 kg scale.

10 In the first step, 100% dialdehyde starch (DAS) was prepared. Sodium periodate (27 kg) was dissolved in 200 L water in a double-walled 300 L vessel equipped with a mechanical stirrer. The solution was cooled to 5°C. To this solution, potato starch (25 kg, 20.5 kg dry matter) was added portion-wise, keeping the temperature below 10°C. The slurry was stirred for 24 hours at 5°C. Then, the sodium iodate salts were removed by decantation after
15 settling of the DAS. The granules were washed with deionised water until no sodium iodate could be detected with potassium iodide and sulphuric acid. This procedure was repeated once and one more time using 21 kg sodium periodate and 20 kg starch. The overall yield of dialdehyde starch was 47 kg of DAS (82 % of theory, due to some losses during the washing procedure).

20 In the second oxidation step, MACS was prepared. DAS (11.75 kg) was slurried in about 150 L deionised water in a 300 L double-walled vessel. Sodium bromide (1.41 kg) was added and subsequently peracetic acid (7.07 kg, 39% activity) was added slowly using a pump running at 20 mL/min. The pH maintained between 4.7 and 5.3 by a pH controller adding 4 M NaOH. The temperature was kept between 15°C and 20°C. After all chemicals
25 were added, the solution was stirred overnight to ensure complete reaction. After reaction, the volume was reduced and part of the sodium acetate salts formed during reaction were removed using a membrane filtration unit (exclusion limit of 10000 D) to obtain a solution containing about 10 % MACS. This procedure was executed 4 times, and the products were mixed. The reaction yield of MACS in the second oxidation step was 42 kg (87 % of
30 theoretical).

A solution (490 kg) containing 8.6 % MACS was obtained. The polymer obtained in this way had similar characteristics regarding molecular weight and charge density as the material described in Example 1.

A tissue paper containing MACS was produced at a paper machine. See Example 10.

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Example 10: Application in a full scale tissue paper machine

With the MACS thus prepared (see Example 9), tissue paper was made on an industrial scale (continuous process) and the properties of the tissue were compared to those obtained with conventional wet strength agents.

- 5 Three kinds of tissues were made using the following composition of pulp: 65% TCF pulp (total chlorine free pulp) and 33% HTCTM pulp (high temperature chemi-thermo-mechanical pulp).

The first run was the reference, in which only PAE (9 kg/ton pulp) was applied. The second run was prepared using PAE (9 kg/ton pulp) and CMC, Hercobond C129 with a degree of substitution of 0.65-0.9, (1.7 kg/ton pulp). In the third run, PAE (9 kg/ton) and 1.7 kg
10 MACS per ton were used. The results with regard to the dry strength, wet strength, and wet tensile index are summarised in Table 3.

*Table 3. Wet and dry strength properties of tissue paper with PAE,
15 PAE/CMC and PAE/MACS, respectively.*

Run	Tissue samples	Dry strength (Nm/g)	Wet strength (Nm/g)	Tensile strength index (%)
1	PAE(ref.)	8.9	2.5	28.1
2	PAE/CMC	11.6	3.2	27.3
3	PAE/MACS	10.8	3.2	29.6

As can be seen from Table 3, both MACS and CMC improve the properties of the tissue with regard to wet and dry strength and CMC and MACS exhibit the same properties.

Claims

1. Use of a water-soluble or water-dispersible polymer having a molecular weight of at least 800, containing 0.25-2.25 aldehyde groups per recurring unit of the polymer and/or at least 5 aldehyde groups per molecule and containing at least 1 anionic group per molecule, the ratio of aldehyde groups to anionic groups being higher than 0.75:1, as a wet strength additive.
2. Use according to claim 1, in which the degree of substitution for aldehyde groups is 0.1-2.95 per recurring unit of the polymer, and the degree of substitution for anionic groups is 0.03-1.0 per recurring unit of the polymer.
3. Use according to claim 1, in which the degree of substitution for aldehyde groups is 0.25-2.25 per recurring unit of the polymer, and the degree of substitution for anionic groups is 0.05-0.4 per recurring unit of the polymer.
4. Use according to any one of claims 1-3, in which the anionic groups comprise carboxylic groups.
5. Use according to any one of claims 1-4, in which the polymer is a polysaccharide.
6. Use according to claim 5, in which the polymer is starch or cellulose or a starch- or cellulose-derived polymer.
7. Use according to claim 5 or 6, in which the aldehyde groups and the anionic groups are present as a result of oxidation of dihydroxyethylene moieties of recurring monosaccharide units.
8. Use according to claim 5 or 6, in which the aldehyde groups and the anionic groups are present as a result of oxidation of hydroxymethyl moieties of monosaccharide units.
9. Use according to any one of the preceding claims, in which anionic groups are present as a result of carboxymethylation.
10. Use according to any one of the preceding claims, in which the polymer further contains cationic groups with a degree of substitution of 0.01-0.50.

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11. Carbohydrate derivative containing 0.10-2.95 aldehyde groups, and 0.03-1.0 anionic groups and 0.01-0.50 cationic groups per recurring unit.
12. A wet strength composition containing 10-90% of a carbohydrate derivative containing 0.10-2.95 aldehyde groups, and 0.03-1.0 anionic groups per recurring unit, and 90-10% of a cationic polymer, the percentages being based on the total of carbohydrate derivative and cationic polymer.
13. A cellulosic fibre treated with a polymer as defined in any one of claims 1-11, or with a mixture according to claim 12.

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION 	()	()
Indicación de que se solicita la concesión de una patente.	()	()
Datos de identificación del solicitante o de la persona que se presenta la solicitud.	()	()
Descripción de la invención	()	()
Dibujos de ser estos 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 fotográfica 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 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.	()	()

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