

Clarke, Modet & C^o

COLOMBIA

118
121

SUPERINDUSTRIA Y COMERCIO
Radicación: 0299179 0068065 Folios: 4
Fecha (IMP): 2005-10-14 12:13:07
Trámite: 011 PCT-PATENT 379 FASE NACI 593 IMPULSO I
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

**SEÑORES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
E.S.D**

**REF EXPEDIENTE No. : 02 99179 /
PATENTE : POLIMEROS QUE CONTIENEN ALDEHIDO COMO
ADITIVOS DE RESISTENCIA A LA HUMEDAD
SOLICITANTE : SCA HIGIENE PRODUCTS ZEIST**

ASUNTO: SOLICITUD ESTUDIO DE FONDO

DILIA RODRÍGUEZ D'ALEMAN, en mi condición de apoderada de la Sociedad solicitante, por el presente escrito atentamente solicito a Usted que habiéndose surtido la publicación de la presente solicitud, en la Gaceta de la Propiedad Industrial No.551 de fecha Abril 29, 2005 se proceda con el estudio de Fondo.

Para tal fin me permito anexar la tasa correspondiente.

Agradezco continuar con el presente trámite.

Señor Jefe,


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

P-457

119 +22

SUPERINDUSTRIA Y COMERCIO
Radicacion : 88893173 88888888
Fecha (HH): 2005-09-14 17:13:07
Tramite : 011 OCT-PATENT 379 FASE INICI 593 IMPULSO ;
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 71,882
FECHA : SEPTIEMBRE 15 DE 2005

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO POPULAR	050-00110-6	35422041	15/09/2005	9,290,00 00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09 OTROS SERVICIOS DE PROPIEDAD I	21 CERTIFICACIONES	10,000.00
TOTAL :			\$ 10,000.00

SON: DIEZ MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

120 723

SUPERINDUSTRIA Y COMERCIO
Radicacion : 82999179 00000005 Folios: 4
Fecha (HH): 2005-10-14 17:13:07
Tramite : 001 PCT-PATENT 379 FASE NACI 593 IMPULSO P
Dependencia: 0000 DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 74,957
FECHA : OCTUBRE 9 DE 2005

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE HOBET Y CO. COLOMBIA	CONSIGNACION	BANCO POPULAR	050-00110-6	40241679	05/10/2005	9,373,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-00	PRORROGA DE TERMINOS	66,000.
		TOTAL :	\$ 66,000.00

SON: SESENTA Y SEIS MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

124
121

SUPERINDUSTRIA Y COMERCIO
Radicación: 02993179 00000000
Fecha (MM): 2005-10-14 17:17:07
Trámite: 011 PCT-PATENTE 379 FASE NACI 393 IMPULSO
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Folios: 4

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 5 - 16,636
FECHA : MARZO 4 DE 2005

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CLARKE MOJET Y CO. COLOMBIA	CONSIGNACION	BANCO POPULAR	050-00110-6	33846602	04/03/2005	604,750.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	25% TRAMITES DE SOL. DE PATENTE D	110,750.00
		TOTAL :	\$ 110,750.00

BOB: CIENTO DIEZ MIL SETECIENTOS CINCUENTA PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL ASUNTO No.

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 02-99179

**EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION-
PCT FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No 551,
DE FECHA 29 DE ABRIL DE 2005, EL TERMINO HABIL SEÑALADO POR LA
LEY EXPIRA EL 29 DE JULIO DE 2005.**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____ **NO** ☒ _____

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

2020

Bogotá, D. C., 23 de Junio de 2006

Doctora

DILIA RODRIGUEZ D'ALEMAN

Representante SCA HIGIENE PRODUCTS ZEIST

ASUNTO

Radicación No. 02-99179

Trámite 002

Evento 001

Actuación 430

Oficio

Folios 019

06953

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

1) Documentos estudiados:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 34 a 68 de la solicitud en estudio.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 15 reivindicaciones en los folios 102 a 105 de la solicitud en estudio.
- c) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 31 de octubre de 2002, y en el momento de la radicación se presentó como solicitud de patente PCT Fase nacional y se reclamó prioridad de las primeras solicitudes presentadas en Europa EP201630.1 y EP201693.9

2) Objeto de la invención

- a) Las reivindicaciones 1 a 15 de la solicitud en estudio se refieren a
 - i) (1.-) Un método para mejorar la resistencia a la humedad de un producto de papel, tejido o no tejido, que comprende aplicar un polímero soluble en agua o dispersable en agua que tiene un peso molecular de al menos 800, que contiene 0,25-2,25 grupos aldehído por unidad recurrente del 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 aldehídos a los grupos aniónicos es mayor de 0,75:1, como un aditivo resistente a la humedad.
 - ii) (11.-) Un derivado de carbohidrato que contiene 0,10 – 2,95 grupos aldehído, y 0,03 – 1,00 grupos aniónicos, y 0,01 – 0,50 grupos catiónicos por unidad recurrente

iii) (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 recorrente y 90 – 10% de un polímero catiónico, el porcentaje esta basado en el total el (sic) derivado de carbohidrato y el polímero catiónico.

iv) (13.-) Una fibra celulósita...

b) El anterior procedimiento busca usar un compuesto definido.

c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a D 21 H 21/20

3) Claridad de la Solicitud

a) El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones establece

"La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

La descripción no es clara toda vez que presenta muchos errores tipográficos, errores de traducción y nombres químicos que no corresponden al de uso corriente. La solicitud deberá presentarse nuevamente, siendo esta revisada por alguien que entienda del arte.

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

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

El capítulo reivindicatorio no es claro toda vez que:

i) Todas las objeciones hechas en el punto 3) a) son aplicables acá

ii) La forma de exponer el grado de sustitución en los polímeros es ambiguo toda vez que no explica sobre que base trabaja los valores establecidos.

iii) No se precisa la materia sobre la cual se solicita protección. Cómo se explicará en el punto 4), la presente solicitud no posee unidad de invención, por lo que no está definida la materia sobre la cual se solicita protección.

- iv) Un proceso es una secuencia lógica de pasos o etapas (plural, no singular) que busca un fin. De acuerdo a lo establecido en la reivindicación 1 así como con sus dependientes, el solicitante pretende que le sea protegido la aplicación (o uso) de una composición. Primero, no hay proceso pues existe una sola acción (aplicar). Segundo lo que se quiere proteger es un uso lo cual no es admitido. Deben eliminarse dichas reivindicaciones.

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

4) Evaluación de la Unidad de Invención

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

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

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

De acuerdo a lo anterior, la presente solicitud no cumple con el requisito de unidad de invención de acuerdo al Art. 25 de la Decisión 486. De continuar con el impedimento, esta oficina procederá a estudiar solo el primer grupo de invenciones que conformen un único concepto inventivo.

5) Reivindicaciones de uso

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

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

Las reivindicaciones 1 a 10 y 13 a 15 se refieren al uso de una composición. Tal como está contemplado en la legislación el uso no se protege. Se protegen los productos o procedimientos, donde el producto este correctamente definido por su conformación o su composición, y los procedimientos por la serie de etapas que busquen un fin. El uso no corresponde ni a un uso ni a un procedimiento. El uso es simplemente la aplicación industrial de esos productos o procedimientos.

Por lo anterior, las reivindicaciones 1 a 10 y 13 a 15 no son patentables de acuerdo al Art. 14 de la Decisión 486.

6) **Determinación del Estado de la Técnica**

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

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

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

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 08 y las más cercanas a ellas, se encontró que antes del 4 de mayo de 2000 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con compuestos poliméricos que contienen aldehído.

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

Nº	Documento	Título	Fecha de Publicación
D1	WO 0011046	Dialdehyde modified anionic and amphoteric polyacrylamides for improving strength of paper	2000.03.02

7) **Evaluación de los requisitos de patentabilidad**

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

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

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

a) **Evaluación de la novedad y el del Nivel Inventivo**

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

"Una invención se considerará nueva cuando no está comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción

escrita u oral, utilización comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

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

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

El documento WO 0011046 (D1) revela composiciones de derivados de carbohidrato con grupos aniónicos y catiónicos, con grupos aldehído. En general, la anterioridad anticipa la presente solicitud.

b) Resumen

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

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	WO 0011046	11 - 12	Novedad
			Nivel inventivo

8) Notificación

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

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


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en la lista, de fecha
30 JUN. 2006

Concepto Técnico N° 992	EXAMINADOR TÉCNICO Código No. 202003	EXAMINADOR JURÍDICO Código No.
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DIALDEHYDE-MODIFIED ANIONIC AND AMPHOTERIC POLYACRYLAMIDES
FOR IMPROVING STRENGTH OF PAPER

Background of the Invention

Field of the Invention

This invention relates to improving the strength of paper and more particularly it relates to dialdehyde modified anionic and amphoteric polyacrylamides which when incorporated in paper result in improved strength

Description of the Prior Art

Several anionic and amphoteric polyacrylamides have been, or are in the process of being, commercialized by Hercules Incorporated for the paper industry. Anionic polyacrylamides comprised of acrylic acid with a small amount of crosslinker are described in US 5,543,448 the disclosure of which reference is hereby incorporated by reference. Amphoteric polyacrylamides comprised of methacryloyloxyethyl-trimethylammonium chloride (MTMAC) and itaconic acid with a small amount of crosslinker are described in WO 98/06888 the disclosure of which reference is hereby incorporated by reference. All of these materials improve the dry strength of paper via electrostatic attraction and hydrogen bonding.

Summary of the Invention

According to the present invention there is provided a composition comprising crosslinked thermosetting, water soluble polymer having nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 6 carbon atoms and salts thereof; moieties derived from water soluble divinyl monomer; and optionally cationic moieties derived from unsaturated monomers containing amino groups or

quaternary ammonium groups, said polymer having aldehyde functionality where the aldehyde functionality is derived from a dialdehyde. There is also provided a composition consisting essentially of crosslinked thermosetting water soluble polymer having nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 6 carbon atoms and salts thereof; and optionally cationic moieties derived from unsaturated monomers containing amino groups or quaternary ammonium groups, said polymer having aldehyde functionality where the aldehyde functionality is derived from a dialdehyde.

Further according to the present invention there are provided processes for preparing the polymer of the present invention; for making paper with such polymer; for making paper with such polymer in combination with a cationic adjunct; and paper comprising polymer of the present invention.

Detailed Description of the Invention

Surprisingly, it has been discovered that the reaction of dialdehydes (such as glyoxal) with anionic and amphoteric polyacrylamides results in improved dry strength and wet strength as well as providing repulpable or temporary wet strength.

The ionic prepolymers of the invention are made from nonionic monomer selected from the group consisting of acrylamide and methacrylamide, anionic monomer, and optionally cationic monomer. The amount of anionic monomer plus cationic monomer comprises from 1 to 80 mole percent of the total of anionic, cationic, and nonionic monomer in the prepolymer. Acrylamide is the preferred nonionic monomer.

Anionic monomers are preferably α,β -unsaturated carboxylic acids having from 3 to 6 carbon atoms and salts thereof. Suitable anionic monomers are e.g., acrylic acid, methacrylic acid, itaconic acid and salts thereof. Acrylic acid and itaconic acid are preferred. The preferable salts are sodium salts.

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Cationic monomers can be unsaturated monomers containing amino groups or quaternary ammonium groups. When monomers containing amino groups are used, cationic sites are obtainable by forming salts of the amino groups with mineral acids. Preferred unsaturated cationic monomers are methacryloyloxyethyltrimethylammonium chloride (MTMAC), acryloyloxyethyltrimethylammonium chloride (ATMAC), diallyldimethylammonium chloride (DADMAC), methacrylamidopropyltrimethylammonium chloride (MAPTAC), methacryloyloxyethylbenzyltrimethylammonium chloride (MBMAC), and the hydrochloride salt of dimethylaminoethylmethacrylate (DMAEMA-HCl). The most preferred cationic monomer is MTMAC.

The ionic prepolymers for use in the invention can have an amount of anionic monomer plus cationic monomer up to about 50 mole percent, preferably up to about 20 mole percent, and most preferably up to about 10 mole percent, of the total of anionic, cationic, and nonionic monomers. The mole percent anionic monomer plus cationic monomer can be at least about 1, preferably at least about 3, and most preferably at least about 5.

The amount of cationic monomer when present can be up to about 25 mole percent, preferably up to about 10 mole percent, and most preferably up to about 5 mole percent. The amount of cationic monomer can be 0, preferably at least about 1 and most preferably at least about 2 mole percent.

The preferred molar ratio of cationic monomer to anionic monomer is at least about 1:10 and can be up to about 10:1, with the most preferred ratio being at least about 1:2 and can be up to about 2:1.

A small amount of water soluble divinyl monomer may also be incorporated to increase the molecular weight of the ionic prepolymer by crosslinking without rendering it insoluble. Suitable divinyl monomers are N,N'-methylenebisacrylamide

ethyleneglycol dimethacrylate and ethyleneglycol diacrylate. Preferably the divinyl monomer is N,N'-methylenebisacrylamide.

Preferred dialdehydes for reaction with the copolymer are glyoxal and C₃ to about C₆ saturated or unsaturated dialdehydes. Examples of such dialdehydes include malonic dialdehyde, succinic dialdehyde, glutaraldehyde, adipic dialdehyde, 2-hydroxyadipic dialdehyde, pimelic dialdehyde, suberic dialdehyde, azelaic dialdehyde, sebacic dialdehyde, maleic aldehyde, fumaric aldehyde, phthalaldehyde, isophthalaldehyde, terephthalaldehyde, and 1,4-diformylcyclohexane. The most preferred dialdehyde is glyoxal.

The amount of dialdehyde used for reaction can be at least from about 0.01 moles for each mole of nonionic moiety (e.g., acrylamide) contained in the prepolymer, preferably at least about 0.1 moles, and most preferably at least from 0.2 moles for each mole of nonionic moiety in the prepolymer. The amount of dialdehyde can be up to about 1, preferably up to about 0.7 and most preferably up to about 0.5 moles for each mole of nonionic moiety in the prepolymer.

The polyacrylamide prepolymers are prepared by free-radical initiated polymerization of acrylamide and an anionic monomer, such as acrylic acid, and optionally a cationic monomer, such as MTMAC. The product resin is prepared by reacting the prepolymer with dialdehyde, such as glyoxal, to a target viscosity followed by acid stabilization. The resulting product is a crosslinked, thermosetting, anionic or amphoteric resin containing aldehyde functionality.

The reaction between the dialdehyde and prepolymer can preferably be carried out at a pH of at least about 5 and it can be up to about 10 and a temperature of at least about 20°C and up to about 80°C for a time sufficient to reach the viscosity target for the product. More preferably the pH is at least about 8 and up to about 9 and the temperature is at least about 25 and up to about 50°C. During the reaction of dialdehyde with the prepolymer some crosslinking of the

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product will occur through reaction of the aldehyde group with another amide-containing polymer chain. The crosslinking is accompanied by an increase in viscosity. The preferable target viscosity for the product is a Brookfield viscosity of at least about 50 cps as an 8.5% solids aqueous solution. The preferred target viscosity can be up to about 500 cps. More preferably the target viscosity is at least about 100 and up to about 300 cps, and most preferably it is at least about 150 and up to about 250 cps.

By imparting cellulose reactive functionality to anionic or amphoteric polyacrylamide compositions, better performance can be achieved. Cellulose reactivity can be imparted by derivatizing some of the acrylamide moieties e.g. with glyoxal. The reaction with glyoxal crosslinks or further crosslinks the resin backbone, which will often boost dry strength effectiveness, and also provides aldehyde functionality which will react with cellulose hydroxyls. The reactions between resin aldehydes and cellulose hydroxyls form reversible covalent bonds (hemiacetals) which boost dry strength performance and provide some reversible (temporary) wet strength.

The resins of the present invention can be added to paper pulp alone in the case of amphoteric resins, or with a cationic adjunct to improve retention in the case of either the anionic or amphoteric versions. The resins of this invention also boost the performance of cationic wet strength or dry strength resins.

Examples of cationic adjuncts include polyaminopolyamide-epi resins (such as Kymene® 557H wet-strength resin available from Hercules Incorporated), cationic starch, polyamines (such as Retan® 203 polyamine available from Hercules Incorporated), polyamine-epi resins (such as Retan® 204 resin available from Hercules Incorporated) and polyethylenimine. Preferred cationic adjuncts are the polyaminopolyamide-epi resins and cationic starch. Most preferred cationic adjuncts are the polyaminopolyamide-epi resins. When used alone the dry strength effectiveness of the amphoteric resins of this invention is comparable to

that obtained with polyaminopolyamide-epi resins. When used in combination with polyaminopolyamide-epi resins, wet and dry strength performance is boosted by over 10% compared to the polyaminopolyamide alone. It is expected that paper treated with these resins alone would exhibit some wet strength (up to 50% of that obtained with polyaminopolyamide wet-strength resins at equal resin loading), and be more repulpable (on an equal strength basis) than paper treated with polyaminopolyamide-epi wet-strength resins.

By the term "cationic wet strength resin" is meant cationic polymers or adjuncts which when used alone in paper impart significant wet strength to the paper.

Polymeric amine/epichlorohydrin resins are selected from the group consisting of polyaminoamide/epichlorohydrin resins, polyalkylenepolyamine/epichlorohydrin resins, aminopolyamine/epichlorohydrin resins, and polyaminoamide urethane/epichlorohydrin resins. The preferred epichlorohydrin is epichlorohydrin.

The most preferred cationic wet strength resins for the practice of the invention are the polyaminoamide/epichlorohydrin resins. Polyaminoamides containing tertiary amines in the backbone are disclosed in U.S. Patent Nos. 4,467,884 and 4,515,857 to Masterton, both of which are incorporated herein by reference in their entireties. If tertiary amines are present in the polyaminoamide or polyamine backbone, quarternary epoxide groups are produced.

Kymene® wet strength resins are the preferred polyaminoamide/epichlorohydrin resins. Some examples of polyaminoamide/epichlorohydrin Kymene® wet strength resins, available from Hercules Incorporated, Wilmington, DE are Kymene® 557H, Kymene® 557LX, Kymene® 557 BLX, Kymene® 557 ULX and Kymene® Plus. In Kymene® 557H adipic acid is reacted with diethylenetriamine to form a polyaminoamide that is alkylated and crosslinked with epichlorohydrin to form a polyaminoamide/epichlorohydrin resin. Kymene® Plus is a higher solids version of

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Kymene® 557H, Kymene® 557LX, Kymene® 557BLX and Kymene® 557ULX are versions of Kymene® 557H that contain low amounts of halide by-products. Polyaminoamide/epichlorohydrin resins containing low amounts of halide by-products are disclosed in U.S. Patent No. 5,171,786, to Miller et al., which is incorporated herein by reference in its entirety. European Patent Application Publication No. 0 468 767A2 to Bower and European Patent Application Publication No. 0 610 967A1 to Blal et al.

Kymene® 450 wet strength resin is a polyaminoamide ureylene/epichlorohydrin resin prepared by reacting oxalic acid methyl bis(aminopropylamine) and urea to form a polyaminoamide ureylene, which is then alkylated with epichlorohydrin. Resins of this type are disclosed in U.S. Patent No. 4,487,884, to Masterton.

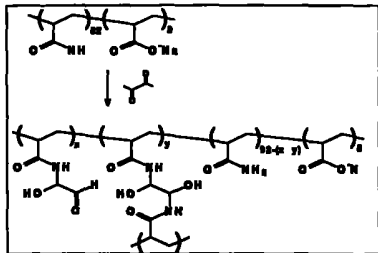
Kymene® 736 is a polyalkylenepolyuremine/epichlorohydrin resin prepared from hexamethylenediamine and epichlorohydrin as described in European Patent Application Publication No. 0606203, October 14, 1992.

The level of cationic adjunct used will generally be in the range of from about 0.1% to about 5% on a dry basis based on the dry weight of pulp. A preferred level is from about 0.2% to about 4% and a more preferred level from about 0.3% to about 3%. The most preferred level will be in the range of from about 0.3% to about 2%.

The synthetic scheme for a resin of the present invention based on an 8 mole percent acrylic acid anionic polyacrylamide is given in Figure 1. Examples of the synthesis of the anionic polyacrylamide prepolymer including ranges of properties and composition, are given in the above referred to US 5,543,468. Preferred prepolymer RSV is 0.5 to 2 dL/g. Preferred composition of acrylic acid is 4-12 mole percent. The prepolymer is diluted to 7 to 10% solids and glyoxal is added at ambient temperature. The mole ratio of glyoxal to acrylamide in the prepolymer ranges from 0.1 to 1.0. Preferred range is 0.15 to 0.5. Most preferred mole ratio is 0.25. The pH of the mixture is raised to about 9 with dilute NaOH. Solution viscosity (Gardner-Holdt) is monitored. After an increase of up to about 6 Gardner-

Holdt viscosity units, the reaction is quenched by reducing the reaction pH to about 3. Final solids range from 7 to 10%, with 8.5% preferred.

Figure 1

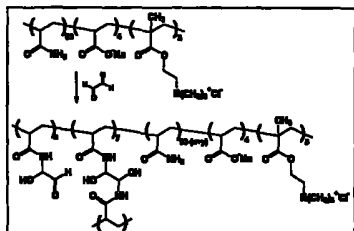


where X can be from 1 to 50, most preferably about 15. Y can be up to 5, most preferably about 1.

The synthetic scheme for a resin of the present invention based on a 4 mole percent acrylic acid/3 mole percent MTMAC amphoteric polyacrylamide is given in Figure 2.

Examples of the synthesis of the amphoteric polyacrylamide prepolymer are given in the above referred to WO 00/08698. Preferred prepolymer RSV is from 0.5 to 2 dL/g. MTMAC and acrylic acid content in the prepolymer are less than 10 mole percent. The reaction with glyoxal is the same as described for the anionic version above.

Figure 2



where X can be from 1 to 50 most preferably about 18. Y can be up to 8, most preferably about 1

The product resins of the present invention are either anionic or amphoteric, crosslinked, thermosetting, and reactive with paper pulp fibers. For the anionic resins, a cationic adjunct or co-additive is usually necessary to retain the material on the anionic fiber surfaces. Such an adjunct can be a non-reactive material such as a retention aid (a polyDADMAC such as Reten® 203 retention aid or a cationic polyacrylamide such as Reten® 1232 retention aid) or a reactive resin (polyaminopolyamide-epi resin, such as Kymene® 567H, resin polyamine-epi resin such as Kymene® 736 resin or glycidated cationic polyacrylamide such as Herculobond® 1386 resin). The amphoteric resins of this invention, due to the presence of the cationic quaternary ammonium groups, can be retained without the use of a cationic adjunct. Retention and performance, however, are usually increased by the use of a cationic adjunct.

When the amphoteric resins of this invention are used alone or when the anionic or amphoteric resins of this invention are used in combination with a non-reactive cationic retention aid, paper dry strength is improved. This dry strength

Improvement is usually better than that obtained with conventional uncrosslinked unreactive dry strength resins. In addition, some wet strength is obtained. Because of the reversible nature of the hemiacetals that give rise to this wet strength, the wet strength is temporary, i.e., it decays rapidly over time. This temporary nature makes paper treated with the resins of this invention more repulpable than conventional polyaminopolyamide-epi wet-strength resins, when compared on an equal wet strength basis.

When the cationic adjunct is a functional additive such as a polyaminopolyamide-epi wet-strength resin, the resins of this invention significantly improve the wet and dry strength performance of the adjunct over non-dialdehyde-modified anionic or amphoteric polyacrylamides.

The scope of the present invention as claimed is not intended to be limited by the following Examples which are given merely by way of illustration. All parts and percentages are by weight unless otherwise indicated.

Example 1

This example describes the synthesis of a glycidyl-modified anionic polyacrylamide with a low crosslink density.

An anionic polyacrylamide comprised of 8 mole percent of acrylic acid and 0.04 mole percent of methylenebisacrylamide with a 0.05% reduced specific viscosity (RSV) measured in 2 mole/l sodium chloride at 30°C in a Ubbelohde viscometer of about 1.2 dL/g (500 g at 22.4% solids) and deionized water (1100 g) were charged at ambient temperature to a 3 neck 2-liter round bottom flask equipped with a mechanical stirrer, glass stirrer shaft with Teflon stir blade, and pH probe. Solids of the mixture was 7.0% by weight. The pH of the mixture was raised from 4.5 to 7.2 using dilute caustic. Glycidol (51.98 g at 40% solids) was added via syringe. The pH was raised to 8.5 with 10% NaOH. The Gardner-Holt viscoity was measured immediately (ASTM method D803) and was found to be an

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E+ The reaction pH was maintained at 8.5 while the Gardner-Holdt viscosity of the mixture was monitored. After 60 minutes, the viscosity was a G+. The reaction was quenched by lowering the pH to 4 with sulfuric acid. Total solids were 7.48%. The sample was stored under refrigeration.

Example 2

This example describes the synthesis of a glyoxal-modified anionic polyacrylamide with a high crosslink density.

The same anionic polyacrylamide prepolymer used to prepare the resin in Example 1 (500 g at 22.4 % solids) was charged to a flask equipped as described in Example 1. The polymer was diluted to 7% solids with deionized water (1100 g). The pH was adjusted to 7.45 with 10% NaOH. With stirring, glyoxal (51.96 g at 40% solids) was added to the flask at ambient temperature. 10% NaOH solution was added to raise the pH of the mixture to 8.5. The Gardner-Holdt viscosity was E+. The pH was maintained at 8.5 while the viscosity was monitored. Once the viscosity increased 4-6 Gardner-Holdt units, the reaction was to be quenched. After 61 minutes, the viscosity had increased to J. The reaction was quenched by reducing the pH to 4.0 with sulfuric acid. Total solids were 7.86%. The mixture was stored under refrigeration.

Example 3

This example describes the synthesis of a glyoxal-modified amphoteric polyacrylamide from a polyacrylamide prepolymer comprised of 4 mole percent of acrylic acid and 3 mole percent of MTMAC.

An amphoteric polyacrylamide comprised of 4 mole percent of acrylic acid and 3 mole percent of MTMAC having an RBV of 0.8 dL/g (131.0 g of a 17.5% solids solution, 22.9 g dry basis) was diluted to 7% solids with 196 g of water. The solution pH was raised from 4.4 to 7 with 4.7 g of 6% caustic. Glyoxal (12.7 g of a 40% solution, 6.07 g dry basis) was added to the solution all at once, at ambient

temperature. The pH of the mixture was raised to 8.5 with 1.36 g of 6% caustic, again at ambient temperature. When the Gardner-Holdt viscosity (initially about "G") reached "M" (an increase of about 6 Gardner units in about 30 minutes), the crosslinking reaction was quenched by adding 2.5 g of 10% sulfuric acid to bring the pH down to 3. Final solids were about 8.6%.

Example 4

This example describes the synthesis of a glyoxal-modified amphoteric polyacrylamide from a polyacrylamide prepolymer comprised of 2 mole of Itaconic acid and 3 mole percent of MTMAC.

An amphoteric polyacrylamide comprised of 2 mole percent of Itaconic acid and 3 mole percent of MTMAC having an RBV of 1.66 dL/g (80.0 g of a 16.4% solids solution, 9.84 g dry basis) was diluted to 7% solids with 80.6 g of water. The solution pH was raised to 7 with 6% caustic. Glyoxal (18.6 g of a 40% solution, 7.42 g dry basis) was added to the solution all at once, at ambient temperature. The pH of the mixture was raised to 8.3 with 6% caustic again at ambient temperature. When the Gardner-Holdt viscosity (initially about "G") reached "I+" (an increase of about 2 Gardner units in about 10 minutes), the crosslinking reaction was quenched by adding 10% sulfuric acid to bring the pH down to 3. Final solids were about 9.9%.

Example 5 and 6 Comparative Examples 1 to 4

These examples describe an evaluation in paper demonstrating the improvement in wet and dry strength performance of a polyaminopolyacrylamide-epi wet-strength resin when used with resins of the invention.

Paper handsheets were prepared from a 50:50 hardwood:softwood bleached kraft dry lap pulp blend refined to about 500 mL Canadian standard freeness. Sheets were generated having 80 lb/3000 sq. ft. basis weight at a papermaking pH

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of about 8. The tensile strengths were determined on two week naturally aged sheets by TAPPI methods T458 and T484. PAPAe = Kymene® 557H polyaminopolyamide-epi resin available from Hercules Incorporated. Pam = polyacrylamide. Ingredients and results are summarized in Table 1.

Table 1

Example	PAPAe (%)	Resin (%)	Dry Tensile (lb/in)	Wet Tensile (lb/in)
C-1	0	0	38.4	1.3
C-2	0.4	0	48.3	7.7
8	0.4	Example 1 (0.5)	47.2	8.1
8	0.4	Example 3 (0.5)	46.1	8.4
C-3	0.4	Acrilan PAM™ (0.5)	48.8	7.7
C-4	0.4	Acquafix PAM™ (0.5)	45.7	8.0

⁸⁴% male percent acrylic acid

⁸⁴% male percent acrylic acid, 3 male percent MTHAC

These examples demonstrate that the resin of this invention boosted the wet and dry strength obtained by the PAPAe resin alone. The wet strength improvements obtained with the resins of the invention were better than that obtained with the polyacrylamides prior to the process of the invention.

Examples 7-9 and Comparative 5 and 6

These examples describe an evaluation in a groundwood newsprint furnish, demonstrating the improvement in dry strength provided by the resin formulation of Example 4.

Paper was prepared on a continuous papermaking former from a 95:5 blend of repulped groundwood newsprint (unrefined) and softwood bleached kraft pulp refined to about 410 mL Canadian standard freeness. Sheets were generated having 42 g/m² basis weight at a papermaking pH of about 4.5 with 1% alum. Control runs (no additives) were prepared at 42 and 45 g/m² basis weight for comparison. Ingredients and results are summarized in Table 2.

Table 2

Example	Basis Weight (g/m ²)	Resin of Example 4 (%)	Dry Tensile (lb/in)
C-5	42	0	8.4
C-6	45	0	8.5
7	42	0.2	8.8
8	42	0.4	9.9
9	42	0.8	10.3

These examples demonstrate that the resin of this invention boosted dry strength of a 42 g/m² sheet to a level even higher than that obtained with a heavier (45 g/m²) sheet without such resin. Higher levels of resin afforded higher strength.

Examples 10-13 and Comparative Examples 7 and 8

These examples describe an evaluation in a recycled linerboard furnish, demonstrating the ability of the resins of this invention to impart both wet and dry strength when used alone and to improve the wet and dry strength performance of a polyaminopolyamide-epi wet-strength resin.

Paper was prepared on a continuous papermaking former from repulped old corrugated containers (OCC) refined to about 400 mL Canadian standard freeness. Sheets were generated having 60 lb/3000 sq. ft. basis weight at a papermaking pH of about 6. All runs contained 1% alum and 0.75% cationic starch. PAPAe = low epi polyaminopolyamide-epi resin (epi:amine ratio = 0.25:1). Ingredients and results are summarized in Table 3.

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Table 3

Example	PAPAE (%)	Resin (%)	Sheller Burst (psi)	Dry Tensile (lb/in)	Ring Crush (lb/in)	Wet Tensile (lb/in)
C-7	0	0	88.5	38.4	48.3	1.7
10	0	Example 3 (0.5)	71.3	40.8	81.3	3.5
11	0	Example 4 (0.5)	88.4	38.5	48.7	2.9
C-8	0.5	0	71.3	38.5	82.4	3.3
12	0.5	Example 3 (0.5)	73.0	42.5	87.3	4.9
13	0.4	Example 4 (0.5)	73.1	43.8	88.6	4.3

Example 14 and Comparative Examples 9 and 10

These examples describe an evaluation in a liquid packaging board furnish, demonstrating the ability of a resin of this invention to improve the wet and dry strength performance of a polyaminopolyamide-epi wet-strength resin

Paper was prepared on a continuous papermaking former from a 70.30 hardwood:softwood bleached kraft pulp blend refined to about 600 mL Canadian standard freeness. Sheets were generated having 180 lb/3000 sq. ft. basis weight at a papermaking pH of about 8. The strength data were determined on two week naturally aged sheets. All runs contained 0.5% cationic starch and 0.2% AKD size. PAPAE = Kymene® 557H polyaminopolyamide-epi resin. Ingredients and results are summarized in Table 4

Table 4

Example	PAPAE (%)	Resin (%)	201 TM (psi)	Sheller Burst (psi)	Dry Tensile (lb/in)	Wet Tensile (lb/in)
C-9	0	0	80.3	101	68.8	2.8
C-10	0.5	0	74.8	123	84.2	18.0
14	0.5	Example 4 (0.5)	88.5	165	93.9	16.9

TM201 sheller burst strength determined by TAPPI method T841

Example 16

This example describes the synthesis of a glyoxal-modified acrylamide/methacrylic acid copolymer

Dilute five hundred grams of a 20% solution of a 10 mole percent methacrylic acid/90 mole percent acrylamide copolymer to 7% solids with 528.8 grams of deionized water in the reactor. Adjust the pH to 7.5 with 10% NaOH. With stirring, add glyoxal (45.0 grams of 40% solution) to the flask at ambient temperature, and add 10% NaOH solution to raise the pH to 8.5. Maintain pH at 8.5 while monitoring the viscosity. The initial Gardner-Holdt viscosity of E increases to J over a period of one hour. Quench the reaction by reducing the pH to 4.0 with sulfuric acid giving a final solids of 7.8%. Store the product under refrigeration.

Example 18

This example describes the synthesis of a glyoxal-modified amphoteric copolymer of DADMAC, acrylic acid, and acrylamide.

Dilute six hundred twenty-five grams of a 10.0% solution of a 5 mole percent acrylic acid/5 mole percent DADMAC/90 mole percent acrylamide copolymer to 7% solids with 808.8 grams of deionized water in the reactor. Adjust the pH to 7.5 with 10% NaOH. With stirring, add glyoxal (43.2 grams of 40% solution) to the flask at ambient temperature, and add 10% NaOH solution to raise the pH to 8.5. Maintain

the pH at 8.8 while monitoring the viscosity. The initial Gardner-Holdt viscosity of D increases to 1 over a period of 80 minutes. Quench the reaction by reducing the pH to 4.0 with sulfuric acid giving a final solids of 7.5%. Store the product under refrigeration.

Examples 17, 18 and Comparative Examples 11, 13

This example describes an evaluation in a liquid packaging board furnish demonstrating the ability of a resin of this invention to improve the dry strength performance of an polyaminopolyamide-epi wet-strength resin with or without added cationic starch.

Paper was prepared on a continuous papermaking former from a 70:30 hardwood:softwood bleached kraft pulp blend refined to about 800 ml. Canadian standard freeness. Sheets were generated having 180 lb/3000 sq. ft. basis weight at a papermaking pH of about 8. The strength data were determined on two week naturally aged sheets. All runs contained 0.2% AKD size. PAPAe = Kymene® 867H polyaminopolyamide-epi resin.

Example	Cationic Starch %	PAPAe %	Resin %	ZDT (psi)
C-11	0	0.3	0	66.2
17	0	0.3	Example 2 (0.3)	66.2
C-12	0.6	0.6	0	61.2
18	0.6	0.6	Example 2 (0.3)	61.1
C-13	1.0	0.3	0	67.7
19	1.0	0.3	Example 2 (0.3)	64.4

Claims

1. A composition comprising crosslinked thermosetting, water soluble polymer having nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 6 carbon atoms and salts thereof; moieties derived from water soluble divinyl monomer and optionally cationic moieties derived from unsaturated monomers containing amino groups or quarternary ammonium groups; said polymer having aldehyde functionality wherein the aldehyde functionality is derived from a dialdehyde.

2. A composition consisting essentially of crosslinked thermosetting, water soluble polymer having nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 6 carbon atoms and salts thereof; and optionally cationic moieties derived from unsaturated monomers containing amino groups or quarternary ammonium groups, said polymer having aldehyde functionality wherein the aldehyde functionality is derived from a dialdehyde.

3. The composition of claims 1-2 wherein the combined amount of anionic and cationic moieties in the polymer is at least about 1 mole % based on the total amount of anionic, cationic and nonionic monomers.

4. The composition of claim 3 wherein the combined amount of anionic and cationic moieties in the polymer is at least about 3 mole %.

5. The composition of claim 3 wherein the combined amount of anionic and cationic moieties in the polymer is at least about 6 mole %.

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8. The composition of claims 1-6 wherein the combined amount of anionic and cationic moieties in the polymer is up to about 50 mole % based on the total amount of anionic, cationic and nonionic moieties.
- 5 7 The composition of claim 6 wherein the combined amount of anionic and cationic moieties in the polymer is up to about 20 mole %.
- 8 The composition of claim 6 wherein the combined amount of anionic and cationic moieties in the polymer is up to about 10 mole %.
- 10 9 The composition of claims 1-6 wherein the amount of cationic moieties is at least about 1 mole %.
- 15 10 The composition of claim 9 wherein the amount of cationic moieties is at least about 2 mole %.
- 11 The composition of claims 1-10 wherein the amount of cationic moieties is up to about 25 mole %
- 20 12. The composition of claim 11 wherein the amount of cationic moieties is up to about 10 mole %.
13. The composition of claim 11 wherein the amount of cationic moieties is up to about 5 mole %
- 25 14 The composition of claims 1-9 wherein the amount of cationic moieties is 0 mole %
15. The composition of claims 1-4 wherein the molar ratio of cationic moieties to anionic moieties is at least about 1:10.
- 30

16. The composition of claim 15 wherein the molar ratio of cationic moieties to anionic moieties is at least about 1:2
- 17 The composition of claims 1-16 wherein the molar ratio of cationic moieties to anionic moieties is up to about 10:1
- 18 The composition of claim 17 wherein the molar ratio of cationic moieties to anionic moieties is up to about 2:1
- 10 19. The composition of claims 1-18 additionally comprising moieties derived from water soluble divinyl monomer
- 20 20 The composition of claims 1-18 wherein the moieties derived from divinyl monomer are selected from the group consisting of *N,N'*-methylenebisacrylamide, ethyleneglycol dimethacrylate, and ethyleneglycol diacrylate.
- 15 21 The composition of claim 20 when the water soluble is divinyl monomer *N,N'*-methylenebisacrylamide
- 20 22. The composition of claims 1-21 wherein the amount of aldehyde functionality is at least about 0.01 mole per mole of nonionic moiety
23. The composition of claim 22 wherein the aldehyde functionality is at least about 0.1 mole per mole of nonionic moiety
- 25 24 The composition of claim 22 wherein the aldehyde functionality is at least about 0.2 mole per mole of nonionic moiety
- 30 25. The composition of claims 1-24 wherein the amount of aldehyde functionality is up to about 1 mole per mole of nonionic moiety

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26. The composition of claim 25 wherein the aldehyde functionality is up to about 0.5 mole per mole of nonionic moiety
- 5 27 The composition of claim 25 wherein the aldehyde functionality is up to about 0.7 mole per mole of nonionic moiety
- 10 28 The composition of claims 1-26 wherein the Brookfield viscosity of the polymer is at least about 50 cps as a 8.5% by weight aqueous solution.
- 15 29 The composition of claim 28 wherein the Brookfield viscosity of the polymer is at least about 100 cps.
- 30 30. The composition of claim 29 wherein the Brookfield viscosity of the polymer is at least about 150 cps.
- 31 The composition of claims 1-30 wherein the Brookfield viscosity of the polymer is up to about 800 cps as a 8.5% by weight aqueous solution.
- 20 32. The composition of claim 31 wherein the Brookfield viscosity of the polymer is up to about 300 cps
33. The composition of claim 31 wherein the Brookfield viscosity of the polymer is up to about 250 cps
- 25 34 The composition of claims 1-33 wherein the aldehyde functionality is derived from dialdehydes selected from the group consisting of glyoxal saturated dialdehydes having from 3 to 8 carbon atoms and unsaturated dialdehydes having from 3 to 8 carbon atoms.
- 30

35. The composition of claim 34 wherein the aldehyde functionality is derived from dialdehydes selected from the group consisting of glyoxal malonic dialdehyde succinic dialdehyde, glutaraldehyde, adipic dialdehyde, 2-hydroxyadipic dialdehyde, pimelic dialdehyde, sebacic dialdehyde, azelaic dialdehyde sebacic dialdehyde maleic aldehyde fumaric aldehyde phthalaldehyde, isophthalaldehyde, terephthalaldehyde, and 1,4-diformylcyclohexane.
- 36 The composition of claim 34 wherein the aldehyde functionality is derived from glyoxal
- 37 The composition of claims 1-36 wherein the anionic moieties are derived from acrylic acid, methacrylic acid itaconic acid and salts thereof
- 15 38. The composition of claims 1-37 wherein the cationic moieties are derived from monomers selected from the group consisting of methacryloyloxymethyltrimethylammonium chloride, acryloyloxymethyltrimethylammonium chloride diallyldimethylammonium chloride, methacrylamidopropyltrimethylammonium chloride, methacryloyloxymethylbenzyltrimethylammonium chloride and the hydrochloride salt of dimethylaminoethylmethacrylate.
- 20 39 The composition of claim 38 wherein the cationic moieties are derived from methacryloyloxymethyltrimethylammonium chloride.
- 25 40 A process for preparing the polymer of claims 1-39 comprising (a) providing a prepolymer comprising nonionic moieties derived from acrylamide, methacrylamide or both; anionic moieties derived from α,β -unsaturated carboxylic acids having from 3 to 6 carbon atoms and salts thereof and optionally cationic moieties derived from unsaturated monomers containing amino groups or quaternary ammonium groups and
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(b) contacting said prepolymer with dialdehyde selected from the group consisting of glyoxal, saturated dialdehydes having from 3 to 8 carbon atoms and unsaturated dialdehydes having from 3 to 8 carbon atoms resulting in crosslinked thermosetting resin containing aldehyde functionality

41 The process of claim 40 wherein the prepolymer is contacted with the dialdehyde at a pH of at least about 5.

42 The process of claim 41 wherein the prepolymer is contacted with the dialdehyde at a pH of at least about 8.

43. The process of claims 40-42 wherein the prepolymer is contacted with the dialdehyde at a pH of up to about 10

44 The process of claim 43 wherein the prepolymer is contacted with the dialdehyde at a pH of up to about 9.

45. The process of claims 40-44 wherein the prepolymer is contacted with the dialdehyde at a temperature of at least about 20°C

46. The process of claim 46 wherein the prepolymer is contacted with the dialdehyde at a temperature of at least about 25°C.

47 The process of claims 40-46 wherein the prepolymer is contacted with the dialdehyde at a temperature of up to about 80°C.

48 The process of claim 47 wherein the prepolymer is contacted with the dialdehyde at a temperature of up to about 50°C

49 The process of claims 40-48 wherein the prepolymer is contacted with the dialdehyde until the resulting resin has a Brookfield viscosity of at least about

50 cps as a 8.5% by weight aqueous solution

50. The process of claim 49 wherein the prepolymer is contacted with the dialdehyde until the resulting resin has a Brookfield viscosity of up to about 500 cps.

51 The process of claim 50 wherein the prepolymer is contacted with the dialdehyde until the resulting resin has a Brookfield viscosity of up to about 300 cps

52 The process of claim 51 wherein the prepolymer is contacted with dialdehyde until the resulting resin has a Brookfield viscosity of up to about 280 cps.

53. The process of claims 49-52 wherein the prepolymer is contacted with the dialdehyde until the resulting resin has a Brookfield viscosity of at least about 100 cps

54 The process of claim 53 wherein the prepolymer is contacted with dialdehyde until the resulting resin has a Brookfield viscosity of at least about 180 cps.

55. The process of claims 40-54 wherein the prepolymer is contacted with the dialdehyde until the resulting resin has a Brookfield viscosity of from about 150 to about 250 cps, and wherein the amount of dialdehyde is from about 0.2 to about 0.5 mole per mole of nonionic moiety in the prepolymer

56. The process of claims 40-55 wherein the prepolymer additionally comprises moieties derived from water soluble dihyal monomer

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57 The process of claims 40-56 wherein the prepolymer additionally comprises moieties derived from water soluble divinyl monomer selected from the group consisting of N,N'-methylenebisacrylamide ethyleneglycol dimethacrylate and ethyleneglycol diacrylate.

58. The process of claim 57 wherein water soluble divinyl monomer is N,N'-methylenebisacrylamide.

59 A process for making paper having improved dry strength and wet strength comprising:
(a) providing an aqueous suspension of pulp fibers;
(b) adding to the aqueous suspension at least one crosslinked thermosetting, water soluble polymer according to any of claims 1-39; and
(c) sheeting and drying the aqueous suspension to obtain paper having better dry strength and wet strength than paper that is substantially the same except that it does not contain said crosslinked, thermosetting polymer

60 A process for making paper having improved strength comprising:
(a) providing an aqueous suspension of pulp fibers;
(b) adding to the aqueous suspension (i) at least one crosslinked thermosetting polymer according to any of claims 1-39 and (ii) at least one cationic adjunct resin; and
(c) sheeting and drying the aqueous suspension to obtain paper having better dry strength and wet strength than paper that is substantially the same except that it does not contain said crosslinked thermosetting polymer

61 The process of claim 60 wherein the cationic adjunct resin is selected from the group consisting of polyaminopolyamide epichlorohydrin resin cationic starch polyamines polyamine epichlorohydrin resins and polyethylenimine.

62. The process of claims 60-61 wherein wherein the cationic adjunct resin is polyaminopolyamide epichlorohydrin resin.

63 Paper comprising at least one crosslinked thermosetting water soluble polymer according to any of claims 1-39

64 Paper comprising
(a) at least one crosslinked thermosetting water soluble polymer according to any of claims 1 -39 and
(b) at least one cationic adjunct resin

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

RADICACIÓN 2-88179

EDICTO No 18088

LA SECRETARÍA GENERAL AD-HOC
HACE SABER

Que esta Superintendencia profirió Resolución No 28192 de 29-OCT-2006. Que el contenido de la parte resolutive es como sigue: El Superintendente de Industria y Comercio

RESUELVE

ARTICULO PRIMERO Negar el privilegio de patente de invención para la solicitud correspondiente a "POLIMEROS QUE CONTIENEN ALDEHIDO COMO ADITIVOS DE

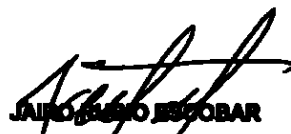
RESISTENCIA A LA HUMEDAD" que entró en fase nacional en virtud del Tratado de Cooperación en Materia de Patentes (PCT).

ARTICULO SEGUNDO Notificar personalmente el contenido de la presente resolución a la doctora Dña María Rodríguez D'Alaman, o a quien haga sus veces, en su calidad de apoderada de Sca Hygiene Products Zeist B.V entregándole copia de la misma advirtiéndole que contra ella procede el recurso de reposición Interpuesto ante el Superintendente de Industria y Comercio, al momento de la notificación o dentro de los 5 días hábiles siguientes a ella

NOTIFÍQUESE Y CÚMPLASE

Dada en Bogotá, D.C. a los 26 OCT 2006

EL SUPERINTENDENTE DE INDUSTRIA Y COMERCIO


JAIME LUIS ESCOBAR

Para notificar a los interesados se fija el presente EDICTO en lugar visible al público en la SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO por el término de (10) diez días hábiles contados a partir de las 8.30 a.m. de hoy

Secretaría General Ad-Hoc 20-NOV-2006 Este edicto se desliza hoy 01-DIC-2006 a las cinco (5:00 p.m.)
Secretaría General Ad-Hoc
EDICTO No 18088