

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D21F	A2	(11) International Publication Number: WO 97/11223 (43) International Publication Date: 27 March 1997 (27.03.97)
(21) International Application Number: PCT/US96/14305 (22) International Filing Date: 6 September 1996 (06.09.96) (30) Priority Data: 195 32 908.2 7 September 1995 (07.09.95) DE (71) Applicant (for all designated States except US): BETZDEARBORN INC. [US/US]; 4636 Somerton Road, Trevose, PA 19053-6783 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): KNIGHT, Paul [GB/GB]; 4 Bridge Gardens, Liverpool (GB). SHERIDAN, Geoffrey, Philip [GB/GB]; 32 East Lane, Sandiway, Northwich, Cheshire (GB). (74) Agents: VON NEIDA, Philip, H. et al.; BetzDearborn Inc., 4636 Somerton Road, Trevose, PA 19053-6783 (US).		(81) Designated States: AU, BR, CA, CN, CZ, JP, KR, MX, NO, NZ, PL, RU, TR, UA, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: METHOD OF CREPING A PAPER (57) Abstract The present invention relates to a method of creping a paper which comprises applying a water-soluble, non-thermosetting polyamidoamine or modified polyamidoamine directly to the surface of the creping drum in an apparatus for producing soft, lightweight paper web suitable for making sanitary paper products such as bathroom and facial tissue, paper towels and napkins.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

Method of Creping a Paper

This invention relates to a method of creping a paper which comprises applying a creping aid composition directly to the creping drum (also known as Yankee or MG cylinder) in an apparatus for producing soft, lightweight paper web suitable for making sanitary paper products such as bathroom and facial tissue, paper towels and napkins.

In the manufacture of creped tissue products the paper web is passed over a rotating drying cylinder (creping drum) and removed and creped from the surface of the drying cylinder by the use of a creping blade often called a doctor blade. It is usual to adhere the paper web to the rotating drying cylinder by the application of adhesive chemicals directly onto the drying cylinder itself, e.g. by spraying. Creping adhesive chemicals which are widely used for this application include polyvinyl alcohols, poly (ethylene vinyl acetate) copolymers, polyvinyl acetate, polyacrylates and thermosetting cationic polyamides of the wet strength resin type which comprise the water-soluble reaction products of an epihalohydrin and a polyamide containing secondary amino groups. These chemicals may be used alone or in combination with each other in order to achieve the desired effect. Generally, these chemicals are used with a release agent in order to control the adhesion of the web to the cylinder surface.

Most of these creping adhesive chemicals and particularly those polyamides of the wet strength resin type become crosslinked by the input of thermal energy and dehydration which occur on the surface of the drying cylinder. If this crosslinking is allowed to take place in an uncontrolled manner due to the variability

of temperature and moisture contents found during the tissue making process, then the coating will become uneven and lead to runnability problems. The control of adhesion becomes even more difficult when the drying cylinder is at elevated temperatures, e.g. 140 to 150°C, since the coatings become more crosslinked.

5 This results in harder, brittle and non-renewable coatings which will give reduced adhesion, reduced protection to both the creping blade and the cylinder and generally inferior tissue quality.

10 It has now been surprisingly found that the use of non-thermosetting polyamidoamines when used alone or in combination with other polymers will provide superior and more controlled adhesion. In other words, when these polyamidoamines are applied to the drying cylinder, the paper web adheres better and in a more

15 controlled uniform manner to the cylinder, even under variable and extreme conditions of cylinder temperature and sheet moisture content such that improved creping takes place.

Thus, the present invention provides a method of creping a paper

20 which comprises applying directly to the surface of the creping drum a water-soluble, non-thermosetting polyamidoamine or modified polyamidoamine.

Prior to the present invention only polyamidoamines or modified

25 polyamidoamines which are thermosetting (crosslinkable) and are generally used as wet strength agents in paper making have been used as adhesion-improving agents in paper creping by direct application to the drying cylinder (see above). In contrast according to the present invention polyamidoamines or modified

30 polyamidoamines are directly applied to the drying cylinder which are non-thermosetting (non-crosslinkable), i.e. they are essentially free of any functional groups which may result in crosslinking. Thus the polyamidoamines or modified polyamidoamines useful in the method of the present invention are non-cross-

35 linkable or already crosslinked.

The polyamidoamines useful in the method of the present invention are prepared by the condensation of aliphatic, cycloaliphatic, araliphatic or heterocyclic (preferably aliphatic) polyamines containing at least two amino groups, at least one of which must be a primary amino group, with a saturated or unsaturated aliphatic or aromatic (preferably aliphatic) dicarboxylic acid having from 4 to 10 carbon atoms or their functional equivalents. To increase their molecular weight it is preferred to react the polyamidoamines or modified polyamidoamines with a substoichiometric amount of crosslinking agent, i.e. a compound which is polyfunctional with respect to the amino groups contained in said condensation product. By using a substoichiometric amount it is secured that the crosslinking agent completely reacts with the polyamidoamine or the modified polyamidoamine so that no further crosslinking can take place on the surface of the drying cylinder under the elevated temperature conditions. In case of incomplete reaction of the crosslinking agent or use of more than substoichiometric amounts of crosslinking agent any functional groups which remain after crosslinking and can result in further crosslinking under the elevated temperature conditions on the surface of the drying cylinder can be "neutralized" by reacting the crosslinked polyamidoamine or modified polyamidoamine with suitable agents. When e.g. an epihalohydrin is used for crosslinking any remaining free epoxy functionality, which could lead to further crosslinking, can be removed by reacting the crosslinked polyamidoamine or modified polyamidoamine with an amine or ammonia.

Preferably the polyamidoamines useful in the method of the present invention are obtained by the condensation of a dicarboxylic acid and an amine containing two primary amino groups and at least one secondary amino group, e.g. diethylenetriamine. The condensation results in polyamidoamines which contain about 10 dicarboxylic acid derived units and the corresponding amount of amine derived units. While these polyamidoamines can be used as such, it is preferred to increase their molecular weight by

crosslinking. Accordingly the condensation product is reacted with a suitable crosslinking agent like epihalohydrin, preferably epichlorohydrin. However, in contrast to the preparation of conventional wet strength agents the crosslinking agent is used in substoichiometric amounts to make sure that no free epoxy functionality is included in the crosslinked polyamidoamine which would make it crosslinkable and thus thermosetting.

Indeed it is known to use crosslinked polyamidoamines or modified polyamidoamines which are useful in the present invention as retention aids in the paper making process. However, such retention aids have never been used as adhesion-improving agents in paper creping for direct application to the surface of the drying cylinder.

In the prior art many modifications of thermosetting polyamidoamines useful as wet strength agents or non-thermosetting polyamidoamines useful as retention aids are described. All these modified polyamidoamines are also useful in the method of the present invention as long as they are non-thermosetting, i.e. crosslinking of the polyamidoamines has been effected by the use of substoichiometric amounts of crosslinking agent or any functional crosslinkable groups remaining after crosslinking have been "neutralized" (see above). Examples for modifications of polyamidoamines which are within the scope of the present invention are disclosed in US-patent 4,501,862, DE-OS 33 23 732, US-patent 4,673,729, DE-PS 23 34 816 (including DE-OS 18 02 435 referred to in this document) and EP-patent 74 558. Preferred modified polyamido amines are disclosed in DE-OS 34 21 557, the disclosure of which is hereby included by reference. These are polyamidoaminepolyamines formed by transamidation of polyamidoamines with polyamines which are obtainable by reacting under substantially anhydrous conditions and at elevated temperatures of at least 150°C

35

(A) at least one water soluble or water dispersible polyamido-amine prepared by the condensation of

- 5 (a) at least one aliphatic, cycloaliphatic or araliphatic polyamine having at least two primary amino groups and at least one secondary or tertiary amino group or a mixture of said polyamine with at least one aliphatic, cycloaliphatic, araliphatic or heterocyclic polyamine containing two primary or two amino groups, each selected from primary or secondary amino groups, and
- 10 (b) at least one C₄-C₁₀ aliphatic dicarboxylic acid or an amide forming derivative thereof; with

- 15 (B) a water soluble low molecular weight polyamine selected from (a) poly(C₂-C₃)alkylenepolyamines having at least two primary amino groups and a molecular weight of from about 150 to 3,000 or (b) reaction products of a low molecular weight amine selected from ammonia, a monoalkyl monoamine, a C₂-C₃ polyalkylene diamine, triamine tetramine or pentamine with
- 20 a polyfunctional compound selected from epihalohydrin or alpha, omega-dihaloalkane, said amine and polyfunctional compound being reacted in amounts such that the ratio of amino nitrogen atom to polyfunctional compound is from about
- 25 0.5:1 to 30:1, the resultant reaction product has at least two primary amino groups and has a weight average molecular weight of from about 150 to 3,000.

and subsequently reacting the polymeric product of (A) and (B)

30 with

- (C) a compound which is polyfunctional with respect to amino groups contained in the product of (A) and (B).

35 The preparation of the polyamidoamines or modified polyamidoamines useful in the method of the present invention is well

known to a skilled man and described in detail in the prior art like the prior art documents cited above.

The molecular weight of the polyamidoamines or modified polyamidoamines useful in the method of the present invention depends on the structure of the specific polyamidoamine or modified polyamidoamine and the particular properties desired for a specific type of paper. In general the molecular weight is above 1,500. In case the molecular weight is increased by crosslinking, it has to be observed that the crosslinked polyamidoamine or modified polyamidoamine is still water-soluble.

The amounts of water-soluble, non-thermosetting polyamidoamines or modified polyamidoamines used in the method of the present invention also depend upon the nature of the tissue grade and softness characteristics to be obtained. In general from 0.05 to 0.3 grams of polymer is required per squaremetre of surface of the drying cylinder. Typically the polymers are applied as aqueous solutions (preferably by spraying) containing about 5 to 50, generally 5 to 20, e.g. about 10% by weight of polymer.

The non-thermosetting polyamidoamines or modified polyamidoamines can be used in combination with other conventional polymers to give improved results and more reliable processing. Typically between 5 to 30% by weight can be added to other polymers like polyvinyl alcohol to enhance adhesion and overall coating performance.

Further it is often advantageous to use the polyamidoamines or modified polyamidoamines useful in the method of the present invention together with usual release agents. These include imidazolines as well as oils such as mineral oils and other hydrophobic components including quaternary surfactants which have a softening effect on the paper web.

EXAMPLE

Different adhesion-improving agents were tested according to the following method:

(1) A 2 gm dry weight polymer film was prepared by heating in a 7 cm diameter aluminium dish at 85°C for 12 hours.

(2) A wet cotton strip (4 cm x 4 cm) was applied to the surface and pressed for 5 minutes using a 1 kg weight.

(3) Adhesiveness was measured by peeling off by hand at an angle of 180°. The degree of adhesiveness was recorded on a scale from 1 to 5 (1 being very adhesive and 5 being not adhesive at all).

(4) The film was then heated for a further 2 hours at 150°C and reassessed.

Product	Adhesiveness	Chemical Type
A*	3	Polyamide (wet strength)
B*	2	Polyvinyl acetate (mol wt 500,000 to 1,500,000)
C*	2	Polyvinyl alcohol
D*	4	Methacrylic/acrylamide (1:2)
E	1	Modified polyamidoamine according to DE-OS 34 21 557
F	1	C/E (4:1)

* Comparative examples

More importantly the films after subjection to 150°C remained uniform and flexible when products E and F were used whilst all others became brittle and broken.

Having thus described the invention, what we claim is:

1. A method of creping a paper comprising applying directly to the surface of a creping drum a water-soluble, non-thermosetting polyamidoamine or modified polyamidoamine.

2. The method as claimed in claim 1 characterized in that the water-soluble, non-thermosetting polyamidoamine or modified polyamidoamine is crosslinked with a compound which is polyfunctional with respect to amino groups contained in the polyamidoamine or modified polyamidoamine.

3. The method as claimed in claim 1 or 2 characterized in that the water-soluble, non-thermosetting polyamidoamine or modified polyamidoamine is crosslinked with an epihalohydrin.

4. The method as claimed in claim 3 characterized in that the epihalohydrin is epichlorohydrin.

5. The method as claimed in any one of the preceding claims characterized in that the water-soluble, non-thermosetting, modified polyamidoamine is a polyamidoamine polyamine formed by transamidation of polyamidoamine with a polyamine.

6. The method as claimed in any one of the preceding claims characterized in that the temperature of the creping drum is between about 100°C and about 150°C.

7. The method as claimed in any one of the preceding claims characterized in that the temperature of the creping drum is between about 130°C and about 150°C.

8. The method as claimed in any one of the preceding claims further characterized in that a release agent is applied to the surface of the creping drum.

9. The method as claimed in any one of the preceding claims further characterized in that an adhesion-improving agent is applied to the surface of the creping drum.