

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 1 258 561 A2**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**20.11.2002 Bulletin 2002/47**

(51) Int Cl.7: **D21H 21/20**

(21) Application number: **02445060.3**

(22) Date of filing: **21.05.2002**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**

Designated Extension States:

**AL LT LV MK RO SI**

• **Wallenius, Hans**

**459 32 Ljungskile (SE)**

• **Struck, Oliver**

**52349 Düren (DE)**

• **Gorzynski, Marek**

**52349 Düren (DE)**

(30) Priority: **18.05.2001 SE 0101810**

(71) Applicant: **SCA Hygiene Products AB**

**405 03 Göteborg (SE)**

(74) Representative: **Egeröd, Lisbeth et al**

**Ström & Gulliksson IP AB**

**Sjöporten 4**

**417 64 Göteborg (SE)**

(72) Inventors:

• **Sandberg, Sussan**

**439 35 Onsala (SE)**

(54) **Wet-strong tissue paper**

(57) A strong and soft tissue paper having a bulk between 2 and 8 cm<sup>3</sup>/g, containing a wet strength agent in the form of a nitrogen-containing polymer having hydrophobic side-chain substituents. The tissue paper before converting has a relative wet strength value (RWS) of at least 45%.

**EP 1 258 561 A2**

**Description****Technical field**

5 **[0001]** The present invention refers to a tissue paper having a bulk between 2 and 8 cm<sup>3</sup>/g, said tissue paper containing an amount of a wet strength agent and having a wet strength index of at least 1 Nm/g.

**Background of the invention**

10 **[0002]** In the papermaking art, wet strength agents like epichlorohydrin-based resins, for example polyaminoamide epichlorohydrin resins have been used for a long time to enhance the strength of paper. Such resins are disclosed in US 3,700,623 and US 3,772,076. The wet strength of a paper relates to its ability to maintain physical integrity and to resist tearing, bursting, and shredding under use, especially under wet conditions. A further important property of wet strengthened paper is the softness, especially for tissue paper or the like. The softness can be described, as the tactile sensation perceived when holding or rubbing a paper across the skin.

15 **[0003]** Although the above epichlorohydrin-based resins in some applications give adequate wet strength properties to paper including tissue paper, it would be desirable to be able to further improve the wet strength and softness properties for tissue paper.

**Object and most important features of the invention**

20 **[0004]** It is an object of the present invention to provide a wet-strong tissue paper having improved softness properties. This has been obtained by the fact that the tissue paper contains a wet strength agent in the form of a nitrogen-containing polymer having hydrophobic side-chain substituents and before converting has a relative wet strength value (RWS) of at least 45%.

25 **[0005]** The relative wet strength value (RWS) is defined as:  $RWS (\%) = WS/DS$  wherein WS = wet strength index and DS = dry strength index.

**[0006]** A preferred example of a nitrogen containing polymer is a polyamine or a polyaminoamide.

**[0007]** The hydrophobic side-chain substituents preferably comprise a hydrophobic chain having 6-40 carbons.

30 **[0008]** The tissue paper according to the invention contains an amount of wet strength agent from 1 to 4 % by weight, preferably between 1.2 to 3 % by weight.

**[0009]** In preferred embodiments the tissue paper before converting has a relative wet strength value (RWS) of at least 43%, preferably at least 45% and more preferably at least 50%. Preferably the relative wet strength value (RWS) is up to 60%.

35 **[0010]** The tissue paper may further contain an amount of a dry strength agent. Examples of preferred dry strength agents are carboxy alkyl polysaccharides, for example carboxy alkyl cellulose.

**[0011]** The tissue paper should preferably have a dry strength index of at least 5 Nm/g and no more than 10 Nm/g.

**[0012]** A tissue paper having the above characteristics is wet strong and soft and it also has a sufficient dry strength for handling in converting operations.

**Description of the invention**

**[0013]** Today the only way of creating a high wet strength is by one or more of the following methods:

- 45
- adding as much wet strength resin as possible;
  - using a high amount of refining energy;
  - adding dry strength chemicals.

50 **[0014]** This strategy leads to a high wet strength and a high dry strength, meaning that the dry strength is only a tool for improving wet strength. The dry strength level in tissue paper therefor usually is higher than necessary, which leads to a stiff and coarse paper.

55 **[0015]** It has according to the invention been found that a soft and wet strong tissue paper having a basis weight between 10 and 50 g/m<sup>2</sup>, a bulk between 2 and 8 cm<sup>3</sup>/g and a wet strength index of at least 1 Nm/g, can be obtained by the fact that the tissue paper contains a wet strength agent in the form of a nitrogen-containing polymer having hydrophobic side-chain substituents and by balancing the wet strength index and dry strength index of the paper so as to provide a relative wet strength index (RWS) of at least 45%, preferably at least 47% and more preferably at least 50%. The RWS value refers to the value before converting operations, such as embossing, gluing, lamination etc., since these may effect the properties of the paper.

**[0016]** Wet strength agents which increase the wet strength of tissue paper without increasing the dry strength are wet strength agents comprising a cationic nitrogen-containing polymer having hydrophobic side-chain substituents and a derivative of a crosslinker. The hydrophobic side-chain substituent may be saturated or unsaturated.

**[0017]** The cationic nitrogen-containing polymer has hydrophobic side-chain substituents and derivatives of a crosslinker attached to the nitrogen atoms of the polymer. The hydrophobic side-chain substituents may be saturated or unsaturated. Examples of suitable nitrogen-containing polymers include well-known available commercial products which may be prepared as described above or according to conventional methods known in the art. Examples of suitable nitrogen-containing polymers include polyaminoamides, alkyl polyamines, polyimines, and polyvinylamines. An example of a preferred crosslinker is epichlorhydrin.

**[0018]** Hydrophobic side-chain substituents are attached to the nitrogen atoms of the nitrogen-containing polymer. The term hydrophobic side-chain substituent is here meant to include hydrophobic groups containing e.g. hydrophobic linear or branched hydrocarbon chains which can be linked, e.g. via a hetero atom by a covalent bond, to a nitrogen atom of the nitrogen-containing polymer. Hydrophobic groups may also include cyclic chains including cyclic hydrocarbons. Combinations of linear, branched and cyclic hydrocarbons are also included in the concept of hydrophobic groups.

**[0019]** The hydrophobic group of the hydrophobic side-chain can contain up to 40 carbon atoms, preferably 6-40 carbon atoms, and most preferably 8-40 carbon atoms.

**[0020]** Such wet strength agents are disclosed in detail in the international patent application no. PCT/SE00/02233, the content of which is included herein as a reference.

**[0021]** The addition to tissue paper of wet strength agents in the form of the nitrogen-containing polymers having hydrophobic side-chain substituents will cause an increase of the wet strength index of the paper, due to the formation of covalent bonds between the cellulose molecules and the nitrogen-containing polymers. This is the same mechanism as in conventional wet strength agents. The addition of conventional wet strength agents will also increase the amount of hydrogen bond sites resulting in an increased dry strength. However due to the presence of the hydrophobic side-chain substituents in the wet strength agents used in the present invention the hydrogen bond sites will decrease. Since the dry strength of paper to a high degree is dependant on the amount of hydrogen bonds, a decrease of the hydrogen bonds will also result in a decrease of the dry strength of the paper.

**[0022]** Thus an increase of the wet strength index of the tissue paper is obtained, without increasing the dry strength index by adding the wet strength agents in the form of the nitrogen-containing polymers having hydrophobic side-chain substituents. In fact a decrease of the dry strength index may even be obtained.

**[0023]** Evaluation of the dry strength of the tissue paper was performed according to the standard method SCAN P 44:81. The wet strength was tested according to SCAN P 58:86. The tensile strength is presented as index values or geometrical mean values of machine and cross direction according to:

$$\sqrt{\text{MDxCD}} / \text{grammage Nm/g.}$$

**[0024]** The tissue paper should preferably contain the wet strength agent in an amount from 1 to 4% by weight, more preferably from 1.2 to 3% by weight. These values refer to the amount of wet strength agent adhering to the fibres and measured according to the so called total nitrogen method. This method is based on flash combustion and is called Dumas Total Nitrogen Analysis. The measuring instrument used is Carlo Erba Instrument NA 1500 supplied by CE Termo Quest. A manual is supplied together with the instrument.

**[0025]** The wet strength agent is preferably in the form of an aqueous dispersion and may be added to an aqueous cellulosic suspension containing the papermaking cellulosic fibers. The wet strength agent may also be added to the produced paper so as to provide a surface treatment of the paper.

**[0026]** The tissue paper should preferably have a dry strength index of at least 5 Nm/g in order to be handled in converting processes such as rolling, unrolling, cutting, embossing, lamination etc. An addition of a dry strength agent, such as a carboxy alkyl polysaccharide, for example carboxy alkyl cellulose, especially carboxy methyl cellulose (CMC), may be necessary in order to obtain a sufficient dry strength of the tissue paper. These dry strength agents are anionic and will contribute in adsorbing more of the cationic wet strength agent to the fibres. The dry strength index should preferably be no more than 10 Nm/g in order to keep the softness as high as possible.

**[0027]** The tissue paper may also contain further additives such as softening agents, absorption enhancing agents, fillers etc.

### **Examples**

**[0028]** Four different wet strength agents were produced according to Example 7 in the international patent applica-

tion no. PCT/SE00/02233. The wet strength agents were designated A, B, C and D, of which D were produced exactly as disclosed in Example 7 of PCT/SE00/02233. while the other three were produced as disclosed but with the modification that varying amounts of dodecyl acrylate were used.

### Test 1

**[0029]** Tissue paper having a basis weight of about 25 g/m<sup>2</sup> and a bulk at 2kPa of about 6-6.5 cm<sup>3</sup>/g was produced on a full scale paper machine. The pulp used was a mixture of 70% by weight CTMP (chemothermomechanical pulp) and 30% by weight sulphate softwood pulp. Varying amounts of the wet strength agents A and B were added. The results obtained are presented in Table 1 below.

Table 1

Wet strength agent	Added amount (kg/t pulp fibers)	Dry strength index (Nm/g)	Wet strength index (Nm/g)	Rel wet strength index RWS (%)
A	7	10,2	3,4	33
A	10	10,1	4,0	40
A	15	8,7	3,8	44
A	20	7,9	4,1	52
B	7	8,4	3,6	43
B	10	8,8	3,7	42
B	15	8,3	4,0	48
B	20	9,0	4,1	46

### Test 2

**[0030]** Tissue paper having a basis weight of about 40 g/m<sup>2</sup> and a bulk at 2kPa of about 5 cm<sup>3</sup>/g was produced on a full scale paper machine. The pulp used was recycled newsprint mixed. The wet strength agent C was used in combination with a dry strength agent in the form of CMC (carboxy methyl cellulose). The results obtained are presented in Table 2 below.

Table 2

Wet strength agent	Added amount Wet strength agent (kg/t pulp fibers)	Added amount CMC (dry strength agent) (kg/t pulp fibers)	Dry strength index (Nm/g)	Wet strength index (Nm/g)	Rel. wet strength RWS (%)
C	16	3	12,9	4,7	33
C	18	3	13,5	4,8	31
C	25	3	-	-	50

### Test 3

**[0031]** Tissue paper having a basis weight of about 26,5 g/m<sup>2</sup> and a bulk at 2kPa of about 2,5 cm<sup>3</sup>/g was produced on a full scale paper machine. The pulp used was recycled newsprint mixed. The wet strength agent D was used in combination with a dry strength agent in the form of CMC (carboxy methyl cellulose). The results obtained are presented in Table 3 below.

Table 3

Wet strength agent	Added amount Wet strength agent (kg/t pulp fibers)	Added amount CMC (dry strength agent) (kg/t pulp fibers)	Dry strength index (Nm/g)	Wet strength index (Nm/g)	Rel. wet strength RWS (%)
D	20	2,3	9,3	4,2	46
D	20	3,3	8,8	5,0	57
D	15	2	8,0	3,8	48
D	15	3	10,6	4,1	39

**[0032]** The above tests show that it is possible to achieve relative wet strength values (RWS) of 45% and higher by using relatively high amounts of the wet strength agents containing hydrophobic side-chain substituents. The wet strength agent may advantageously be combined with an anionic dry strength agent in order to adsorb more of the cationic wet strength agent to the fibres.

### Claims

1. Tissue paper having a bulk between 2 and 8 cm<sup>3</sup>/g, said tissue paper containing an amount of a wet strength agent and having a wet strength index of at least 1 Nm/g,  
**characterized in**  
**that** the tissue paper contains a wet strength agent in the form of a nitrogen-containing polymer having hydrophobic side-chain substituents and before converting has a relative wet strength value (RWS) of at least 45%.
2. Tissue paper as claimed in claim 1,  
**characterized in**  
**that** the nitrogen containing polymer is a polyamine or a polyaminoamide.
3. Tissue paper as claimed in claim 2,  
**characterized in**  
**that** the hydrophobic side-chain substituents comprise a hydrophobic chain having 6-40 carbons.
4. Tissue paper as claimed in any of the preceding claims,  
**characterized in**  
**that** it contains a wet strength agent in an amount from 1 to 4% by weight, preferably from 1.2 to 3% by weight.
5. Tissue paper as claimed in any of the preceding claims,  
**characterized in**  
**that** it before converting has a relative wet strength value (RWS) of at least 47%., preferably at least 50%.
6. Tissue paper as claimed in any of the preceding claims,  
**characterized in**  
**that** it before converting has a relative wet strength value (RWS) of up to 60%.
7. Tissue paper as claimed in any of the preceding claims,  
**characterized in**  
**that** it also contains an amount of a dry strength agent.
8. Tissue paper as claimed in claim 7,  
**characterized in**  
**that** the dry strength agent is a carboxy alkyl polysaccharide.
9. Tissue paper as claimed in claim 8

**characterized in**

**that** the carboxy alkyl polysaccharide is a carboxy alkyl cellulose.

10. Tissue paper as claimed in any of the preceding claims,

**characterized in**

**that** it has a dry strength index of at least 5 Nm/g.

11. Tissue paper as claimed in claim 10,

**characterized in**

**that** it has a dry strength index of no more than 10 Nm/g.