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(54) **PAPER PRODUCT AND METHOD FOR PRODUCTION THEREOF AND USE THEREOF**

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(57) **ABSTRACT**

The invention relates to a method for the production of flat paper products with increased relative wet tensile strength and softness from a pulp suspension in which a block copolymer is added to the pulp suspension and/or the paper product is treated during production thereof or subsequently with the block copolymer. The invention likewise relates to a paper product produced in this manner. Paper products of this type are used in particular as tissue products.

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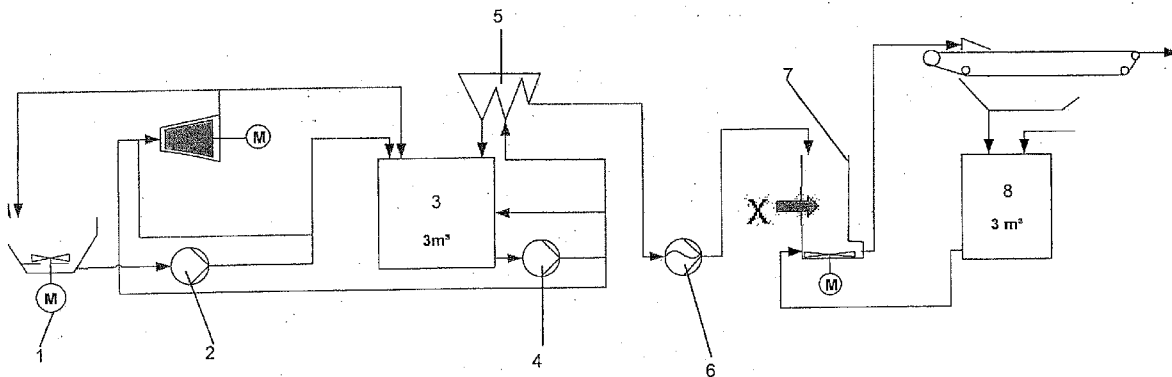
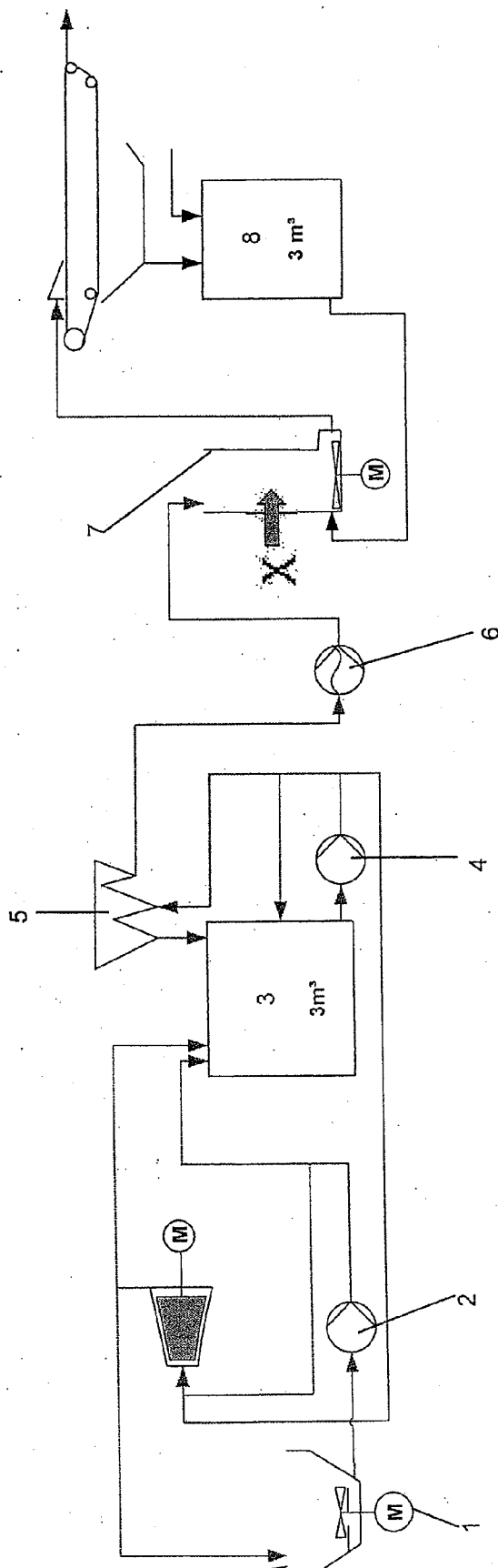


Fig. 1



**PAPER PRODUCT AND METHOD FOR  
PRODUCTION THEREOF AND USE  
THEREOF**

**[0001]** The invention relates to a method for the production of flat paper products with increased relative wet tensile strength and softness from a pulp suspension in which a block copolymer is added to the pulp suspension and/or the paper product is treated during production thereof or subsequently with the block copolymer. The invention likewise relates to a paper product produced in this manner. Paper products of this type are used in particular as tissue products.

**[0002]** The cellulose fibres used in paper production are negatively charged. For a simple and economical paper production method known to the person skilled in the art, it is most favourable if treatment chemicals, e.g. wet-strength agents, are metered directly into the aqueous pulp suspension (pulp) with which then the paper is produced. The technical tissue production process is explained subsequently in brief. The aqueous cellulose pulp is then placed on the machine wires in the technical process, formed there and partially dewatered and subsequently passes into the drying part of the tissue machine. The so-called Yankee cylinder has a surface temperature of approx. 140° C., above that there is gas drying with hood temperatures around approx. 450° C. During an extremely short contact time of a few milliseconds on the cylinder, the curing process of the wet-strength agents begins, said process being terminated during the subsequent storage of the finished tissue web (so-called "subsequent ripening").

**[0003]** Since the cellulose fibres used in paper production are negatively charged, a potential wet-strength agent must be cationic (positively charged) and water-soluble or water-dispersible in order that it can adhere to the cellulose fibre in the aqueous pulp medium during application. The use of conventional wet-strength agents which are based on epichlorohydrin or on polyacrylamide in the paper or tissue industry is regarded as the present state of the art and science. These wet-strength agents are normally added, in the case of household tissues, in quantities of 8 to 10 kg/tonne. The cellulose fibres of the paper or tissue hold together in the dry state in the network of a sheet by means of fibre-fibre contact points which are based on van der Waals' or hydrogen bonds. These bonds are very water-sensitive, i.e. the wetter the tissue becomes the looser these bonds become. In order now to be able to produce so-called wet-strength papers, such as e.g. kitchen or household towels or other toilet tissues, wet-strength agents are added which have the task of forming bonds which are resistant at least temporarily to water. According to the present state of the art, various chemically-based polymer wet-strength agents are available in paper or tissue production, which are described for example in "Paper-making Chemistry" (book 4, ISBN: 9789525216042, Editor: Leo Neimo, published in cooperation with the Finnish Paper Engineers' Association and TAPPI, pp. 288-301). There are used predominantly melamine formaldehyde resins (MF), as described for example in U.S. Pat. No. 4,461,858, and cationic polymers based on polyamide-epichlorohydrin and polyamidine-epichlorohydrin (PAE), as described for example in U.S. Pat. No. 2,926,116, U.S. Pat. No. 2,926,154, U.S. Pat. No. 3,733,290, U.S. Pat. No. 4,566,943, U.S. Pat. No. 4,605,702.

**[0004]** It is disadvantageous with the above-mentioned wet-strength agents, on the one hand, that the treated tissue

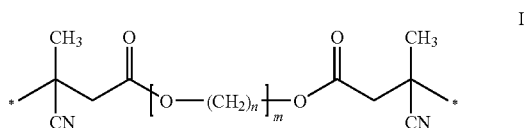
does in fact have increased wet strength but this has the consequence of reduced softness. This must then be achieved by an additional mechanical treatment of the tissue. A further disadvantage of PAEs is the production-related content of organic halogen compounds. WO 00/40639 describes a PAE-based wet-strength agent with a low-content of organically bonded chlorine. Furthermore, water-dispersible wet-strength agents based on polyisocyanate are described in DE 196 40 205 A1, which are obtained by conversion of the initial components polyisocyanate, polyalkyleneoxide polyether alcohol of a quaternised aminopolyalkyleneoxide polyether alcohol and also possibly further aids and supplements.

**[0005]** Furthermore, it is known from DE 698 14 359 T2 that e.g. polyethylene imine belongs to the temporary wet-strength agents. Furthermore it is known to the person skilled in the art that polymers which have a low glass-transition point (room temperature or below) have soft properties. DE 689 16 860 describes in detail a method for the production of absorbent structures in which the absorbing structures are produced from mixed paper raw materials, one of which is treated with a latex with an elastomer core. The softness is hereby achieved by the soft rubber latex. In order that the lattices adhere to the cellulose fibre in the wet method, these have a polymer shell based on oleyl-polyethoxylate which carries a quaternary functional (trimethyl)-ammonium group at the terminal end of the ethoxylate chain. However it is disadvantageous with this method that the soft lattices are of a hydrophobic (=water-repellent) nature and hence negatively affect the absorption power of the paper produced therefrom in the case of a single "one batch" application. Therefore the operation must take place with this method with different pulps, only one being treated with the latex. In a further step, the pulp suspension treated with latex is mixed with an untreated pulp in order thus to achieve the water-absorbent effect of the paper. WO 96/333 10 describes a method for the production of soft-creped tissue which is obtained by a specially controlled production process, mainly by mechanical treatment.

**[0006]** Starting herefrom, it was the object of the present invention to overcome the problems known from the state of the art. It was therefore an aim to increase the wet strength of paper products without having to accept negative effects on the softness of the products. Likewise the absorbability of the paper product should not be negatively influenced. A further object of the present invention resided in making possible an application which is as simple as possible of the pre-treatment chemicals in the cellulose pulp and in providing an ecologically safe treatment chemical.

**[0007]** This object is achieved by the method having the features of claim 1 and also by the paper product having the features of claim 14. The further dependent claims represent advantageous developments. A use according to the invention is cited in claim 29.

**[0008]** According to the invention, a method for the production of flat paper products with increased relative wet tensile strength and softness from a pulp suspension is provided, in which a block copolymer with the blocks A and B is added to the pulp suspension and/or the paper product is treated during production thereof or subsequently with the block copolymer. It is a particular feature of the present invention that A is a segment with at least one connectable group for cellulose and has a weight average molecular weight in the range of 300 to 3,000,000 g/mol and B represents a polyalkylene glycol segment of the general formula I



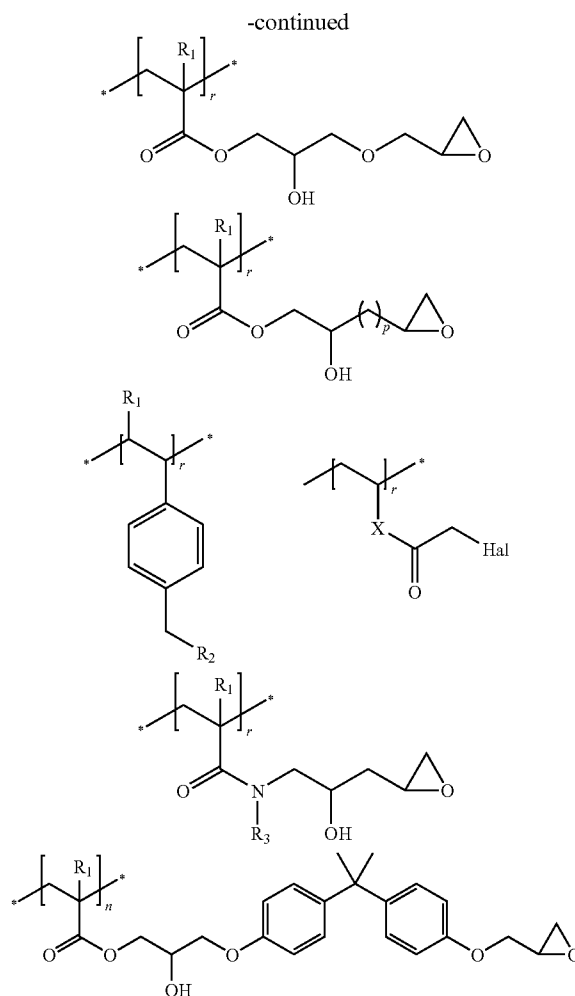
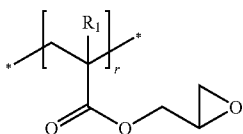
with  $n=2$  to  $6$  and  $m$  being chosen such that the weight average molecular weight of segment B is in the range of  $400$  to  $50,000$  g/mol.

**[0009]** A simple application in the production of paper products, ideally in the aqueous pulp suspension, requires that the polymer systems used for the treatment are water-soluble or water-dispersible. These requirements were able to be fulfilled by the application of copolymer systems which are constructed from soft segments, i.e. flexible polymer blocks with low  $T_g$ , and adhesive segments, i.e. polymer blocks with a cationic structure, also in combination with chemically reactive groups. Adhesive segments are required in order to achieve adhesion of the chemicals to the charged pulp fibre, whilst the reactive segments, during the further processing process by a chemical reaction, effect a covalent crosslinking of the chemical with the fibre and also the fibres to each other and hence increase the wet tensile strength of the paper product. At the same time, the soft segment effects elasticity between the fibres so that the increase in wet tensile strength is not achieved at the expense of softness, as is the case with the systems known to date from the state of the art.

**[0010]** Surprisingly, it was now able to be established that the block copolymers provided according to the invention can be applied in the simplest manner, the production thereof also being possible in the simplest manner. The synthesis strategy resides in converting a precursor compound which contains soft polyalkylene glycol segments in a simple manner to form block copolymers by copolymerisation with suitable monomers. A particularly simple synthesis is hereby possible by the use of PEG azo initiators which degrade thermally into polymer PEG biradicals and hence leads to the formation of for example A-B-A block copolymers which are particularly preferred.

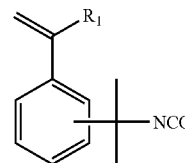
**[0011]** The production of such macro-azo initiators (MAI) is described for example in Takahashi et al., Journal of Polymer Science, Part A, Polymer Chemistry, Vol. 35, 69-76 (1997) or also in Smith "Die Makromolekulare Chemie 1003", 301-303 (1967) and state of the art.

**[0012]** Segment A is selected preferably from the group consisting of glycidyl, benzylhalogenide,  $\alpha$ -halogenacyl, isocyanate, anhydride, azide, tosylate and mesylate. A few representatives are cited subsequently by way of example.



with  $p=1$  to  $12$ ,  $r=3$  to  $3,000$ ,  $R_1=H$  or  $CH_3$  and  $R_2=$ halogen, tosylate or mesylate,  $R_3=H$ , if  $R_1=CH_3$  and  $R_3=CH_3$ , if  $R_1=H$  and also  $X=O$  or  $NR_4$  with  $R_4=H$  or  $CH_3$ .

**[0013]** As a further variant according to the invention, segment A can be formed as a homopolymer from a monomer of the general formula II,



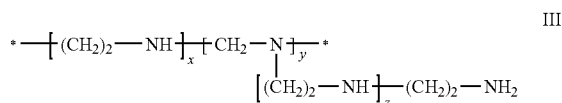
wherein  $R_1=H$ . If  $R_1=CH_3$ , then the monomer of the general formula II can be copolymerised together with at least one further radically polymerisable comonomer selected from the group consisting of aliphatic and aromatic methacrylic acid esters, aliphatic and aromatic acrylamides and styrene which can also be substituted with  $NR_5$ ,  $OR_5$  and/or  $COOR_5$  with  $R_5=C_1-C_{12}$  alkyl or aryl. This is likewise possible for  $R_1=H$ .

The aromatic substituent in formula II can be disposed in ortho-, meta- or para-position.

**[0014]** Basically all methacrylic acid esters, acrylamides and styrenes which are substituted with the remaining radicals, in the case of which R<sub>5</sub> is not hydrogen, can be used here.

**[0015]** The weight average molecular weight of segment A is preferably in the range of 1,000 to 1,000,000 g/mol, whilst the weight average molecular weight of segment B is preferably in the range of 400 to 10,000 g/mol.

**[0016]** In a further preferred variant, the block copolymer can in addition be coupled to a polymer amine, in particular a polyethylene imine and/or a polyvinyl amine. A polyethylene segment of the general formula III



which is coupled with formation of a graft copolymer, x, y and z being chosen such that the weight average molecular weight is in the range of 500 to 3,000,000 g/mol, in particular 500 to 1,000,000 g/mol, is particularly preferred.

**[0017]** Another particularly preferred variant concerns coupling to poly-4-vinylpyridine.

**[0018]** In the case of the previously described coupling to a polymer amine, a graft copolymer is present which has a backbone made of the polymer amine and grafts made of the block copolymer. However, the converse variant is also possible in that the graft copolymer comprises a backbone made of the block copolymer and grafts made of the polymer amine.

**[0019]** The polyalkylene glycol is preferably polyethylene glycol.

**[0020]** According to the invention, a paper product with increased relative wet tensile strength and softness is likewise provided, which contains cellulose fibres which are crosslinked with a block copolymer with the blocks A and B of the previously described structure.

**[0021]** Paper products of this type are used in particular as tissue products.

**[0022]** The subject according to the invention is intended to be explained in more detail with reference to the subsequent FIGURE and examples without wishing to restrict said subject to the special embodiments shown here.

**[0023]** FIG. 1 shows, with reference to a schematic representation, the course of the production process according to the invention for paper products.

#### EXAMPLE 1

Synthesis of poly(glycidyl methacrylate)-block-poly(ethylene glycol)-block-poly(glycidyl methacrylate)

**[0024]** The macro-azo initiators listed in Table 1 were used.

TABLE 1

macro-azo initiator	molecular weight [g/mol]	molecular weight of the segment	mol azo group per 1 g
VPE-0201	15,000-30,000	2,000	0.45 mmol/g (1/14)

TABLE 1-continued

macro-azo initiator	molecular weight [g/mol]	molecular weight of the segment	mol azo group per 1 g
VPE-0401	25,000-40,000	4,000	0.24 mmol/g (1/25)

#### EXAMPLE 1.1

Triblock Copolymer Made of VPE-0401 and Glycidyl Methacrylate (1:1)

**[0025]** Macro-azo initiator VPE-0401 [WAKO], 20 g 1,4-dioxane [ACROS, p.a., stabilised] and subsequently 7.64 g glycidyl methacrylate [ALDRICH, 97%] are weighed into a Schlenk flask. After degassing with N<sub>2</sub>, the flask is sealed with a septum and the reaction solution is brought to polymerisation with agitation on the oil bath at 85° C. overnight. After cooling to room temperature, the product is converted with agitation into diethylether (glycidyl methacrylate is soluble in Et<sub>2</sub>O, the product in dioxane). The polymer is freed of the remaining solvent in Petri dishes in the vacuum drying cabinet over P<sub>2</sub>O<sub>5</sub>. The yield is 93% of the theoretical.

#### EXAMPLE 1.2

Triblock Copolymer Made of VPE-0201 and Glycidyl Methacrylate (1:1)

**[0026]** 8.0 g macro-azo initiator VPE-0201 [WAKO], 20 g 1,4-dioxane [ACROS, p.a., stabilised] and subsequently 8.0 g glycidyl methacrylate [ALDRICH, 97%] are weighed into a Schlenk flask. After degassing with N<sub>2</sub>, the flask is sealed with a septum and the reaction solution is brought to polymerisation with agitation on the oil bath at 85° C. overnight. After cooling to room temperature, the product is converted with agitation into diethylether (glycidyl methacrylate is soluble in Et<sub>2</sub>O, the product in dioxane). The polymer is freed of the solvent in Petri dishes in the drying cabinet over P<sub>2</sub>O<sub>5</sub>. The yield is 93% of the theoretical.

#### EXAMPLE 1.3

Production of Solutions for the Sheet Formation Tests

**[0027]** Production of 1% Aqueous Active Substance Dispersions

**[0028]** A specific quantity of polymer (see Table 2) was dissolved in 4.5 g dioxane (material see Table 2).

**[0029]** 45 g water were then added to this solution with intensive agitation. Thereafter, the corresponding quantity of polyethylene imine (PEI) was added immediately with agitation. The dispersion was agitated for a further 30 minutes and then was ready for use.

**[0030]** The individual batches are listed in Table 2.

TABLE 2

OM 17 - A1	triblock copolymer PGLMA-PEG-PGLMA OM 17	0.40 g polymer 0.1 g PEI 4.5 g dioxane
OM 18 - B1	triblock copolymer PGLMA-PEG-PGLMA OM 18	0.40 g polymer 0.1 g PEI 4.5 g dioxane

TABLE 2-continued

OM 17 - C1	triblock copolymer PGLMA-PEG-PGLMA OM 17	0.35 g polymer 0.15 g PEI 4.5 g dioxane
OM 18 - D1	triblock copolymer PGLMA-PEG-PGLMA OM 18	0.35 g polymer 0.15 g PEI 4.5 g dioxane
OM 17 - E1	triblock copolymer PGLMA-PEG-PGLMA OM 17	0.30 g polymer 0.2 g PEI 4.5 g dioxane
OM 18 - F1	triblock copolymer PGLMA-PEG-PGLMA	0.30 g polymer 0.2 g PEI

TABLE 2-continued

OM 17 - G1	OM 18 triblock copolymer PGLMA-PEG-PGLMA	4.5 g dioxane 0.25 g polymer 0.25 g PEI
OM 18 - H1	OM 17 triblock copolymer PGLMA-PEG-PGLMA OM 18	4.5 g dioxane 0.25 g polymer 0.25 g PEI 4.5 g dioxane

**[0031]** Furthermore, solutions made of PEI and Servamine were produced for comparison.

**[0032]** The results are presented in Table 3.

TABLE 3

chemicals kg/t pulp	basis weight [g/m <sup>2</sup> ]	thickness [mm]	permeability [ml/min]	tensile strength (dry) [N]	tensile strength (wet) [N]	breaking length (dry) [m]	breaking length (wet) [m]	wet/dry [%]	tensile strength [mNm/m]
0	79.3	0.12	1450	50.3	0.6	4311	51	1.2	1350
1.5 Servamine KZC 14	80.7	0.12	1300	49.7	5.1	4185	429	10.3	1350
1.5 Servamine KZC 20	80.3	0.12	1250	49.8	3.9	4215	330	7.8	1450
3 A: triblock copolymer OM17; 0.40 g polymer 0.10 g PEI	80.3	0.12	1600	46.6	2.3	3944	195	4.9	1300
9 A: triblock copolymer OM17; 0.40 g polymer 0.10 g PEI	79.7	0.12	1750	47.8	6.2	4076	529	13.0	1300
3 B: triblock copolymer OM18; 0.40 g polymer 0.10 g PEI	79.7	0.12	1500	47.0	1.9	4008	162	4.0	1400
9 B: triblock copolymer OM18; 0.40 g polymer 0.15 g PEI	80.3	0.12	1700	49.1	5.5	4155	465	11.2	1350
3 C: triblock copolymer OM17; 0.35 g polymer 0.15 g PEI	80.7	0.13	1500	47.5	3.1	4000	261	6.5	1250
9 C: triblock copolymer OM17; 0.35 g polymer 0.15 g PEI	80.3	0.13	1750	51.6	7.4	4367	626	14.3	1450
3 D: triblock copolymer OM18; 0.35 g polymer 0.15 g PEI	79.3	0.12	1650	45.2	2.5	3874	214	5.5	1350
9 D: triblock copolymer OM18; 0.35 g polymer 0.15 g PEI	80.7	0.13	1800	52.6	6.4	4429	539	12.2	1500
3 E: triblock copolymer OM17; 0.30 g polymer 0.20 g PEI	81.3	0.13	1400	49.5	3.4	4138	284	6.9	1400
9 E: triblock copolymer OM17; 0.30 g polymer 0.20 g PEI	81.0	0.12	1450	59.0	8.4	4950	705	14.2	1300
3 F: triblock copolymer OM17; 0.30 g polymer 0.20 g PEI	80.0	0.12	1450	50.3	2.3	4273	195	4.6	1250
9 F: triblock copolymer OM18; 0.30 g polymer 0.20 g PEI	80.7	0.12	1550	59.5	9.5	5011	800	16.0	1350
3 G: triblock copolymer OM17; 0.25 g polymer 0.25 g PEI	80.7	0.12	1250	49.9	3.1	4202	261	6.2	1350
9 G: triblock copolymer OM17; 0.25 g polymer 0.25 g PEI	81.3	0.12	1400	61.2	9.7	5116	811	15.8	1400
3 H: triblock copolymer OM18; 0.25 g polymer 0.25 g PEI	80.7	0.12	1350	51.3	3.0	4320	253	5.8	1400
9 H: triblock copolymer OM18; 0.25 g polymer 0.25 g PEI	80.0	0.12	1450	59.3	10.8	5037	917	18.2	1350
3 graft copolymer OM20 (high-molecular polyethylene imine)	81.7	0.13	1300	48.3	1.6	4018	133	3.3	1400
9 graft copolymer OM20 (high-molecular polyethylene imine)	80.3	0.12	1350	60.6	9.2	5129	779	15.2	1300
3 graft copolymer OM21 (high-molecular polyethylene imine)	80.0	0.12	1350	54.5	2.6	4630	221	4.8	1300
9 graft copolymer OM21 (high-molecular polyethylene imine)	79.7	0.12	1300	61.9	9.1	5278	776	14.7	1350

**[0033]** The preparation of the solutions can also be effected for example such that the PEI is added firstly to the polymer dioxane solution and the latter is placed in water subsequently with agitation or water is added to the dioxane solution with agitation.

#### EXAMPLE 2

Synthesis of poly(glycidyl methacrylate)-block-poly(ethylene glycol)-block-poly(glycidyl methacrylate)

**[0034]** The macro-azo initiators listed in Table 4 were used.

TABLE 4

macro-azo initiator	molecular weight [g/mol]	molecular weight of the segment	mol azo group per 1 g
VPE-0201	15,000-30,000	2,000	0.45 mmol/g (1/14)
VPE-0401	25,000-40,000	4,000	0.24 mmol/g (1/25)

**[0035]** 20% solution of triblock copolymer (poly(glycidyl methacrylate)-block-poly(ethylene glycol)-block-poly(glycidyl methacrylate)) in 1,4-dioxane

**[0036]** 280.0 g macro-azo initiator (50.0 g VPE-0401 [WAKO]+230.0 g VPE-0201 [WAKO]) are firstly mixed well and then distributed equally to three 1 l flasks. In total 325 g glycidyl methacrylate [ALDRICH, 97%] are added to respectively one third (93.3 g). With N<sub>2</sub> introduction, 250 ml 1,4-dioxane [ACROS, p.a., stabilised] are added per flask.

**[0037]** These reaction solutions are brought to polymerisation with agitation on the oil bath at 80° C. overnight. After cooling to room temperature, all the reaction solutions are combined and diluted with 1,4-dioxane to 3000 g in order to obtain a 20% solution. They are filled into 2 bottles (respectively 1.5 kg) with information about the dry content. The dry content is determined with drying scales [Sartorius moisture analyser] (3 h/120° C.):

**[0038]** solids content<sub>1</sub>=20%

**[0039]** solids content<sub>2</sub>=20%

**[0040]** Production of the Aqueous Solutions:

**[0041]** High-molecular polyethylene imine (PEI) (Aldrich (Best.-no. 181978, CAS [25987-06-8]) Mw ~75,000, Mn ~60,000, 50% aqueous solution) was used, which was diluted with water before the beginning of the test to a 25% solution.

#### EXAMPLE 2.1

Variant 1:1 (Material Copolymer for PEI)

**[0042]** Production of a 0.5% solution:

**[0043]** 1.5 kg of the approx. 20% solution are added together to 1.2 kg of a 25% aqueous PEI solution with agitation and diluted with 117.2 kg water with rapid agitation (30 min) to form a 0.5% solution.

#### EXAMPLE 2.2

Variant 1:1.3

**[0044]** 1.3 kg of the approx. 20% solution are added together to 1.387 kg of a 25% aqueous PEI solution with agitation and diluted with 118.68 kg water with rapid agitation (30 min) to form a 0.5% solution.

**[0045]** The solutions produced under a) and b) are used immediately and metered in within 7 h.

#### EXAMPLE 3

Paper Production with the Solutions Produced in Example 2.1 and 2.2.

**[0046]** The solutions produced in example 2.1 and 2.2 were metered in at position X so that different active substance concentrations per tonne of produced paper could be set. The paper production is represented schematically in FIG. 1.

**[0047]** Pulp used:

**[0048]** Grapho Celeste TCF tissue, SCA Hygiene Products AB, Östrand, Sweden

**[0049]** Degree of beating: 13 SR unbeaten, 18 SR beaten.

**[0050]** Machine Parameters:

**[0051]** Operating width: 0.5 m

**[0052]** Running speed: 20 m/min

**[0053]** Differential speed forming wire: TAD wire: -12%

**[0054]** Drying method: UCTAD (uncreped through air dried)

**[0055]** Temperature throughflow air: approx. 100° C.

**[0056]** The pulp is delivered in bales. The corresponding quantity respectively of pulp sheets was removed in order to obtain a pulp suspension with a consistency of approx. 3%. For this purpose, approx. 44 sheets were beaten in 800 l water for 20 minutes in the pulper. The degree of beating of the beaten suspension was 13 SR. Subsequently, the pulp suspension was beaten with a recirculating beating until a degree of beating of 18 SR was achieved. A flat cone refiner was used as beating unit.

**[0057]** After conclusion of the beating, the pulp suspension was diluted in the pulper 1 to a consistency of 2.4% and was subsequently transferred into the machine chest 3. From the machine chest, the pulp suspension is pumped into the stock level boxes 5 with a pump 4. The required quantity of pulp suspension is pumped via a monopump 6 into the recipient vessel 7 (Fluffer, HBX-pump). The excess proportion of stock suspension runs back into the machine chest 3. Deposition of the fibres is prevented by the constant movement in the machine chest 3.

**[0058]** The recipient vessel 7 is a small container which is equipped with an agitator. The stock suspension is forced into the headbox by the movement which is produced. In order to obtain good formation, the stock suspension is diluted to a consistency of approx. 0.5%. Backwater 8 which is formed during the dewatering in the forming zone is used as diluting water.

**[0059]** Because of the high turbulences and the low consistency in the recipient vessel, the latter was selected as metering point for the chemicals. The dewatering of the pulp suspension is effected on a long wire paper machine by means of wire table, foils and vacuum boxes. From the forming wire, the paper web is transferred through a vacuum box to the TAD wire, the TAD wire having a speed which is less by 12%. The paper web located on the TAD wire is moved over a through-flow drying cylinder. Here hot air at approx. 100° C. is blown through the paper web and the wire so that a final wetness of 5% can be set when rolling up.

**[0060]** The thus produced raw materials can be processed on processing lines to form single or multilayer kitchen towels.

[0061] The thereby achieved results are represented in Table 5.

TABLE 5

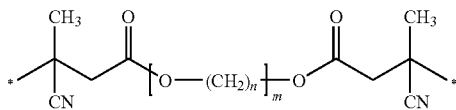
number of layers		6 kg/t variant a	6 kg/t variant b	9 kg/t variant c	9 kg/t variant d
basis weight	g/m <sup>2</sup>	22.5	21.5	22.1	21.8
thickness	μm	552	555	565	573
tensile strength	N/m	417.5	316.7	477.5	494.3
md					
tensile strength cd	N/m	191.9	165.1	162.8	153.0
stretch md	%	14	12	14	15
stretch cd	%	5	5	5	5
tensile strength	N/m	52.1	43.2	69.7	61.3
md (wet)					
tensile strength	N/m	24.4	21.3	24.3	24.3
cd (wet)					
rel. tensile strength md	%	12	14	15	12
rel. tensile strength cd	%	13	13	15	16

The measuring values mentioned in the table were determined according to the following methods:  
 basis weight: DIN EN ISO 12625-6  
 thickness: DIN EN ISO 12625-3  
 dry tensile strength md machine direction: DIN EN ISO 12625-4  
 dry tensile strength cd cross direction: DIN EN ISO 12625-4  
 stretch md machine direction: DIN EN ISO 12625-4  
 stretch cd cross direction: DIN EN ISO 12625-4  
 wet tensile strength md machine direction: DIN EN ISO 12625-5  
 wet tensile strength cd cross direction: DIN EN ISO 12625-5  
 relative wet tensile strength = wet tensile strength/dry tensile strength

1. A method for the production of flat paper products with increased relative wet tensile strength and softness from a pulp suspension in which a block copolymer with the blocks A and B is added to the pulp suspension and/or the paper product is treated during production thereof or subsequently with the block copolymer,

wherein

A is a segment with at least one connectable group for cellulose and has a weight average molecular weight in the range of 300 to 3,000,000 g/mol and B represents a polyalkylene glycol segment of the general formula I

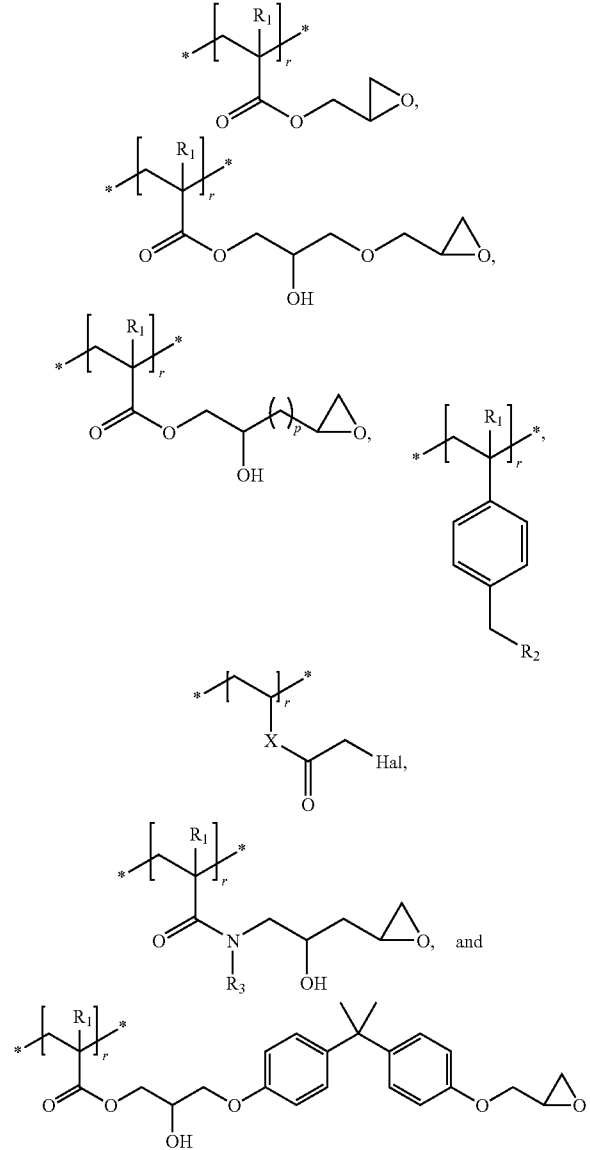


with n=2 to 6 and m being chosen such that the weight average molecular weight of segment B is in the range of 400 to 50,000 g/mol.

2. The method according to claim 1,

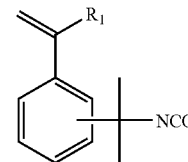
wherein segment A is selected from the group consisting of glycidyl, benzylhalogenide, α-halogenacyl, isocyanate, anhydride, azide, tosylate and mesylate.

3. The method according to claim 1, wherein segment A is selected from the group consisting of:



with p=1 to 12, r=3 to 3,000, R<sub>1</sub>=H or CH<sub>3</sub> and R<sub>2</sub>=halogen, tosylate or mesylate, R<sub>3</sub>=H, if R<sub>1</sub>=CH<sub>3</sub> and R<sub>3</sub>=CH<sub>3</sub>, if R<sub>1</sub>=H and also X=O or NR<sub>4</sub> with R<sub>4</sub>=H or CH<sub>3</sub>.

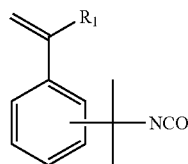
4. The method according to claim 1, wherein segment A is formed from a monomer of the general formula II



with R<sub>1</sub>=H.



5. The method according to claim 1, wherein segment A is formed from a monomer of the general formula II,



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with  $R_1 = \text{H}$  or  $\text{CH}_3$ ,

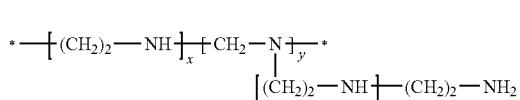
together with at least one further radically polymerisable comonomer selected from the group consisting of aliphatic and aromatic methacrylic acid esters, aliphatic and aromatic acrylamides and styrene which can also be substituted with  $\text{NR}_5$ ,  $\text{OR}_5$  and/or  $\text{COOR}_5$  with  $R_5 = \text{C}_{1-12}$  alkyl or aryl.

6. The method according to claim 1, wherein the weight average molecular weight of segment A is in the range of 1,000 to 1,000,000 g/mol.

7. The method according to claim 1, wherein the weight average molecular weight of segment B is in the range of 400 to 10,000 g/mol.

8. The method according to claim 1, wherein the block copolymer is in addition coupled to a polymer amine.

9. The method according to claim 8, wherein the block copolymer is coupled in addition to a polyethylene imine segment of the general formula III with formation of a graft copolymer,



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x, y and z being chosen such that the weight average molecular weight is in the range of 500 to 3,000,000 g/mol.

10. The method according to claim 8, wherein the block copolymer is coupled in addition to poly-4-vinylpyridine.

11. The method according to claim 8, wherein the graft copolymer has a backbone made of the polymer amine and grafts made of the block copolymer.

12. The method according to claim 8, wherein the graft copolymer has a backbone made of the block copolymer and grafts made of the polymer amine.

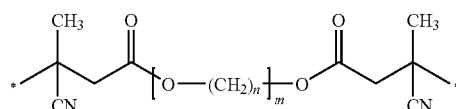
13. The method according to claim 1, wherein polyethylene glycol is used as polyalkylene glycol.

14. The method according to claim 1, wherein a free glycidyl function of the polyalkylene glycol is coupled via the amine groups to the polyethylene imine.

15. A paper product with increased relative wet tensile strength and softness which contains cellulose fibres which are crosslinked with a block copolymer with the blocks A and B,

wherein A is a segment with at least one connectable group for cellulose and has a weight average molecular weight in the range of 300 to 3,000,000 g/mol and

B represents a polyalkylene glycol segment of the general formula I



I

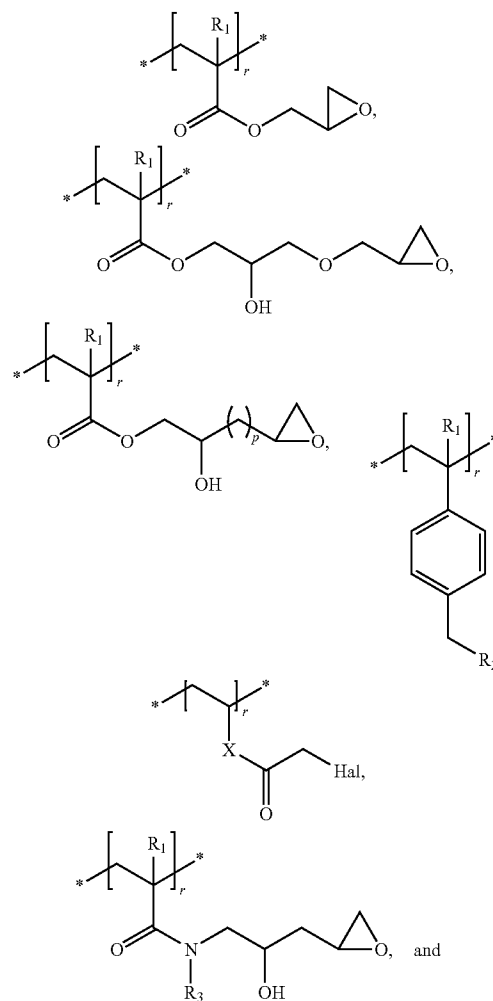
n being chosen such that the weight average molecular weight of segment B is in the range of 400 to 50,000 g/mol.

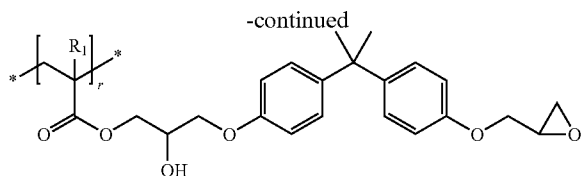
16. The paper product according to claim 15,

wherein segment A is selected from the group consisting of glycidyl, benzylhalogenide,  $\alpha$ -halogenacyl, isocyanate, anhydride, azide, tosylate and mesylate.

17. The paper product according to claim 15,

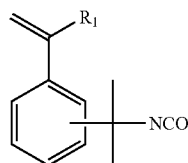
wherein segment A is selected from the group consisting of





with  $p=1$  to  $12$ ,  $r=3$  to  $3,000$ ,  $R_1=H$  or  $CH_3$  and  $R_2$ =halogen, tosylate or mesylate,  $R_3=H$ , if  $R_1=CH_3$  and  $R_3=CH_3$ , if  $R_1=H$  and also  $X=O$  or  $NR_4$  with  $R_4=H$  or  $CH_3$ .

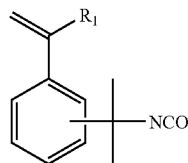
**18.** The paper product according to claim 15, wherein segment A is formed from a monomer of formula II



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with  $R_1=H$ .

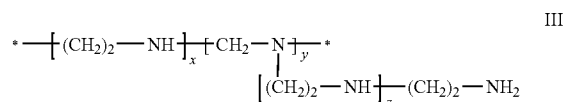
**19.** The paper product according to claim 15, wherein segment A is formed from a monomer of formula II



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with  $R_1=H$  or  $CH_3$  together with at least one further radically polymerisable comonomer selected from the group consisting of aliphatic and aromatic methacrylic acid esters, aliphatic and aromatic acrylamides and styrene which can also be substituted with  $NR_5$ ,  $OR_5$  and/or  $COOR_5$  with  $R_5=C_1-C_{12}$  alkyl or aryl.

- 20.** The paper product according to claim 15, wherein the weight average molecular weight of segment A is in the range of 1,000 to 1,000,000 g/mol.
- 21.** The paper product according to claim 15, wherein the weight average molecular weight of segment B is in the range of 400 to 10,000 g/mol.
- 22.** The paper product according to claim 15, wherein the block copolymer is in addition coupled to a polymer amine.
- 23.** The paper product according to claim 22, wherein the block copolymer is coupled in addition to a polyethylene imine segment of the general formula III with formation of a graft copolymer,



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$x$ ,  $y$  and  $z$  being chosen such that the weight average molecular weight is in the range of 500 to 3,000,000 g/mol.

- 24.** The paper product according to claim 22, wherein the block copolymer is coupled in addition to poly-4-vinylpyridine.
- 25.** The paper product according to claim 22, wherein the graft copolymer has a backbone made of polyethylene imine and grafts made of the block copolymer.
- 26.** The paper product according to claim 22, wherein the graft copolymer has a backbone made of the block copolymer and grafts made of the polyethylene imine.
- 27.** The paper product according to claim 22, wherein the polyethylene imine is linear.
- 28.** The paper product according to claim 22, wherein the polyethylene imine is branched.
- 29.** The paper product according to claim 15, wherein the polyalkylene glycol is polyethylene glycol.
- 30.** The paper product according to claim 15, wherein a free glycidyl function of the polyalkylene glycol is coupled via the amine groups to the polyethylene imine.
- 31.** The paper product according to claim 15 which is a tissue product.

\* \* \* \* \*