



US 20050109476A1

(19) **United States**

(12) **Patent Application Publication**
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(10) **Pub. No.: US 2005/0109476 A1**

(43) **Pub. Date: May 26, 2005**

(54) **MEDIUM FOR INCREASING THE
ABSORPTION CAPACITY OF PAPER PULP
FOR STARCH**

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(21) Appl. No.: **11/023,835**

(22) Filed: **Dec. 28, 2004**

(30) **Foreign Application Priority Data**

Jul. 21, 2003 (EP) 1 384 811

Publication Classification

(51) **Int. Cl.⁷ D21H 17/00**

(52) **U.S. Cl. 162/158; 162/175; 162/168.2**

(57) **ABSTRACT**

The present invention relates to a medium for increasing the absorption capacity for starch of paper or paper pulp in a fibre slurry for paper manufacture, the medium containing cereal meal and/or starch, in particular rye meal, together with a polymer with vinylamine units.

MEDIUM FOR INCREASING THE ABSORPTION CAPACITY OF PAPER PULP FOR STARCH

TECHNICAL FIELD

[0001] The present invention relates to a means for increasing the absorption capacity of paper pulp, such as is used in paper manufacture, for starch or starch-containing products.

[0002] The present invention is suitable for use in conventional methods of producing paper, paperboard or cardboard and for devices usually used for this purpose, which devices are generally known.

[0003] The present invention is especially suitable for manufacture from waste paper.

BACKGROUND

[0004] As a starting material for paper manufacture, an aqueous suspension is prepared from the starting materials such as the fibrous constituents and optionally other paper auxiliaries. The aqueous suspension will hereinafter be referred to as the fibre slurry, and the solid materials contained therein as the paper pulp.

[0005] For the purpose of improving properties such as the resistance of paper to tearing during the manufacturing process, it is known to add starch as a sizing agent to paper pulp from which sheet paper is ultimately obtained.

[0006] For paper manufacture, the fibre slurry containing the paper pulp—as yet without the starch additive—in suspension, is introduced in the form of a web on to a band-like sieve which contains dewatering elements. After partial dewatering, the web passes through a so-called sizing press, in which the application of starch to the already partially dried web takes place. In this operation, the starch is applied as an aqueous suspension, with the result that the moisture content and thus the drying necessary to achieve the finished, dried paper web is increased.

[0007] It would therefore be desirable to already add the starch to the fibre slurry. By this means, the sizing press and the supplementary drying measures could be dispensed with, as a result of which the equipment and the time required to produce the paper, and thus the cost, could be crucially reduced. Adding the starch to the fibre slurry has already been experimented with. However, the starch proved to be only inadequately absorbed by the paper pulp, with the result that the starch content of the paper web obtained is too low to achieve the desired effects, in particular increasing the resistance to tearing.

THE INVENTION

[0008] The aim of the present invention was therefore to make it possible to already add starch to the fibre slurry so that the resulting paper web has a starch content sufficiently high to enable the sizing press and the associated process control which is also necessary to be dispensed with during paper manufacture.

[0009] According to the invention, this aim is achieved with a medium for increasing the absorption capacity of paper pulp for starch, which medium contains cereal meal and/or starch and a polymer with vinylamine units, and is

obtainable by mixing the cereal meal and/or the starch and the polymer with vinylamine units in an extruder.

[0010] The invention further relates to a method of paper manufacture in which a medium containing cereal meal and/or starch and a polymer with vinylamine units is added to the fibre slurry.

[0011] The invention also relates to the use of a medium containing cereal meal and/or starch and a polymer with vinylamine units for increasing the starch content of the paper pulp, particularly in the fibre slurry.

[0012] Cereal meals contain a high proportion of starch, with possible variation in the proportion and composition of the starch depending on the cereal type.

[0013] The meal preferably used according to the invention is a rye meal or a meal of a type of cereal in which the proportion and composition of the starch corresponds to or is similar to that of rye.

[0014] The meal may be a commercially available meal.

[0015] Preferably-used starches are rye-meal starch, or a starch which, in its composition, in particular its content of amylose and amylopectin, corresponds to or is similar to that of rye starch.

[0016] The cereal meal and/or the starch may be added to the medium according to the invention in each case either in the pure form or as a mixture.

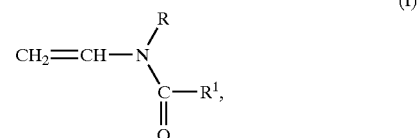
[0017] The medium according to the invention additionally contains a polymer with vinylamine units.

[0018] This may be a homopolymer or a copolymer.

[0019] These may be obtained in a way which is known per se, by radical polymerisation of N-vinylcarboxylic acid amides and subsequent at least partial hydrolysis of the amide functional group to form the corresponding amine functional group.

[0020] Examples of suitable monomers and comonomers, and methods of producing polymers with vinylamine units may be found in EP 0 553 135 B1, EP 0 758 344 B1, WO 98/45536 and WO 00/60167, which for this purpose are referred to in their entirety.

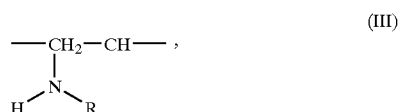
[0021] Suitable polymers with vinylamine units are polymers obtained by polymerisation of N-vinylcarboxylic acid amides of the formula



[0022] wherein R, R¹=H or C₁ to C₆-alkyl, alone or in the presence of other therewith copolymerisable monomers, and hydrolysis of the resulting polymers with acids or bases with cleavage of the group



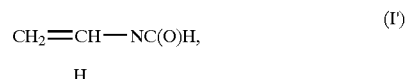
[0023] and with formation of the vinylamine units of the formula



[0024] wherein R has the meaning assigned in formula (I).

[0025] Suitable formula (I) monomers are, for example, N-vinylformamide, N-vinyl-N-methyl-formamide, N-vinyl-N-ethylformamide, N-vinyl-N-propylformamide, N-vinyl-N-isopropylformamide, N-vinyl-N-butylformamide, N-vinyl-N-sec.butylformamide, N-vinyl-N-tert.butylformamide, N-vinyl-N-pentylformamide, N-vinylacetamide, N-vinyl-N-ethylacetamide and N-vinyl-N-methylpropionamide, N-vinylacetamide, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinylpropionamide, N-vinyl-N-methylpropionamide and N-vinylbutyramide.

[0026] N-Vinyl Formamide



[0027] is preferably used according to the invention.

[0028] Copolymers of monomers (I) and (I') contain, for example,

[0029] 1) 99 to 1 mol-% of N-vinylcarboxylic acid amides of formula (I), and

[0030] 2) 1 to 99 mol-% of other, therewith copolymerisable, monoethylenically unsaturated monomers.

[0031] Examples of copolymerisable, monoethylenically unsaturated monomers are vinyl formate, vinyl acetate, vinyl propionate, N-vinylpyrrolidone, acrylic acid, methacrylic acid, esters, amides and nitriles of acrylic acid or methacrylic acid, and the C₁- to C₄-alkyl vinyl ethers.

[0032] Preferred polymers with vinylamine units are hydrolysed copolymers of

[0033] 1) N-vinyl formamide (I') and

[0034] 2) Vinyl formate, vinyl acetate, vinyl propionate, acrylonitrile and N-vinylpyrrolidone, as well as hydrolysed homopolymers of N-vinylformamide.

[0035] The degree of hydrolysis of the N-vinylformamide units in the homopolymers and copolymers is 2 to 100%, preferably 30 to 100%, and especially 75 to 100 mol-%. The molar mass of the polymers with vinylamine units has a value of up to 1 million, and is preferably within the range

10 000 to 600 000 and especially preferably within a range of 400 000 to 500 000 (determined by light scatter).

[0036] Homopolymers, especially of N-vinyl formamide, are preferably used according to the invention.

[0037] The preferred homopolymers are completely hydrolysed. As defined by the invention, the term "completely hydrolysed" also includes substantially completely hydrolysed polymers in the sense that, although the hydrolysis should theoretically run to completion, there may be departures therefrom which process controls render unavoidable.

[0038] Polyvinylamines which are especially preferred according to the invention are completely, or substantially completely, hydrolysed homopolymers of N-vinyl formamide as monomers having a molar mass within a range from 400 000 to 500 000.

[0039] A suitable example thereof is marketed by the company BASF under the product designation CATIOFAST VFH.

[0040] The medium according to the invention preferably contains 5 to 30 wt %, especially 10 to 25 wt %, of polymers with vinylamine units (with reference to the native meal with its natural water content).

[0041] According to requirements, the medium may also contain a larger or smaller quantity of polymer with vinylamine units, provided that the fibre slurry is guaranteed to have the desired starch content.

[0042] If the cereal meal is wholly or partially replaced by starch, the content data must be adjusted accordingly.

[0043] The medium according to the invention may also contain water, which either originates from the natural content of the meal or of the starch and/or was added in the course of the manufacturing process and was incompletely removed during subsequent drying.

[0044] According to requirements, the medium according to the invention may contain additives which may be desirable for paper manufacture.

[0045] The medium according to the invention may be obtained by intimate mixing of the ingredients, meal and/or starch, polymer with vinylamine units, water if applicable and optionally other additives.

[0046] The mixing preferably takes place in an extruder.

[0047] One extruder which is suitable for the extrusion is a co-rotating twin-screw extruder. An example of a suitable twin-screw extruder is an extruder such as that marketed by the company Bühler under the product designation BCTA.

[0048] The extruder may be coupled to a preconditioner.

[0049] The extrusion usually takes place at a temperature of 100 to 170° C., especially of 130 to 155° C.

[0050] The extrusion preferably takes place during addition of water. The water may be added in the liquid state or also at least partially as vapour, for example via a preconditioner. The water is usually added in a quantity of up to 30 wt %, preferably 5 to 20 wt %, with reference to the meal and/or starch content.

[0051] The product obtained by extrusion may then be converted into a form suitable for use. For example, it may

be milled to form a granulate. Beyond this, the particle size of the granulate is not critical. It is usually of the order of 0.5 to a few millimetres, for example of the order of 0.75 mm.

[0052] If required, the extrudate, like the granulate, may be subjected to drying. The drying preferably precedes cooling of the extrudate. The drying with cooling may be carried out in the usual way, which is known per se.

[0053] A medium which is preferred according to the invention is obtained by extrusion of rye meal with 10 to 25 wt % of polymer with vinylamine units, preferably with addition of 5 to 15 wt % of water, in each case with reference to the rye-meal content.

[0054] The granulate, which contains starch and/or a cereal meal modified with a polymer with vinylamine units, is added to the fibre slurry for paper manufacture in a quantity sufficient to adjust the starch content of the paper pulp to the desired value.

[0055] It has been demonstrated that the paper pulp is capable of excellent retention of the starch and/or cereal meal modified with a polymer with vinylamine units, yielding a paper web which has the starch content required for adequate tear resistance. The addition of starch via a sizing press can therefore be dispensed with according to the invention.

[0056] In the case of a medium according to the invention which contains rye meal, addition of a quantity corresponding to 3 to 5 wt % of rye meal with reference to the fibre slurry is sufficient.

[0057] The invention also comprises an improved method of paper manufacture, in which an adequate starch content of the paper pulp may be adjusted as early as in the fibre slurry, with the result that application of the starch to the paper web with the use of a sizing press may be dispensed with. To this end, medium according to the invention is added to the fibre slurry with the paper pulp for paper manufacture in a quantity sufficient to adjust the desired starch content in the paper web to be produced or the finished paper web. If, for example, a preferred medium according to the invention is used, which is obtained by extrusion of rye meal with 10 to 25 wt % of polymer with vinylamine units, it is sufficient to add a quantity corresponding to 3 to 5 wt % of rye meal (with reference to the fibre slurry).

[0058] In what follows, the preparation of the medium according to the invention will be explained in greater detail with the use of examples.

[0059] A conventional rye meal and, as the polymer with vinylamine units, CATIOFAST VFH of the company BASF were used for carrying out the examples.

[0060] All runs of experimental series 1 to 4 were carried out with a Bühler BCTG extruder with a co-rotating twin screw.

[0061] In experimental series 2 to 4, a Bühler BCTC preconditioner was connected upstream of the extruder, via which preconditioner the individual ingredients were fed to the extruder. In selected runs, water in the form of water vapour was additionally fed in via the preconditioner (reported separately).

[0062] Definitions:

N	Screw speed (rpm)
WW	Added water [wt %]
PC	Preconditioner
Polymer	Polymer with vinylamine units [wt %], with reference to the meal content

[0063] Rye meal with its natural water content was used for the series of experiments.

[0064] Experimental Series 1:

Parameter	Variation
Extruder design series: DNDL	Housing diameter (extruder) constant at L/D 40
Meal throughput [kg/h]	Constant at 50
Polymer [wt %]	10; 17.5; 25
N [rpm]	100; 85; 70
WW [wt %]	5; 10; 15

[0065] Conduct of the Experiment:

Polymer	10		17.5			25			
	WW/N	100	85	100	85	70	100	85	70
15	1						6		8
10			3		4			5	
5	2						7		9
Run									
	1	2	3	4	5	6	7	8	9
N [rpm]	100	100	85	85	85	100	100	70	70
Pulp pressure [bar]	45	50	55	51	50	40	50	50	65
Extrusion temperature [° C.]	145	165	151	136	138	136	148	126	138
Cutter speed [%]	50								
H ₂ O ext. [kg/h]	7.5	2.5	5	5.2	5	7.5	2.5	7.5	2.5
Polymer ext. [kg/h]	5.1	5.1	5.1	8.7	12.5	12.5	12.5	12.5	12.5

[0066] The throughput of the mixture of meal, water and polymer through the extruder was a constant 50 kg/h for runs 1 to 9.

[0067] In runs 1 to 9, the water and polymer fraction was added in two batches to the mixture to be extruded, part being added prior to introduction into the extruder and part being added to the mixture in the extruder, in the above table described as “H₂O ext.” and “polymer ext.” In this series, the “polymer ext.” was added via housing 2 and the “H₂O ext.” via housing 1 of the extruder, which comprised 5 housings.

[0068] Experimental Series 2:

[0069] In the runs shown here, the rye meal was introduced at a constant rate of 200 kg/h. The polymer was introduced at a constant 10 wt % of the introduced meal (20 kg/h).

[0070] In runs 4, 5, 6 and 7, water was added in the form of water vapour. In the runs with the switch in the “off” position, water (liquid) and polymer, but no water vapour, were introduced via the preconditioner.

[0071] The runs were conducted as follows:

PC		off		>95° C.		
N	WW	10	15	0	5	10
150				8	6	7
200		2	3		5	4
250		1				

	Run							
	1	2	3	4	5	6	7	8
N [rpm]	250	200	200	200	200	150	150	150
Torque [%]	45	54	46	31	36	41	35	49
Pulp pressure	69	87	70	36	40	50	44	64
Extrusion temperature [° C.]	155	155	147	146	155	152	148	159
PC temperature [° C.]	—	—	—	98	99	99	99	100
Rye meal [kg/h]	200							
Water [%]	10	10	15	10	5	5	10	—
Polymer [%]	10	10	10	10	10	10	10	10

[0072] The granulated extrudate was dried and cooled, during which operation it was collected in a drier (Bühler OTW 50) for 5 minutes, kept in the drier for a further 5 minutes and then transferred to a cooler. After cooling to room temperature, the granulate was decanted.

[0073] Experimental Series 3:

PC		off									>95° C.					
N	WW	5			10			15			0		5		10	
150		17			16				15		19	20			21	
200						13		14						18		
250		10	11		12				9		23	24				
		Run														
		9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
N [rpm]	250	250	250	250	200	200	150	150	150	200	150	150	150	250	250	250
Torque [%]	32	36	42	32	39	35	50	57	58	29	43	38	33	33	28	28
Pulp pressure	90	124	57	104	104	91	87	116	128	46	61	60	47	47	47	47
Extrusion temperature [° C.]	134	163	168	154	149	140	135	146	158	146	156	150	144	173	165	165
PC temperature [° C.]	—									95	98	98	98	99	99	99
Rye meal [kg/h]	200															
Water [%]	15	5	5	5	10	10	15	5	5	5	—	—	10	—	—	—
Polymer [%]	10	10	15	15	10	15	10	15	10	15	10	15	10	10	15	15

[0074] The drying and cooling of the extruded granulate was performed as in experimental series 2.

[0075] Experimental Series 4:

[0076] The addition of meal was varied for experimental series 4.

No. 24	Polymer: 10%	250 kg/h	150 rpm
No. 25	Polymer: 10%	300 kg/h	200 rpm
No. 26	Polymer: 10%	400 kg/h	250 rpm
Run			
	24	25	26
N [rpm]	150	200	250
Torque [%]	48	46	55
Pulp pressure	61	63	78
Extrusion temperature [° C.]	151	154	157
PC temperature [° C.]	95	93	89
Rye meal [kg/h]	250	300	400
Water [%]	5	5	5
Polymer [%]	10	10	10

[0077] The drying and cooling of the granulated extrudate was as in the previous experimental series.

[0078] The results showed that, by addition of the granulates obtained in experimental series 1 to 4, the starch content of the paper pulp in a fibre slurry for paper manufacture could be adjusted to the desired value without difficulty, with the result that a paper with good resistance to tearing could be obtained without the need to add further starch via a sizing press as a supplementary measure.

[0079] With the aid of the present invention, therefore, the sizing press and the equipment connected downstream thereof, such as drying elements, may be completely dispensed with, with the result that significantly more simple and cheaper machinery for paper manufacture is feasible.

1. A medium for increasing the absorption capacity of paper pulp for starch, comprising:

at least one of cereal meal and starch;

and a polymer with vinylamine units;

said medium obtainable by mixing the said at least one of cereal meal and the starch and the polymer with vinylamine units in an extruder.

2. A medium according to claim 1, wherein the medium is obtainable by mixing cereal meal with 5 to 30 wt % of polymer with vinylamine units, with reference to the cereal meal, in an extruder.

3. A medium according to claim 1 wherein the cereal meal is rye meal.

4. A medium according to claim 1, wherein the starch is rye starch.

5. A medium according to claim 1, wherein the polymer with vinylamine units is a homopolymer and/or a copolymer.

6. A medium according to claim 1 containing rye meal and 5 to 30 wt % of polymer with vinylamine units, with reference to the rye meal content.

7. A medium according to claim 1, wherein the polymer with vinylamine units is a completely hydrolysed homopolymer of N-vinylformamide.

8. A method of preparing a medium for increasing the absorption capacity of paper pulp for starch, characterised in that at least one of cereal meal and starch, and a polymer with vinylamine units are mixed in an extruder.

9. A method according to claim 8, wherein water is additionally added.

10. A method according to claim 8, wherein water is added entirely or partially in the form of water vapour.

11. A method according to claim 8, wherein rye meal is used as the cereal meal.

12. A method according to claim 8, wherein the content of polymer with vinylamine units is 5 to 30 wt %, with reference to the cereal-meal fraction.

13. A method according to claim 8, wherein a twin-screw extruder is used as the extruder.

14. A method according to claim 8, wherein a completely hydrolysed homopolymer of N-vinyl formamide is used as the polymer with vinylamine units.

15. A medium according to claim 1, wherein cereal meal and/or starch and a polymer with vinylamine units for adjusting the starch content in the paper pulp of a fibre slurry for paper manufacture.

16. A method of paper manufacture, wherein a medium according to claim 1 is added to the fibre slurry with the paper pulp.

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