

The present invention relates to a process for trash removal in papermaking.

In the last decades, the papermaking industry has succeeded in reducing the specific fresh water consumption and the specific waste water amount to a considerable extent by concentrating and closing the water circuits in the paper manufacture. The reason for said concentration is to avoid loss of matter with waste water on the one hand, and, on the other hand, the official requirements with respect to composition and amount of discharged waste water according to the law concerning waste-water-emission.

Many new problems have arisen due to this concentration of the water amount. As a result of the increased portion of circuit water, the temperature of the pulp system in some cases increases to a considerable extent. Thus, increased slime formation may result. Higher electrolyte concentrations in the process water lead to an earlier corrosion. Due to the anaerobic zones within the water cycle, problems with respect to odour may result.

However, the major problem relating to water circuit concentration is the enrichment of organic substances in the recycled water, the so-called "trash". According to Auhorn "Wochenblatt für Papierfabrikation 112, 37-48 (1984)" said matter consist of dissolved or colloidally dissolved anionic oligomers or polymers, and non-ionic hydrocolloids. In the production and processing of cellulose, wood pulp, and waste paper they are formed as lignanes or polysaccharides or oligosaccharides deriving from hemicellulose. Other trash originates from the anionic auxiliaries used in papermaking.

The concentration of these water-soluble substances considerably increases with an increasing concentration of recycled water.

When wood-containing paper is made, the circuit water of paper machines is extremely loaded with such trash.

The trash impairs the paper manufacture in many respects. It influences pulp beating due to less fibre swelling and delayed beating effect; it leads to increased sedimentation in the circuit and in the pulp flow of a paper making machine.

In addition, a deterioration of the retention, drainage, sheet formation, and of the paper strength are to be observed. The efficiency of nearly all chemical auxiliary agents is affected by these disturbing substances. Examples include retention aids and dewatering auxiliary agents, wet and dry strength agents, sizing agents, defoamers, bleaching chemicals, and dyes. The trash concentration may become a limiting factor for the cycle concentration.

Formerly, these problems could widely be prevented by adding the then usual aluminium sulfate. The high adsorption capacity of the intermediate Al-complexes relieves the recycled water of inorganic and organic impurities. In today's neutral operation, there is the problem that aluminium sulfate can no longer be employed as precipitation and fixing agent. This also results from the increasing use of calcium carbonate as coating and filling pigment for economic and qualitative considerations.

Owing to the increased use of calcium carbonate, production problems in the processing of calcium carbonate-containing coating refuse and of waste paper in the acidic pH-range have considerably increased.

Thus, there was the problem of eliminating the trash from the recycled water of paper mills with simultaneously minimizing the use of the previous aluminium sulfate.

First attempts to solve this problem are known. According to Arheilger and von Medvey, "Wochenblatt für Papierfabrikation 114, 958-961 (1986)", highly wood-containing, coated paper is produced by using calcium carbonate without adding alum. This was achieved by the addition of polydiallyldimethyl ammonium chloride (PolyDadmac) to the circuit water. However, PolyDadmac does not seem to have all of the positive characteristics of alum. For example, severe difficulties with respect to combatting slime formation occurred which were overcome not until other agents were employed.

Additionally, in contrast to alum, chromophoric substances were also fixed by PolyDadmac to such an extent that the addition of fixing agents in industrial scale resulted in a whiteness decrease of approximately 1.5 points of whiteness, causing a significant cost increase for bleaching agents.

Thus, the problem of finding substitutes for aluminium sulfate to eliminate trash and which do not have negative side effects still exists.

DE-A 36 20 065 opens up another path: Special drainage, retention, and flocculating agents are used, namely high-molecular, water-soluble polymers of N-vinylamides developing their efficacy not until trash, which contains as accompanying substances phenolic groups-containing oligomers and/or polymers of the substances of wood, is present. For this reason, these special N-vinylamide-polymers are insensitive to pitch-like resins which are always present in concentrated or closed water circuits in paper manufacturing.

The disadvantage of this method is the fact that trash removal does not take place and, in particular, that the flocculating, drain-

age and retention agents based on cationic polymers which are normally used in the paper industry cannot be employed.

A process to prevent the deposition of pitch-like resins in paper-making is known from DE-A-27 34 001, wherein a water-soluble, linear, cationic polymer based on a quaternized aminoalkyl ester of acrylic or methacrylic acid is added to the paper pulp. It is said that through the addition of these polymers, the pitch-like resins are dispersed and separated or retained in the pulp in finely divided form and that there are no interferences caused by other additives which may be present in the pulp. Said pitch-like resins are water-insoluble disturbing agents.

Accordingly, it is the object of the present invention to remove dissolved or colloiddally dissolved trash in papermaking without having to make use of aluminium sulfate and allowing to use the known and proven auxiliary agents based on cationic polymers as drainage auxiliary agent, retention and flocculating agents without impairing their effect.

In accordance with the present invention this object is achieved according to claim 1 by using polymers (homopolymers and/or copolymers) based on quaternized dimethylaminopropyl(meth)acrylamide which are added to the pulp flow and/or to the circuit water, these polymers having an intrinsic viscosity of less than 150 ml/g, measured in 10%-wt. sodium chloride solution.

The polymers used according to the present invention advantageously consist of 50 to 100%-wt. quaternized dimethylaminopropyl(meth)acrylamide and 0 to 50%-wt. acrylamide, acrylic acid, methacrylic acid, acrylamidomethylpropane sulfonic acid, or of mixtures of these cationic and anionic monomers.

The dimethylaminopropyl(meth-)acrylamide is quaternized with the conventional and known quaternizing agents, e.g., dimethyl sulfate, dimethyl carbonate, benzyl chloride, methyl chloride, or ethyl bromide.

The polymers are used in an amount of 0.05 up to 1%-wt., relative to the dry weight of the paper produced, that means in addition to the usual auxiliary agents, by adding them to the pulp flow and/or circuit water. It is preferred that the polymer used as trash remover according to the present invention is employed in an amount of 0.2 to 0.8, relative to the dry weight of the produced paper.

Advantageously, the total amount of polymer added for trash removal can be distributed over several feeders.

Surprisingly, the polymers used according to the present invention result in the following:

- a) the trash contained in the plant water is fixed to the paper fibre and
- b) the degree of whiteness of the paper such produced is not impaired by the trash adsorption.

The polymers used according to the present invention and serving as trash removers are preferably used in neutral operation without the addition of aluminium sulfate. However, it is also possible to use these products in combination with aluminium sulfate according to the pseudoneutral operation.

The polymers used according to the present invention are of particular advantage in papermaking processes where the water circuit is closed by more than 90%.

The invention will be illustrated in greater detail by the following examples:

If not indicated to the contrary, the parts given are parts by weight.

A) Production of the Polymers

Polymer 1:

250 parts of acrylamidopropyltrimethyl ammonium chloride are dissolved in 750 parts of water. A pH-value of 5.0 is adjusted. Heating to 75°C is effected under introduction of nitrogen gas. After the addition of 0.6 parts of potassium peroxodisulfate the polymerization starts.

The final temperature of 90°C is achieved within 5 minutes. After cooling, the product has a viscosity of 1050 mPa.s, the intrinsic viscosity amounts to 120 ml/g.

Polymer 2:

180 parts of acrylamidopropyltrimethyl ammonium chloride and 180 parts of acrylamidomethylpropane sulfonic acid are dissolved one after the other in 568 parts of water. A pH of 5.0 is adjusted using 72 parts of 45% caustic soda solution.

Heating to 75°C is effected under introduction of nitrogen gas. After the addition of 0.6 parts of potassium peroxodisulfate the polymerization starts. The final temperature of 92°C is reached within 10 minutes. After cooling, the product has a viscosity of 860 mPa.s, the intrinsic viscosity amounts to 75 ml/g.

Polymer 3:

200 parts of acrylamidopropyltrimethyl ammonium chloride are dissolved in 709 parts of water. After addition of 50 parts of acrylic acid, pH 5.0 is adjusted by using 41 parts of 45% caustic soda solution. Under introduction of nitrogen gas, heating to 75°C is effected. After adding 0.4 parts of potassium peroxodisulfate the polymerization starts. The final temperature of 94°C is reached within 7 minutes. After cooling, the product has a viscosity of 750 mPa.s, the intrinsic viscosity amounts to 98 ml/g.

Polymer 4:

210 parts of methacrylamidopropyltrimethyl ammonium chloride are dissolved in 638 parts of water. After addition of 90 parts of methacrylic acid, a pH of 5.0 is adjusted by using 62 parts of 45% caustic soda solution. Under introduction of nitrogen gas, heating to 75°C is effected. The polymerization starts after 0.8 parts of potassium peroxodisulfate have been added. The final temperature of 91°C is achieved within 15 minutes. After cooling, the product has a viscosity of 890 mPa.s, the intrinsic viscosity amounts to 105 ml/g.

Polymer 5:

210 parts of methacrylamidopropyltrimethyl ammonium chloride and 30 parts of acrylamidomethylpropane sulfonic acid are dissolved one after the other in 646 parts of water. After addition of 60 parts of acrylic acid, a pH of 5.0 is adjusted using 54 parts of 45% caustic soda solution. After the addition of 0.8 parts of potassium peroxodisulfate, the polymerization starts. The final temperature of 94°C is reached within 12 minutes. After cooling,

the product has a viscosity of 740 mPa.s, the intrinsic viscosity amounts to 88 ml/g.

Polydimethyldiallyl ammonium chloride having an intrinsic viscosity of 95 ml/g was used as comparative polymer in the examinations with respect to technical application.

B) Examinations with respect to the technical application:

The following methods are commonly used to demonstrate the trash removal:

1. The action of cationic dewatering and retention agents is reduced by the anionic trash. After addition of the trash removers, the drainage and retention efficiency is improved and determined quantitatively.

2. The degree of whiteness achieved in the paper is measured according to DIN 53145. A reduced whiteness of the paper is caused by fixing certain trash and chromatophores to the paper fibres.

According to nature, the degree of whiteness is highest without control agents; as compared to the comparative substances the trash removers according to the present invention reduce said degree to a considerably lower extent.

1. Pulp drainage, Schopper-Riegler-method

The apparatus is described in "Zellstoff Papier, 5th edition, VEB publishers, Leipzig, pages 387-388". It was modified such that both outflow ports discharged into a common receiving vessel. Thus, the degree of beating is no longer measured, but only the pulp drainage determined.

A waste paper pulp having a solids content of 4% was used. 3 g oven-dry pulp are diluted with tap water (hardness 3.57 mmole/l; 20°dH) to a volume of 300 ml. The fixing agent is diluted to a volume of 300 ml and added to the pulp suspension. The suspension is poured over thrice. Subsequently, the dewatering auxiliary agent is diluted to 400 ml and added to the suspension. Then this system is poured over once and drained in the Schopper-Riegler-apparatus.

The time for 700 ml of drain is determined.

The drainage for the blank reading is carried out without control agent and drainage auxiliary agent; in the case of the zero value, the trash remover is omitted but drainage auxiliary agent added. 25% cationic polyacrylamide is used as drainage auxiliary agent.

Drainage tests Schopper-Riegler
(Time in seconds for 700 ml of filtrate)

	Drainage auxiliary agent (%)			
	0.00	0.01	0.02	0.03
Blank reading :	255			
Zero value :		121	83	67
Trash remover 1: 0.3%		89	71	59
Trash remover 1: 0.6%		78	65	54
Trash remover 2: 0.3%		96	76	63
Trash remover 2: 0.6%		86	69	57
Trash remover 3: 0.3%		93	74	62
Trash remover 3: 0.6%		82	64	57
Trash remover 4: 0.3%		92	71	61
Trash remover 4: 0.6%		82	65	55
Trash remover 5: 0.3%		94	74	63
Trash remover 5: 0.6%		83	66	56
Comparison : 0.3%		115	81	65
Comparison : 0.6%		105	76	61

2. Determination of Retention (Britt-Jar-Test)

The apparatus used for the determination of the retention is described in "New methods for monitoring retention", Tappi, February 1976, vol. 59, no. 2, KW. Britt and J.E. Unbehend. 2.5 g oven-dry pulp (90% wood pulp and 48° S.R., 10% chalk as 71% slurry, with 60% having a particle size of smaller than 2 μ m) are diluted with tap water (hardness 3.57 mmole/l; 20° dH) to 400 ml

volume. After addition of the trash remover, the suspension is poured over 10 times. Subsequently, the retention auxiliary is added as 0.01% solution, and the suspension is poured over thrice. After dilution to 500 ml with water, the suspension is placed into the Britt-Jar-tester and stirred at a rotation of 800 rpm for 15 seconds. Under continued stirring, the discharge valve is opened for 30 seconds and the filtrate collected. After filtering the filtrate over a vacuum filter provided with a "Schwarzbandfilter" [black band-filter] the accepted stock not subjected to retention is determined by drying.

The retention is given as percentage of that portion of accepted stock which did not undergo retention to the total accepted stock.

Britt-Jar-Test
(Retention %)

	Drainage auxiliary agent (%)		
	0.00	0.02	0.03
Blank reading :	48.9		
Zero value :		57.1	61.6
Trash remover 1: 0.3%		66.5	71.3
Trash remover 1: 0.6%		69.8	75.4
Trash remover 2: 0.3%		64.6	70.8
Trash remover 2: 0.6%		68.4	75.1
Trash remover 3: 0.3%		64.3	70.1
Trash remover 3: 0.6%		68.9	74.3
Trash remover 4: 0.3%		65.2	69.9
Trash remover 4: 0.6%		69.2	74.8
Trash remover 5: 0.3%		64.8	69.3
Trash remover 5: 0.6%		68.2	73.9
Comparison : 0.3%		58.3	62.7
Comparison : 0.6%		63.9	67.3

3. Determination of the degree of whiteness

a) Sheet formation

An amount of 2.5 g OD of the waste paper pulp having a solids concentration of 4% is diluted with tap water to a volume of 500 ml. The trash remover or pitch control agent is added in an amount of 0.4%, relative to oven-dry pulp, as a 0.5% solution and

stirred with a magnetic stirrer at 500 rpm for 30 seconds. Subsequently, the drainage aid, a 25% cationic polyacrylamide, is added in an amount of 0.03% as 0.01% solution, and stirring is continued for 30 seconds. 4 litres of tap water are placed in the sheet former and are brought to bubbling by blowing in air. Now, the pulp suspension is added and drawn off after mixing.

The surfacing cardboard is placed on the formed sheet, and the sheet is drawn off the wire. Subsequently, it is dried in the vacuum dryer for 10 minutes followed by oven-drying at 110°C for 5 minutes. The zero value is obtained without fixing agent.

b) Measurement of whiteness

Following DIN 53145, the degree of whiteness of the sheets thus made is determined. The measurements were carried out using the Elrepho-apparatus of Zeiss; the filter no. 7 calibrated against MgO was used.

Measurement of whiteness degree

	Whiteness (%)
Zero value	65.9
Trash remover 1	62.8
Trash remover 2	63.2
Trash remover 3	62.7
Trash remover 4	61.3
Trash remover 5	61.9
Comparison	57.3



CLAIMS

1. A process for the removal of dissolved or colloiddally dissolved trash during papermaking by adding trash removers, characterized in that polymers are used as trash removers which consist of

- a) 50 to 100%-wt. quaternized dimethylaminopropyl acrylamide or dimethylaminopropyl methacrylamide, and
- b) 0 to 50%-wt. acrylamide, acrylic acid, methacrylic acid, acrylamidomethylpropane sulfonic acid, or mixtures of these monomers,

said polymers having an intrinsic viscosity of less than 150 ml/g, measured in a 10%-wt. sodium chloride solution.

2. The process according to claim 1 characterized in that the polymers are used in an amount of 0.05 to 1, preferably 0.2 to 0.8%-wt., relative to the dry weight of the manufactured paper.

3. The process according to claim 1 or 2 characterized in that the quaternized dimethylaminopropyl(meth-)acrylamide has been quaternized with dimethyl sulfate, methyl chloride, ethyl bromide, dimethyl carbonate, or benzyl chloride.

4. The process according to claim 1 characterized in that the total amount of the added polymer is distributed over several feeders.

5. The process according to claim 1 characterized in that the polymers are used in combination with cationic paper auxiliaries.

6. The process according to claim 1 characterized in that the polymers are used in combination with aluminum sulfate.



7. The process according to claim 1 characterized in that the water circuit is closed up by more than 90% during papermaking.