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- (72) NAGARAJAN, R., US
- (72) WONG SHING, Jane B., US
- (71) NALCO CHEMICAL COMPANY, US
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- (30) 1997/04/25 (08/845,795) US
- (54) PROCESSUS AMELIORE DE FABRICATION DU PAPIER
- (54) IMPROVED PAPERMAKING PROCESS

(57) L'invention revendiquée comprend un processus de fabrication du papier consistant à former une boue de cellulose aqueuse à papier, à soumettre la boue liquide à une ou à plusieurs étapes de cisaillement, à lui ajouter, après l'addition de la charge minérale et avant au moins une des étapes de cisaillement, une quantité efficace d'un polymère de dispersion choisi dans le groupe constitué des copolymères d'acrylamide et de sel quaternaire diméthylaminoéthylacrylate-chlorure de méthyle (DMAEA.MCQ), de sel quaternaire diméthylaminoéthylméthacrylate-chlorure de méthyle (DMAEM.MCQ), de quaternaire diaméthylaminoéthylacrylate-chlorure de benzyle (DMAEA.BCQ) et de sel quaternaire diamnéthylaminoéthylméthacrylate-chlorure de benzyle (DMAEM.BCO) de diallyldiméthylammonium (DADMAC), à cisailler la boue liquide, à lui ajouter une microparticule choisie dans le groupe composé de produits organiques comme des copolymères d'acide polyacrylique et de produits inorganiques comme un sol de bentonite et de silice pour former une feuille et à assécher la feuille pour en faire une feuille de papier.

(57) The claimed invention comprises a papermaking process comprising forming an aqueous cellulosic papermaking slurry, subjecting the slurry to one or more shear stages, adding to the slurry a mineral filler prior to at least one of the shear stages, adding to the slurry after the addition of the mineral filler and prior to at least one of the shear stages an effective amount of a dispersion polymer selected from the group consisting of copolymers of acrylamide dimethylaminoethylacrylate methyl chloride quaternary salt (DMAEA.MCQ), dimethylaminoethylmethacrylate methyl chloride quaternary salt (DMAEM.MCQ), dimethylaminoethylacrylate benzvl chloride quaternary salt (DMAEA.BCQ) and dimethylaminoethylmethacrylate benzyl chloride quaternary salt (DMAEM.BCO) diallyldimethylammonium chloride (DADMAC), shearing the slurry, adding a microparticle selected from the group consisting of organics such as copolymers of polyacrylic acid. inorganics such as bentonite and silica sol, draining the slurry to form a sheet, and drying the sheet to form a paper sheet.

Abstract of the Invention

The claimed invention comprises a papermaking process comprising forming an aqueous cellulosic papermaking slurry, subjecting the slurry to one or more shear stages, adding to the slurry a mineral filler prior to at least one of the shear stages, adding to the slurry after the addition of the mineral filler and prior to at least one of the shear stages an effective amount of a dispersion polymer selected from the group consisting of copolymers of acrylamide and dimethylaminoethylacrylate methyl chloride quaternary salt (DMAEA.MCQ), dimethylaminoethylmethacrylate methyl chloride quaternary salt (DMAEM.MCQ), dimethylaminoethylacrylate benzyl chloride quaternary salt (DMAEA.BCQ) and dimethylaminoethylmethacrylate benzyl chloride quaternary salt (DMAEM.BCQ) and diallyldimethylammonium chloride (DADMAC), shearing the slurry, adding a microparticle selected from the group consisting of organics such as copolymers of polyacrylic acid, inorganics such as bentonite and silica sol, draining the slurry to form a sheet, and drying the sheet to form a paper sheet.

Background of the Invention

1. Field of the Invention

The present invention is in the technical field of papermaking and more particularly in the technical field of wet-end additives to papermaking furnish.

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2. Description of the Prior Art

In the manufacture of paper an aqueous cellulosic suspension or slurry is formed into a paper sheet. The cellulosic slurry is generally diluted to a consistency (percent dry weight of solids in the slurry) of less than 1 percent and often below 0.5 percent ahead of the paper machine, while the finished sheet must have less then 6 weight percent water. Hence the dewatering aspects of papermaking are extremely important to the efficiency and cost of the manufacture.

The dewatering method of the least cost in the process is drainage, and thereafter more expensive methods are used. for instance vacuum, pressing, evaporation and the like, and in practice a combination of such methods are employed to dewater, or dry the sheet to the desired water content. Since drainage is both the first dewatering method employed and the least expensive, improvement in the efficiency of drainage will decrease the amount of water required to be removed by other methods and hence improve the overall efficiency of dewatering and reduce the cost thereof.

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Another aspect of papermaking that is extremely important to the efficiency and cost of the manufacture is retention of furnish components on and within the fiber mat being formed during papermaking. A papermaking furnish contains generally particles

that range in size from about the 2 to 3 millimeter size of cellulosic fibers, to fillers at a few microns, and to colloids. Within this range are cellulosic fines, mineral fillers (employed to increase opacity, brightness and other paper characteristics) and other small particles that generally, without the inclusion of one or more retention aids, would in significant portion pass through the spaces (pores) between the cellulosic fibers in the fiber mat being formed during papermaking.

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One method of improving the retention of cellulosic fines, mineral fillers and other furnish components on the fiber mat is the use of a coagulant/flocculant system, added ahead of the paper machine. In such a system there is first added a coagulant, for instance a low molecular weight cationic synthetic polymer or a cationic starch to the furnish, which coagulant generally reduces the negative surface charges present on the particles in the furnish, particularly cellulosic fines and mineral fillers, and thereby accomplishes a degree of agglomeration of such particles, followed by the addition of a flocculant. Such flocculant generally is a high molecular weight anionic synthetic polymer which bridges the particles and/or agglomerates, from one surface to another, binding the particles into large agglomerates. The presence of such large agglomerates in the furnish as the fiber mat of the paper sheet is being formed increases retention. The agglomerates are filtered out of the water onto the fiber web, where unagglomerated particles would to a great extent pass through such paper web.

While a flocculated agglomerate generally does not interfere with the drainage of the fiber mat to the extent that would occur if the furnish were gelled or contained an amount of gelatinous material, when such flocs are filtered by the fiber web the pores

thereof are to a degree reduced, reducing the drainage efficiency therefrom. Hence the retention is being increased with some degree of deleterious effect on the drainage.

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Another system employed to provide an improved combination of retention and dewatering is described in United States Patent No. 4,753,710 and United States Patent No. 4,913,775, inventors Langley et al., issued respectively June 28, 1988 and April 3, 1990, incorporated hereinto by reference. In brief, such method adds to the aqueous cellulosic papermaking suspension first a high molecular weight linear cationic polymer before shearing the suspension, followed by the addition of bentonite after shearing. The shearing generally is provided by one or more of the cleaning, mixing and pumping stages of the papermaking process, and the shearing breaks down the large flocs formed by the high molecular weight polymer into microflocs, and further agglomeration then ensues with the addition of the bentonite clay particles.

Another system uses the combination of cationic starch followed by colloidal silica to increase the amount of material retained on the web by the method of charge neutralization and adsorption of smaller agglomerates. This system is described in United States Patent No. 4,388,150, inventors Sunden et al., issued June 14, 1983.

Dewatering generally, and particularly dewatering by drainage, is believed improved when the pores of the paper web are less plugged, and it is believed that retention by adsorption in comparison to retention by filtration reduces such pore plugging.

Greater retention of fines and fillers permits, for a given grade of paper, a reduction in the cellulosic fiber content of such paper. As pulps of less quality are

employed to reduce papermaking costs, the retention aspect of papermaking becomes even more important because the fines content of such lower quality pulps is greater generally than that of pulps of higher quality.

Greater retention of fines, fillers and other slurry components reduces the amount of such substances lost to the white water and hence reduces the amount of material wastes, the cost of waste disposal and the adverse environmental effects therefrom.

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Another important characteristic of a given papermaking process is the formation of the paper sheet produced. Formation is determined by the variance in light transmission within a paper sheet, and a high variance is indicative of poor formation. As retention increases to a high level, for instance a retention level of 80 to 90 percent, the formation parameter generally abruptly declines from good formation to poor formation. It is at least theoretically believed that as the retention mechanisms of a given papermaking process shift from filtration to adsorption, the deleterious effect on formation, as high retention levels are achieved, will diminish, and a good combination of high retention with good formation is attributed to the use of bentonite in U. S. Patent No. 4.913.775.

It is generally desirable to reduce the amount of material employed in a papermaking process for a given purpose, without diminishing the result sought. Such add-on reductions may realize both a material cost savings and handling and processing benefits.

It is also desirable to use additives that can be delivered to the paper machine without undue problems. An additive that is difficult to dissolve, slurry or otherwise

disperse in the aqueous medium may require expensive equipment to feed it to the paper machine. When difficulties in delivery to the paper machine are encountered, the additive is often maintained in aqueous slurry form by virtue of high energy input equipment. In contrast, additives that are easily dissolved or dispersed in water require less energy and expense and their uniformity of feed is more reliable.

Summary of the Invention

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The claimed invention comprises a papermaking process comprising forming an aqueous cellulosic papermaking slurry, subjecting the slurry to one or more shear stages, adding to the slurry a mineral filler prior to at least one of the shear stages, adding to the slurry after the addition of the mineral filler and prior to at least one of the shear stages an effective amount of a dispersion polymer selected from the group consisting of copolymers of acrylamide and dimethylaminoethylacrylate methyl chloride quaternary salt (DMAEA.MCQ), dimethylaminoethylmethacrylate methyl chloride quaternary salt (DMAEM.MCQ), dimethylaminoethylacrylate benzyl chloride quaternary salt (DMAEA.BCQ) and dimethylaminoethylmethacrylate benzyl chloride quaternary salt (DMAEM.BCQ) and diallyldimethylammonium chloride (DADMAC), shearing the slurry, adding a microparticle selected from the group consisting of organics such as copolymers of polyacrylic acid, inorganics such as bentonite and silica sol, draining the slurry to form a sheet, and drying the sheet to form a paper sheet.

Description of the Preferred Embodiments

According to the invention, a water soluble polymer is added to a cellulosic slurry before the formation of a paper product. The water soluble polymer should become

substantially dispersed within the slurry before formation of the paper product in any case. The microparticle of the invention is added after shearing of the slurry. The addition of the polymer in an aqueous medium, for instance as a water solution or dispersing, facilitates the dispersion of the polymer of the slurry. In a preferred embodiment, the polymer is added to the cellulosic slurry before the processing steps of draining and forming the paper sheet.

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The present process is believed applicable to all grades and types of paper products, and further applicable for use on all types of pulps including, without limitation, chemical pulps, including sulfate and sulfite pulps from both hard and soft woods and acid pulps, thermo-mechanical pulps, mechanical pulps, recycle pulps and ground wood pulps, although it is believed that the advantages of the process of the present invention are best achieved when the pulp employed is of the chemical pulp type, particularly alkaline chemical pulp.

In preferred embodiment the filler used in the cellulosic slurry is anionic, or at least partially anionic. Other mineral, or inorganic, fillers may, however, be used, such as calcium carbonate, clay, titanium dioxide, or talc or a combination may be present.

The amount of alkaline inorganic filler, such as one of the alkaline carbonates, generally employed in a papermaking stock is from about 10 to about 30 parts by weight of the filler, as CaCO₃, per hundred parts by weight of dry pulp in the slurry, but the amount of such filler may at times be as low as about 5, or even about 2, parts by weight, and as high as about 40 or even 50 parts by weight, same basis.

The reduced specific viscosities of the polymers and copolymers as reported herein were determined in 0.125M sodium nitrate solution from published data.

Similarly, all molecular weights of the polymers as reported herein are the approximate weight average molecular weights of the polymers.

The dispersion polymerization process used to manufacture the polymers of the invention offer numerous advantages which have previously been unavailable. Since the polymers of the invention are synthesized entirely in water, no oil solvent is required. This is significant since:

1) the polymers of the invention do not present a fire hazard;

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- 2) oil is not added to the water which is to be treated (more environmental friendly);
 - dissolution of the polymers of the invention requires only the addition of water,
 no special activators are needed;
 - 4) the ability of the polymers of the invention to dissolve/invert is superior to that of oil dispersion latexes; and
- 5) the polymers of the invention may be diluted to virtually any concentration by using appropriately concentrated salt water.

Another major advantage is that the bulk viscosity of the polymer is low, unlike some oil dispersion latex polymers. This physical property enables any standard chemical pump to deliver the material at the injunction site.

A new class of water-soluble dispersion polymers have been discovered to be more effective in increasing drainage and retention than currently available chemical treatments. As will be discussed in more detail below, the polymer dispersion of the

invention is prepared in an aqueous solution of a polyvalent anionic salt. The polymer dispersion of the invention achieves fine particle sizes and aqueous solubilities not available with other polymers used for this application. Furthermore, there does not appear to be a problem with overfeeding the polymer dispersion which is a drawback with latex polymers.

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According to the method, the dispersion polymer of the invention is added to a cellulosic papermaking slurry. The polymer is added in an effective amount of from 0.5 to about 100 ppm. More preferably, the amount of the polymer added is from 2 to about 40 ppm: and most preferably from about 4 to about 25 ppm. It is believed, that there does not appear to be a maximum dosage at which the polymers adversely affect the system. At some higher doses the beneficial effect may plateau, and on a cost basis such higher doses, probably above about 100 ppm, are not cost effective. The polymers of the invention are preferably added to the system in neat form. However, in some applications, the polymers can be added as an aqueous solution.

The preferred polymers of the invention are manufactured by Hymo Corporation, Japan. Methods for manufacturing the polymer dispersion used in the invention is described in detail in U. S. Patent No. 5,006,590 and U. S. Patent No. 4,929,655, assigned to Kyoritsu Yuki Co., Ltd., Tokyo, Japan. The disclosures of these two patents are incorporated herein by reference.

In the preferred embodiment of the invention, an organic or inorganic microparticle is added to the slurry after the introduction of shear. Preferably, the organic microparticle is a medium molecular weight anionic polymer such as the copolymers of

acrylic acid described in U.S. Patent No. 5,098,520, the disclosure of which is incorporated herein by reference, or medium molecular weight anionic sulfonated polymers such as those described in U.S. Patent No. 5,185,062, the disclosure of which is incorporated herein by reference. The inorganic microparticle may be preferably chosen from among bentonite and silica sol.

According to the invention, the dispersion polymer used to treat the cellulosic papermaking slurry may further be prepared from a water-soluble monomer mixture containing at least 5 mole % of a cationic monomer represented by the general formula (I):

$$CH_{2}=C \longrightarrow R_{1}$$

$$O=C \longrightarrow A_{1} \longrightarrow B_{1} \longrightarrow N \longrightarrow CH_{2} \longrightarrow X_{1}^{\bigcirc}$$

$$R_{2}$$

$$O=C \longrightarrow A_{1} \longrightarrow B_{1} \longrightarrow N \longrightarrow CH_{2} \longrightarrow X_{1}^{\bigcirc}$$

$$R_{3}$$

$$(I)$$

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wherein R_1 is H or CH_3 ; R_2 and R_3 are each an alkyl group having 1 to 2 carbon atoms; A_1 is an oxygen atom or NH; B_1 is an alkyl group having 2 to 4 carbon atoms or a hydroxypropyl group and X_1 is a counter anion.

The above water-soluble monomer mixture is soluble in the aqueous solution of the polyvalent anionic salt. The polymer generated from the monomer mixture is, however, insoluble in the aqueous polyvalent anionic salt solution. The polymer of the

monomer mixture can also be used as the seed polymer. The seed polymer is described in detail below.

The above cationic monomer represented by the general formula (I) preferably is a quaternary ammonium salt obtained by the reaction of methyl chloride or benzyl chloride and dimethylaminoethyl acrylate, diethylaminoethyl acrylate, dimethylaminohydroxypropyl acrylate, dimethylaminopropyl acrylamide, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, diethylaminoethyl methacrylate and dimethylaminopropyl methacrylamide.

The concentration of the above-mentioned monomers in the polymerization reaction mixture is suitably in the range of 1.0 to 30% by weight for the methyl chloride quaternary ammonium salt. Preferably, the concentration is from about 10 to about 20% by weight. For the benzyl chloride quaternary ammonium salts, the concentration in the polymerization reaction mixture is suitably in the range of from about 1.0 to about 35% by weight. Preferably, the concentration is from about 10 to about 20% by weight.

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Monomers preferably copolymerized with the cationic monomer are represented by the general formula (I) includes acrylamide, methacrylamide and the cationic monomers represented by the general formula (II):

wherein R₄ is H or CH₃; R₅ and R₆ are each an alkyl group having 1 to 2 carbon atoms;

A₇ is H or an alkyl group having 1 to 2 carbon atoms; A₂ is an oxygen atom or NH; B₂ is an alkyl group having 2 to 4 carbon atoms or a hydroxypropyl group and X₂ is a counter anion.

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Preferable monomers represented by the formula (II) include the ammonium salts of dimethylaminoethyl acrylate, diethylaminoethyl acrylate, dimethylaminopropyl acrylamide and dimethylhydroxypropyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dimethylaminopropyl methacrylamide, diethylaminopropyl methacrylamide and dimethylhydroxypropyl methacrylate as well as the methylated and ethylated quaternary salts. Among the more preferable cationic monomers represented by the general formula (II) are the salts and methylated quaternary salts of dialkylaminoethyl acrylate and dialkylaminoethyl methacrylate.

The polyvalent anionic salt to be incorporated in the aqueous solution according to the present invention is suitably a sulfate, a phosphate or a mixture thereof. Preferable salts include ammonium sulfate, sodium sulfate, magnesium sulfate, aluminum sulfate, ammonium hydrogen phosphate, sodium hydrogenphosphate and potassium

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hydrogenphosphate. In the present invention, these salts may be each used as an aqueous solution thereof having a concentration of 15% or above.

A dispersant is present in the aqueous anionic salt solution in which the polymerization of the above monomers occurs. The dispersant is a water-soluble high molecular weight cationic polymer. The dispersant is soluble in the above-mentioned aqueous salt solution. The dispersant is preferably used in an amount of from 1 to 10% by weight based on the total weight of the monomers. The dispersant is composed of 20 mole % or more of cationic monomer units represented by the formula (II). Preferably the residual mole % is acrylamide or methacrylamide. The performance of the dispersant is not greatly affected by molecular weight. However, the molecular weight of the dispersant is preferably in the range of 10,000 to 10,000,000 daltons. According to one embodiment of the invention a multifunctional alcohol such as glycerin or polyethylene glycol is coexistent in the polymerization system. The deposition of the fine particles is smoothly carried out in the presence of these alcohols.

For the polymerizations a usual water-soluble radical-forming agent can be employed, but preferably water-soluble azo compounds such as 2,2'-azobis(2-amidinopropane) hydrochloride and 2.2'-azobis(N.N'-dimethyleneisobutylamine) hydrochloride are used.

According to one embodiment of the invention, a seed polymer is added before the beginning of the polymerization of the above monomers for the purpose of obtaining a fine dispersion. The seed polymer is a water-soluble cationic polymer insoluble in the aqueous solution of the polyvalent anionic salt. The seed polymer is preferably a

polymer prepared from the above monomer mixture by the process described herein.

Nevertheless, the monomer composition of the seed polymer need not always be equal to that of the water-soluble cationic polymer formed during polymerization. However, like the water-soluble polymer formed during polymerization, the seed polymer should contain at least 5 mole percent of cationic monomer units represented by the general formula (I). According to one embodiment of the invention, the seed polymer used in one polymerization reaction is the water-soluble polymer prepared in a previous reaction which used the same monomer mixture.

Examples

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The following examples are presented to describe preferred embodiments and utilities of the invention and are not meant to limit the invention unless otherwise stated in the claims appended hereto. In the following examples, common terms used throughout have the following meanings.

Microparticle A (colloidal silica)

Dispersed silica in water with a particle size of 4 nm.

Microparticle B

Copolymer of acrylic acid

Microparticle C (bentonite)

Hydrated suspension of powdered bentonite in water.

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Dispersion Polymers

Polymer A	10 mole% DMAEA.BCQ	RSV 19.6 dl/g
Polymer B	10 Mole % DMAEA.MCQ	RSV 21.4 dl/g
Polymer C	20 mole % DMAEA.MCQ	RSV 27.6 dl/g

Latex Polymer

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Polymer D 10 mole% DMAEA.MCQ RSV 19.7 dl/g

The Reduced Specific Viscosity (RSV) was measured at a concentration of

0.045% polymer in a solution of 0.125M NaNO₃ solution.

Britt Jar Test

The Britt Jar Test employed in Examples 1 to 3 used a Britt CF Dynamic

Drainage Jar developed by K. W. Britt of New York State University, which generally

consists of an upper chamber of about 1 liter capacity and a bottom drainage chamber, the

chamber being separated by a support screen and a drainage screen. Below the drainage

chamber is a downward extending flexible tube equipped with a clamp for closure. The

upper chamber is provided with a variable speed, high torque motor equipped with a 2
inch 3-bladed propeller to create controlled shear conditions in the upper chamber. The

test was conducted by placing the cellulosic stock in the upper chamber and then

subjecting the stock to the following sequence:

Time	Action
0 seconds	Commence shear stirring at 750 rpm, (add
	starch, if needed).
10	Add the cationic polymer, increase speed to
seconds	2000 rpm.
40	Reduce shear stirring to 750 rpm.
seconds	
50	Add the microparticle.
seconds	
60	Open the tube clamp to commence drainage,
seconds	and continue drainage for 30 seconds.

The material so drained from the Britt jar (the "filtrate") is collected and diluted with water to one-fourth of its initial volume. The turbidity of such diluted filtrate, measured in Formazin Turbidity Units or FTU's, is then determined. The turbidity of such a filtrate is inversely proportional to the papermaking retention performance; the lower the turbidity value, the higher is the retention of filler and/or fines. The turbidity values were determined using a Hach Spectrophotometer, model DR2000.

The turbidity values (in FTU) that were determined were converted to (Percent Improvement) values using the formula:

Percent Improvement = 100 X ($Turbidity_u$ - $Turbidity_t$)/ $Turbidity_u$

where $Turbidity_u$ is the turbidity reading result for the blank for which no polymer or microparticle, and wherein $Turbidity_l$ is the turbidity reading result of the test using polymer, or polymer and microparticle.

Filtration Test

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The filtration tests used in Examples 1 to 8 measured the drainage (water removal) rate of the test stock subjected to the various chemical treatments. A filtration cell, mounted upright on a stand, was used. The capacity of this cell is about 220 milliliters. A 200 mesh drainage screen (76µm screen with 8% opening) served as the filter medium. The stock was filtered by gravity. The filtrate was collected in a cup placed on a weighing balance below the cell. This balance was interfaced with a computer so that the displayed weight was recorded continuously over time. The computer automatically recorded the change of weight over time.

The cellulosic stock was treated in the aforementioned Britt jar. The treated stock was transferred to the cell and filtered until completion. The rate of filtrate collection is an indication of the drainage performance; the higher the filtrate collection rate, the higher is the improvement in drainage.

15 Test Stocks

Alkaline Test Stock

The cellulosic stock or slurry used in Examples 1 to 3 and 8 was comprised of 70 weight percent fiber and 30 weight percent filler, diluted to an overall consistency of 0.5 percent with formulation water. The fiber was a 60/40 blend by weight of bleached hardwood Kraft and bleached softwood Kraft, separately beaten to a Canadian Freeness value range of from 320 to 360 C.F.S. The filler was a commercial calcium carbonate, provided in dry form. The formulation water contained 60 ppm calcium hardness (added

as CaCl₂), 18 ppm magnesium hardness (added as MgSO₄) and 134 ppm bicarbonate alkalinity (added as NaHCO₃). The pH of the final thin stock was pH 7.2.

Acid Test Stock

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The cellulosic stock or slurry used in Examples 4 to 5 was comprised of 93 weight percent fiber and 7 weight percent filler, diluted to an overall consistency of 0.54 percent with formulation water. The fiber was a 50/50 blend by weight of bleached hardwood Kraft and bleached softwood Kraft, separately beaten to a Canadian Freeness value range of from 320 to 360 C.F.S. The fillers were clay as predispersed kaolin and titanium dioxide, commercially provided in dry form. The pH was adjusted to pH 4.00 using dilute sulfuric acid, following which alum (0.005% of final slurry) and sizing agent rosin (0.0025 wt% of final slurry) were added. The formulation water contained 60 ppm calcium hardness (added as CaCl₂). 18 ppm magnesium hardness (added as MgSO₄) and 134 ppm bicarbonate alkalinity (added as NaHCO₃).

Corrugated Coated Test Stock

The stock used in Examples 6 and 7 was obtained as thick stock (consistency of 4.11 %) from a paper mill. It was a mixture of OCC, newsprint, and boxboard. It was diluted to an overall consistency of 0.8% with formulation water containing 60 ppm calcium hardness (added as CaCl₂). 18 ppm magnesium hardness (added as MgSO₄) and 134 ppm bicarbonate alkalinity (added as NaHCO₃). The final pH of the thin stock was pH 6.5. The percent ash of the thin stock was 7.3 wt%.

Example 1

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Using the alkaline test stock described above, the Britt jar test, also described above was employed to determine the retention performances of dispersion Polymer A in comparison to the inverse emulsion Polymer D, with microparticle A as the microparticle. In each test, cationic potato starch was charged to the test stock in the amount of 10 lb/ton of dry weight of slurry solids. The various programs tested are shown below in Table 1. The test results are reported in Table 1 below as diluted filtrate turbidity values (FTU) and (Percent Improvement), as defined earlier, for each of the programs tested.

The drainage performance of these programs was measured for the same alkaline furnish using the filtration test described above. In each test starch was charged to the test stock in the amount of 10 lb/ton of dry weight of slurry solids. The results are shown for each of the programs tested in Figure 1 as graphs of collected filtrate weight versus time.

Example 2

Using the alkaline test stock described above, the Britt jar test, also described

above was employed to determine the retention performances of dispersion Polymer B in

comparison to the inverse emulsion Polymer D, with microparticle A as the

microparticle. In each test, cationic potato starch was charged to the test stock in the

amount of 10 lb/ton of dry weight of slurry solids. The various programs tested are shown below in Table 2. The test results are reported in Table 2 below as diluted filtrate turbidity values (FTU) and (Percent Improvement), as defined earlier, for each of the programs tested.

The drainage performance of these programs was measured for the same alkaline furnish using the filtration test described above. In each test starch was charged to the test stock in the amount of 10 lb/ton of dry weight of slurry solids. The results are shown for each of the programs tested in Figure 2 as graphs of collected filtrate weight versus time.

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Table I
Britt Jar Retention Tests
Alkaline Furnish

No.	Polymer	Polymer Dosage lb/ton	Microparticle A Dosage lb/ton	Turbidity (FTU)	Percent Improvement
	blank	0	0	359.5	-
1	Α	1.6	0	289	20
2	Α	1.6	2	84	77
3	D	1.6	0	291	19
4	D	1.6	2	162	55

Table II Britt Jar Retention Tests Alkaline Furnish

No.	Polymer	Polymer Dosage lb/ton	Microparticle A Dosage lb/ton	Turbidity (FTU)	Percent Improvement
	blank	0	0	359.5	
1	В	1.6	0	252	30
2	В	1.6	2	74	79
3	D	1.6	0	291	19
4	D	1.6	2	162	55

Example 3

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Using the alkaline test stock described above, the Britt jar test, also described above was employed to determine the retention performances of dispersion Polymer C in comparison to the inverse emulsion Polymer D, with microparticle A as the microparticle. In each test, cationic potato starch was charged to the test stock in the amount of 10 lb/ton of dry weight of slurry solids. The various programs tested are shown below in Table 3. The test results are reported in Table 3 below as diluted filtrate turbidity values (FTU) and (Percent Improvement), as defined earlier, for each of the programs tested.

Table III
Britt Jar Retention Tests
Alkaline Furnish

No.	Polymer	Polymer Dosage lb/ton	Microparticle A Dosage lb/ton	Turbidity (FTU)	Percent Improvement
	blank	0	0	359.5	
1	С	16	0	266	26
2	С	1.6	2	120	67
3	D	1.6	0	291	19
4	D	1.6	2	162	55

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Example 4

Using the acid test stock described above, the filtration test, also described above was employed to determine the drainage performances of dispersion Polymer A in comparison to the inverse emulsion Polymer D, with microparticle A as the microparticle. The results are shown for each of the programs tested in Figure 3 as graphs of collected filtrate weight versus time.

Example 5

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Using the acid test stock described above, the filtration test, also described above was employed to determine the drainage performances of dispersion Polymer A in comparison to the inverse emulsion Polymer D, with microparticle B as the microparticle. The results are shown for each of the programs tested in Figure 4 as graphs of collected filtrate weight versus time.

Example 6

Using the corrugated coated test stock described above, the filtration test, also described above was employed to determine the drainage performances of dispersion Polymer A. with microparticle A as the microparticle. The results are shown for each of the programs tested in Figure 5 as graphs of collected filtrate weight versus time.

15 Example 7

Using the corrugated coated test stock described above, the filtration test, also described above was employed to determine the drainage performances of dispersion Polymer A. with microparticle B as the microparticle. The results are shown for each of the programs tested in Figure 6 as graphs of collected filtrate weight versus time.

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Example 8

Using the alkaline test stock described above, the filtration test, also described above was employed to determine the drainage performances of dispersion Polymer A in comparison to the inverse emulsion Polymer D, with microparticle C as the microparticle. In each test, cationic potato starch was charged to the test stock in the amount of 10 lb/ton of dry weight of slurry solids. The results are shown for each of the programs tested in Figure 7 as graphs of collected filtrate weight versus time.

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Changes can be made in the composition, operation and arrangement of the method of the present invention described herein without departing from the concept and scope of the invention as defined in the following claims:

Claims

- 2 **1.** A papermaking process comprising forming an aqueous cellulosic papermaking slurry, subjecting the slurry to one or more shear stages, adding to the slurry a mineral
- filler prior to at least one of the shear stages, adding to the slurry after the addition of the mineral filler and prior to at least one of the shear stages
- an effective amount of a cationic dispersion polymer selected from the group consisting of copolymers of acrylamide and dimethylaminoethylacrylate methyl chloride
- 8 quaternary salt, dimethylaminoethylmethacrylate methyl chloride quaternary salt, dimethylaminoethylacrylate benzyl chloride quaternary salt,
- dimethylaminoethylmethacrylate benzyl chloride quaternary salt and diallyldimethylammonium chloride;
- shearing the slurry;
 - adding a microparticle selected from the group consisting of a copolymer of
- acrylic acid. bentonite and silica sol;
 - draining the slurry to form a sheet; and
- drying the sheet to form a paper sheet.
 - 2. The process of claims 1 wherein the dispersion polymer has a molecular weight of
- 2 from about 10,000 to 10,000,000 daltons.
 - 3. The process of claim 1 wherein the slurry is drained on a papermaking screen and
- 2 is pumped to the site of the papermaking screen prior to draining.

- 4. The process of claim 1 wherein the slurry is selected from the group consisting of
- an acid pulp slurry, alkaline chemical pulp slurry, thermo-mechanical pulp slurry, mechanical pulp slurry recycle pulp slurry and ground wood pulp slurry.
 - 5. The process of claim 1 wherein the mineral filler is selected from the group
- 2 consisting of titanium dioxide, clay and, tale calcium alkaline carbonate.
 - 6. The process of claim 1 wherein the mineral filler is added to the slurry in an
- 2 amount of from about 2 to about 50 parts per hundred parts by weight of dry pulp contained in the slurry.
 - 7. The process of claim 1 wherein the concentration of methyl chloride quaternary
- 2 salt is from about 1.0 to about 30 mole percent.
 - 8. The process of claim 7 wherein the concentration of methyl chloride quaternary
- 2 salt is from about 10 to about 20 mole percent.
 - 9. The process of claim 1 wherein the concentration of benzyl chloride quaternary
- 2 salt is from about 1.0 to about 35 mole percent.
 - 10. The process of claim 9 wherein the concentration of benzyl chloride quaternary
- 2 salt is from about 10 to about 20 mole percent.













