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(54) **RETENTION SYSTEM**

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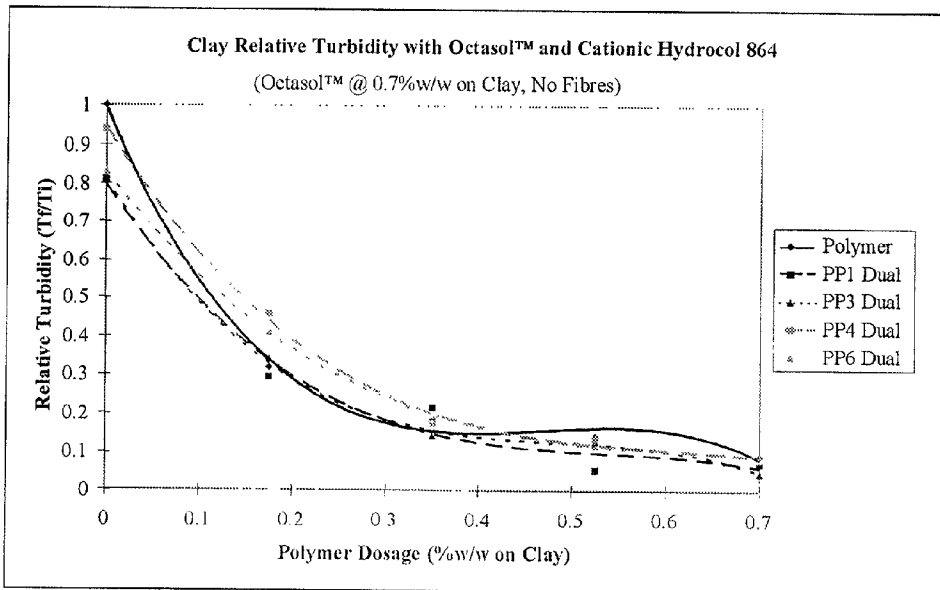
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(57) **ABSTRACT**

There is provided a method for flocculating one or more particulate materials present in a dispersion, the method comprising contacting the dispersion with (i) fibrous cationic colloidal alumina microparticles; and (ii) a cationic polymer and/or a non-ionic polymer.

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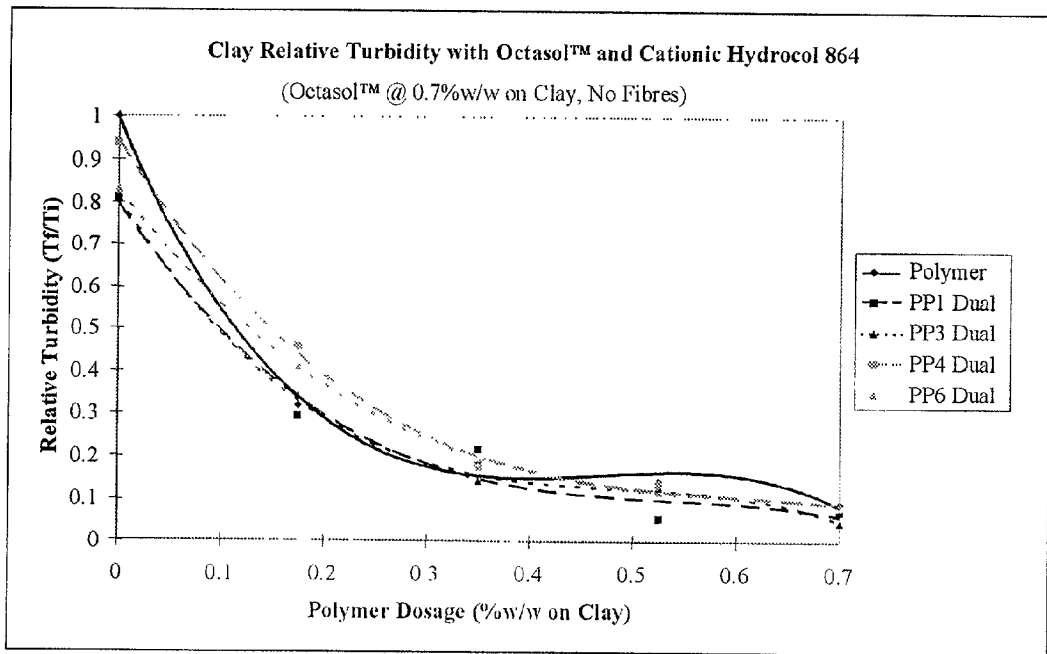


Figure 1. Clay Relative Turbidity with Octasol™ and Cationic Hydrocol 864

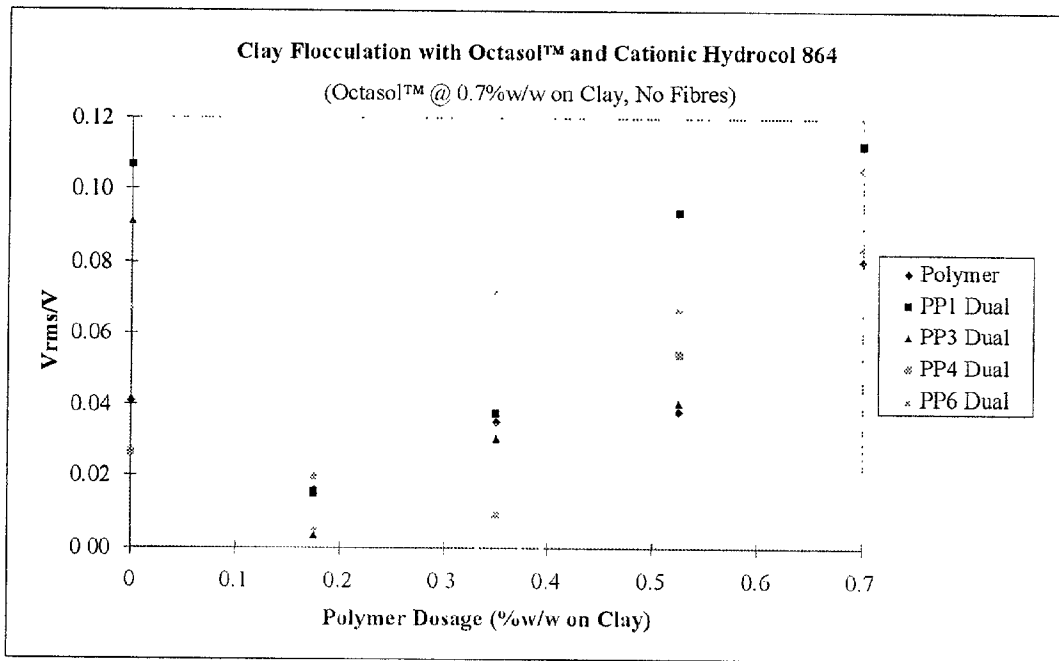


Figure 2. Clay Flocculation with Octasol™ and Cationic Hydrocol 864

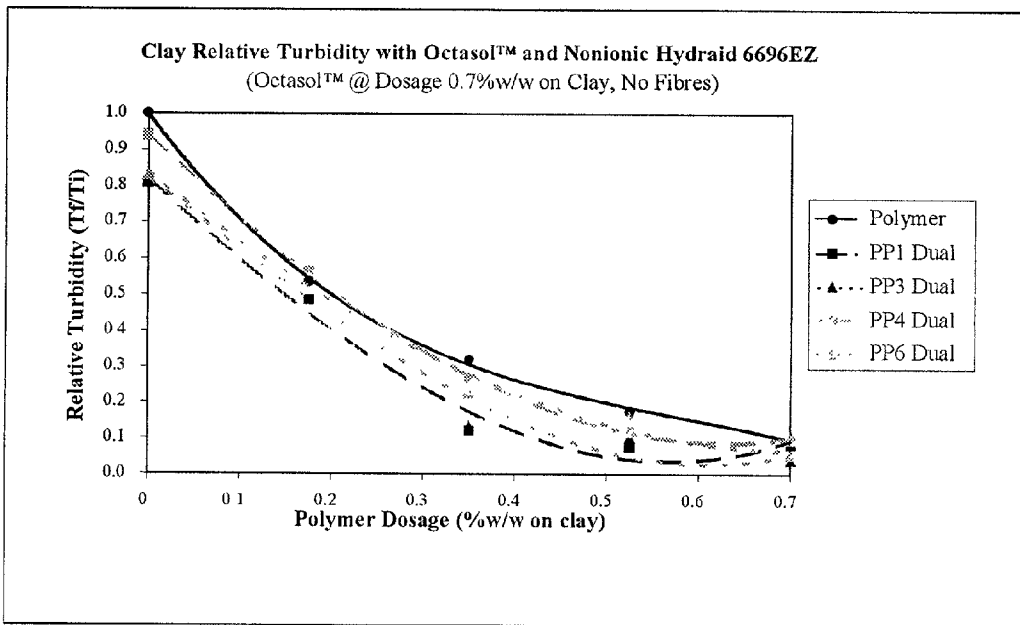


Figure 3. Clay Relative Turbidity with Octasol™ and Non-ionic Hydrad 6696EZ

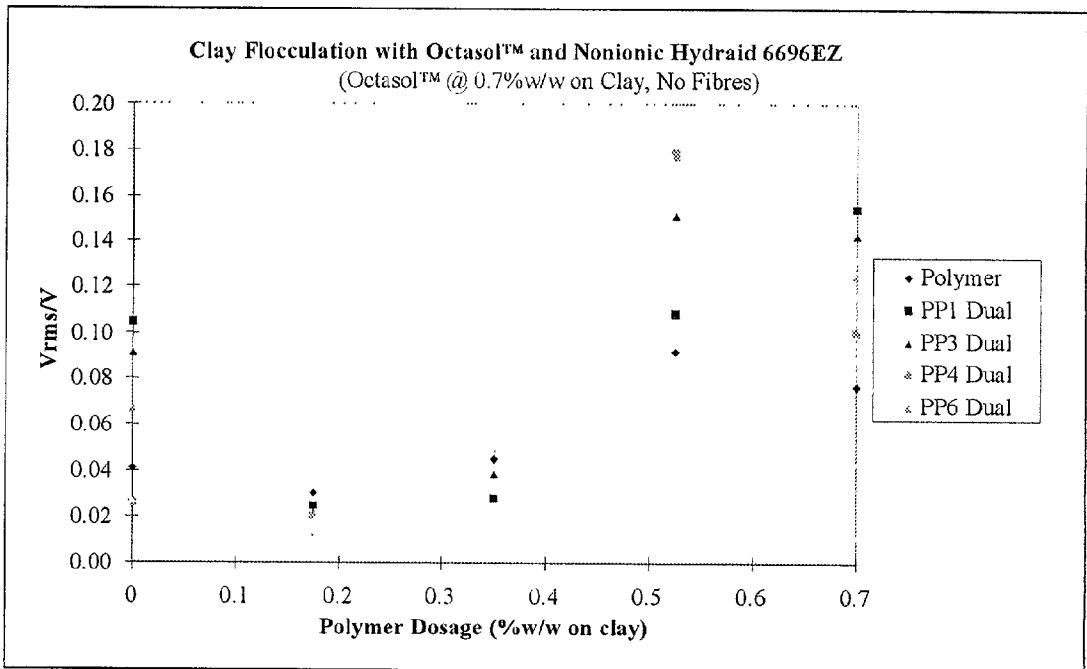


Figure 4. Clay Flocculation with Octasol™ and Non-ionic Hydrad 6696EZ

RETENTION SYSTEM

[0001] The present invention relates to a retention system. In particular the present invention relates to a method for flocculating one or more particulate materials present in a dispersion. The present invention utilises fibrous cationic colloidal alumina microparticles.

[0002] Retention aids are employed to bond papermaking stock components together and reduce loss to white water by either coagulation or flocculation of small particles, and then entrapment or attachment of the flocs onto the larger cellulosic fibres. Papermaking stock is essentially a suspension of particles ranging from 2-3 mm down to a few nanometers in dimensions, the distribution of which depends on the type of filler used and the degree of refining and cleanliness of the pulp.

[0003] Charge neutralisation is the predominant mechanism in coagulation of small particles in papermaking stock. Retention has been recognised for many years as one of the most important aspects of papermaking. Careful application of retention aids may provide many process benefits and economic benefits, such as optimised wet-end running conditions, improved paper properties, maximised raw material yield, and reduced effluent load.

[0004] In recent years trends in paper and board production have contributed to the need for improved retention systems. These trends have included the need for better paper quality, higher machine speeds, greater filler levels, the use of mechanical pulps and recycled fibres and of course environmental pressures. This drive to improve sheet quality, increase paper machine productivity, and control rising furnish costs continues to escalate the demands placed on wet end chemistries.

[0005] Papermaking often compromises one desirable benefit in order to gain more of another desired benefit. An example of this is use of single high molecular weight polymer drainage/retention aids on paper machines. Simple (single polymer) retention aid systems often lack flocculation power under highly turbulent conditions. To obtain high retention of fines on high-speed paper machines, dual-polymer or microparticle retention systems have been developed. Dual-polymer retention aid systems have gained popularity particularly for the manufacture of low basis weight papers (e.g., tissue paper) or filler-containing papers (fine paper, magazine paper) under severe retention conditions.

[0006] Dual-polymer systems have been used for many years with varying degrees of success. Generally speaking, they have comprised of a combination of the low molecular weight cationic polymer, such as a polyamine, and a high molecular weight polyacrylamide. The cationic polymer is normally added early in the stock to neutralise much of the anionic material present and create an environment in which the polyacrylamide can function effectively. The polyacrylamide functions by bridging flocculation and there may be a need to compromise between optimum retention and paper properties.

[0007] Microparticulate retention aid systems are normally based on negatively charged inorganic colloids and positively charged synthetic or natural polymers. The main

difference between the systems is usually the type of microparticle used. Currently used commercial anionic microparticulate retention aid systems include

[0008] Compozil—colloidal silica used in conjunction with cationic starch (available from EKA Nobel AB, Sweden); and

[0009] Hydrocol—sodium montmorillonite (bentonite clay) used with cationic polyacrylamide (available from Ciba, UK).

[0010] The performance of chemical flocculants as retention aids in papermaking may depend on factors such as the point of addition and the shear levels experienced. A high shear level often leads to the break-up of flocs formed, which is beneficial for paper formation, but it also leads to the detachment of fillers deposited on fibres and thus reduces filler retention. A high degree of reflocculation, especially with regard to the flocculation of fillers to fibres when the shear subsides is therefore a desirable characteristic of a retention aid system. This ability to reflocculate after floc breakage is a feature normally ascribed to the microparticle-containing flocculant systems.

[0011] In commercial microparticle systems, strong flocculation of fillers and fibres is first achieved by addition of the cationic component, which is normally a high molecular weight polymer (e.g., cationic starch or cationic polyacrylamide). After periods of high shear, e.g., in pumps, screens, and pipe constrictions, during which flocs are partly disrupted to floc fragments, the flocs can reform when the high shear subsides. Close to the headbox, the negatively charged particle sol is added, which leads to greater flocculation through charge interaction with the cationic polymers adsorbed onto particle surfaces.

[0012] The results of microparticulate coagulation can be very significant and even dramatic when compared to standard retention aid systems. They may include improved retention (stronger flocculation), faster dewatering (drainage) on the wire and press section of the paper machine, greater overall control and flexibility and improved paper properties.

[0013] The retention of filler particles is of great economic and process benefit. However, it also poses a complicated problem and it is difficult to predict the effect of changes in the wet-end of the papermaking system on the retention of filler. Selection of the best retention aid programme depends on the type of fillers used, filler loading, anionic trash content, type and amount of starch, whether the sheet is sized or not, and the mechanical shear of the machine, etc. Consideration also has to be given to the level of retention desired, and the corresponding loss in formation allowable. Increasing the use of retention agents leads to higher chemical costs, so the payback in terms of increased productivity and filler saving is a factor. Reliable selection of a suitable retention aid system is largely dependent on the chemistry of the system.

[0014] To-date much of the literature on microparticle applications in the papermaking industry has concerned anionic microparticles used in conjunction with a high molecular weight cationic polymer. However, a synthetic cationic polymeric microparticle with a range of particle sizes and charge densities has been used as a retention aid for negatively charged fibres and positively charged precipitated

calcium carbonate particles [H Ono and Y Deng, 1996 CPPA International Paper and Coating Chemistry Symposium, Canada, pp 175-184, Jun. 11-13 (1996)].

[0015] Colloidal silica has previously been treated to make it cationic, and used as a retention aid system in conjunction with either an anionic or cationic polymer [K Moberg, TAPPI Papermakers Conference Proceedings, Volume 1, 115-127, (April 1993), TAPPI Press, Atlanta, Ga.]. This system has not been commercialised.

[0016] Cationic colloidal silica microparticles, where aluminium atoms have replaced some of the surface silica, are also known. U.S. Pat. No. 4,798,653 describes a system where anionic polyacrylamide is used with a cationic silica sol, where the polyacrylamide dosage ranges from 0.01 to 1.0% w/w, and the microparticle between 0.01 and 2.0% w/w. It is recommended that the polymer has a medium to high molecular weight and low charge density.

[0017] A similar cationic colloidal silica is described in U.S. Pat. No. 4,946,557. This teaching uses a cationic polyacrylamide. The order of addition of the two components is largely influenced by the size of the silica particles. Better results are reported with small silica particles when the polymer is added first, but for larger particles the silica should be added first.

[0018] Silica-containing anionic microparticulate systems can be expensive in use. Moreover, silica sols rendered cationic by incorporation of polyvalent metallic ions (e.g., Al^{3+}) in the silica surface are unstable with respect to disproportionation under normal conditions of use and either have to be prepared and used quickly or require the use of additional stabilising components such as phosphate, carbonate, borate and the like. [U.S. Pat. No. 4,798,653; U.S. Pat. No. 4,946,557].

[0019] A major disadvantage of bentonite-containing anionic microparticulate systems is that bentonite (Na^+ -montmorillonite) is classed as a carcinogen, so particular care must be taken in its handling and transportation [K Johnson, In: 51st APPITA Annual General Conference Proceedings, pp 325-328, Apr. 28-May 2, 1997].

[0020] The present invention alleviates problems of the prior art.

[0021] Aspects of the present invention are defined in the appended claims.

[0022] The present invention aims to provide a cationic fibrous alumina colloidal compound or composition useful in retention, drainage and dewatering of papermaking that is stable in storage, safe to use and cost-effective.

[0023] The present invention aims to provide a method to improve the effectiveness in retaining the fine mineral fillers such as clay or calcium carbonate with paper fibres using a new inorganic cationic microparticulate retention system based on a synthetic water-based fibrous colloidal alumina with a high surface charge.

[0024] The present invention aims to provide a drainage/retention aid that is less shear- and pH-sensitive as compared to conventional high molecular weight cationic acrylamide-derived polymers.

[0025] The present invention may provide a composition comprising (i) fibrous cationic colloidal alumina microparticles; and (ii) a non-ionic polymer and/or cationic polymer, and a method for using the same or the constituents thereof to improve the effectiveness in retaining the fine mineral fillers such as clay or calcium carbonate with paper fibres using a new retention system based on a synthetic water-based fibrous colloidal alumina with a high surface charge.

[0026] The present invention may provide a drainage/retention aid composition comprising (i) fibrous cationic colloidal alumina microparticles; and (ii) a cationic polymer and/or a non-ionic polymer and a method for using the same or the constituents thereof that is less shear- and pH-sensitive as compared to conventional drainage/retention aids comprising high molecular weight cationic acrylamide-derived polymers.

[0027] The present invention may provide a new inorganic cationic microparticulate retention composition comprising (i) fibrous cationic colloidal alumina microparticles; and (ii) a cationic polymer and/or a non-ionic polymer, and a method for using the same or the constituents thereof to improve the effectiveness in retaining fine mineral fillers such as clay or calcium carbonate with paper fibres.

[0028] The present invention may provide a synthetic water-based colloidal alumina composition with high positive surface charge and controllable particle size and a method for using the same or the constituents thereof. The composition may be useful in wet-end papermaking processes, particularly for the retention of fine particulate fillers such as clay or calcium carbonate.

[0029] The flocculant system of the present invention (i.e. a composition comprising (i) fibrous cationic colloidal alumina microparticles; and (ii) a cationic polymer and/or a non-ionic polymer and the method for using the same) was found to be relatively resilient to shear stress and insensitive to common papermaking process pH variations. This new flocculant system and method was found to give comparable results to a commercial anionic microparticle system in terms of retention and sheet formation when compared on a pilot paper machine and in the laboratory.

[0030] The flocculant system and method of the present invention is stable under normal conditions of storage and use and does not present handling problems nor require application of additional stabilising components.

[0031] Unlike most other microparticles used in the papermaking industry, the flocculant system of the present invention is cationic and fibrous in shape. Consequently, there is little or no conformational changes of the alumina fibres once adsorbed or for reduced effects from penetration into the pores of cellulosic fibres, due to the rigid structure of the alumina particles.

[0032] Furthermore, the other advantages of using the flocculant system of the present invention instead of water-soluble retention aids include more effective patch formation on adsorption and higher charge density which may be easily controllable by the synthesis chemistry.

[0033] The total cationic demand of the pulp furnish in papermaking can be reduced by using cationic microparticles and there is no accumulation of the microparticles in a closed white water system because of the strong adsorption

of the cationic sol onto negatively charged substrates. The presence of anionic polymer will form a co-bridge with the adsorbed cationic microparticle, which will significantly increase flocculation efficiency.

[0034] Alumina

[0035] In the present specification by the term "fibrous" it is meant products which are composed of fibres.

[0036] The term "fibre" is used in accordance with the customary meaning and includes fibrils and aggregates of fibrils which form relatively long thread-like structures.

[0037] The term "fibril" is used to refer to products which when viewed under the electron microscope appear to be single particles as opposed to structures formed of aggregates of a number of separate members. The term "fibrous" encompasses materials in which the fibrils are discrete and relatively unaggregated.

[0038] Preferably the fibrils are particles with an aspect ratio of $\geq 3:1$, preferably $\geq 20:1$ and/or preferably with a uniformity of diameter along the length of the particle. Depending on the specific process conditions used in preparation, the fibrous alumina may be in the form of fibrils or small fibres which have one or more dimensions in the colloidal range. Such fibrils can form aggregates of larger fibres made up of assemblies of fibrils disposed parallel to the length of the fibres. Such fibrous alumina as used in the present specification will preferably have the boehmite crystal lattice.

[0039] In the present specification by the term "cationic" it is meant that the compound/composition is ionic and has a positive charge.

[0040] In the present specification by the term "colloidal" it is meant a heterogeneous system consisting of one substance (the disperse phase) finely divided and distributed throughout a second substance (the continuous phase). Generally speaking, the disperse phase has dimensions in the range of 1 to 1000 nm (1 μm).

[0041] In the present specification by the term "alumina" it is meant any compound consisting essentially of aluminium and oxygen (i.e. aluminium oxide).

[0042] The alumina may be α -alumina, β -alumina, γ -alumina or a mixture thereof. Preferably the alumina is acicular (fibrous) boehmite alumina (α -alumina). In this aspect preferably the acicular (fibrous) boehmite alumina (α -alumina) may be obtained under acidic hydrothermal conditions (according to U.S. Pat. No. 2,915,475 or WO 97/41063).

[0043] Preferably the alumina is fibrillar hydrated α -alumina, known as boehmite alumina (formula: $\alpha\text{-Al}(\text{OH})_3$) or basic alumina monohydrate, optionally obtained in accordance with a process described in WO 97/41063. The fibrils each consist of a crystal of boehmite alumina. The particles contain surface-bound acetate groups (chemisorbed CH_3COO^-) and have a high positive surface charge which is responsible for the colloidal stability of the system and the other useful properties of the product. In water, these cationic boehmite colloid particles are stabilised by electrical double-layer repulsion.

[0044] In the present specification by the term "microparticles" it is meant particles having an average maximum dimension of 1000 nm.

[0045] Preferably the "microparticles" are non-deformable particles (spherical, plate-like or fibrous in shape)

[0046] Neither the particle size nor surface charge of the cationic microparticles is, alone, critical to the performance of the present invention. The present invention is advantageous provided the microparticles can disperse and be dispersed in the suspension, such as an aqueous pulp suspension, and can readily interact with the components which are present in the suspension.

[0047] The microparticles of the present invention may form or be in the form of water-insoluble dispersions. In such dispersions the microparticles may exist both as discrete particles and aggregates of said particles.

[0048] In a preferred aspect the microparticles have surface area of greater than 50 m^2/g .

[0049] The microparticles may be in one aspect of the present invention inorganic colloidal particles.

[0050] The particle size nor surface charge of the cationic microparticles is not, per se, critical to the invention provided that the microparticles can disperse and be dispersed into an aqueous pulp suspension and readily interact with the anionic components which are present in the aqueous pulp suspension or the non-ionic and cationic substances of the invention.

[0051] Preferably the alumina is prepared according to the methods exemplified in WO 97/41063 or PCT/GB99/02841.

[0052] Preferably the alumina is made from isolated solid basic aluminium acetate or other similar aluminium containing salt or starting material under acidic hydrothermal conditions.

[0053] Cationic/Non-Ionic Polymer

[0054] The cationic polymer may be selected from polyacrylamide, polyethylene imine, polyamines, polycyandiamide formaldehyde polymers, amphoteric polymers, diallyl dimethyl ammonium chloride polymers, diallylaminoalkyl (meth)acrylate polymers, and dialkylaminoalkyl (meth)acrylamide polymers, a copolymer of acrylamide and diallyl dimethyl ammonium chloride, a copolymer of acrylamide and dialkylaminoalkyl (meth)acrylates, a copolymer of acrylamide and dialkylaminoalkyl (meth)acrylamides, a polymer of dimethylamine and epichlorohydrin, and natural and semi-synthetic polymers including cationic starch.

[0055] The cationic polymer may be selected from water-soluble copolymers of acrylamide or methacrylamide which carry or are capable of carrying a cationic charge when dissolved in water. The cationic copolymers include the following examples: copolymers of (meth)acrylamide with dimethylaminoethyl methacrylate (DMAEM), dimethylaminoethyl acrylate (DMAEA), diethylaminoethyl acrylate (DEAEA), diethylaminoethyl methacrylate (DEAEM) or their quaternary ammonium forms made with dimethyl sulfate or methyl chloride, Mannich reaction modified polyacrylamides, diallylcyclohexylamine hydrochloride (DACHA HCl), diallyldimethylammonium chloride (DADMAC), methacrylamidopropyltrimethylammonium chloride (MAPTAC) and allyl amine (ALA).

[0056] Copolymers of dialkyl aminoalkyl(meth)acrylates (in cationic form) and (meth)acrylamide may be used as the cationic polymer of the present invention. As discussed in

U.S. Pat No. 5,571,380 it is known in the polymer art that acrylamide-containing polymers may contain a minor amount of acrylic acid or acrylic acid salt mer units due to inadvertent hydrolysis of some acrylamide mer units, even though the polymer is not subjected to conditions that would hydrolyze a substantial proportion of the acrylamide. It is believed that the presence of a minor proportion of hydrolyzed acrylamide mer units (or hydrolyzed methacrylamide mer units) will disable the performance of a cationic polymer that otherwise meets the requirements for use in the present process. Further, it is believed that the presence of up to about 5 mole percent anionic mer units in the polymer is not harmful to the polymer's performance. Hence the term "cationic" as used herein includes polymers containing a minor amount of anionic mer units, although of course the primary nature of the polymer remains cationic.

[0057] The charge density of the cationic polymer may be no greater than 60%.

[0058] The non-ionic polymer may be selected from polymers formed from at least one monomer chosen from acrylamide, methacrylamide, and N-tertiary butyl acrylamide.

[0059] The molecular weight of the cationic/non-ionic polymer may be no greater than 30,000,000, preferably 500,000 to 30,000,000, more preferably 1,000,000 to 30,000,000, more preferably 5,000,000 to 30,000,000.

[0060] Composition

[0061] Preferably the cationic/non-ionic polymer:alumina ratio may be from 10:1 to 1:10, more preferably from 2:1 to 1:2, yet more preferably approximately 1:1.

[0062] The method of the present invention may contact one or more additional components with the dispersion. These components may also be present in the composition of the present invention. These components include cationic starch (including potato starch, and maize starch), fillers, sizing additives (including alum and rosin), pitch control agents, extenders (including anilex), biocides and brightening agents.

[0063] Possible inorganic or mineral fillers include alkaline carbonates, such as calcium carbonate, titanium dioxide, kaolin clay, and the like. The amount of inorganic filler typically employed in a papermaking stock is from about 10 to 30 parts by weight of the filler, as CaCO_3 , per hundred parts by weight of dry pulp in the slurry. The amount of filler may, at times, be as low as about 5, or even about 2, parts by weight, or as high as about 50, or even 80 or 90, parts by weight, per hundred parts by weight of dry pulp in the slurry.

[0064] Method

[0065] As described above the flocculant system and method of the present invention was found to be relatively resilient to shear stress and insensitive to pH variations. Therefore the components of the present invention may be contacted with the dispersion at any point of a paper making process including contact with the thick stock, the thin stock or at high shear points. The dual system of the present invention was found to give comparable results to a commercial anionic microparticle system in terms of retention and sheet formation when compared on a pilot paper machine and in the laboratory.

[0066] The dosage amount of cationic microparticles and/or the cationic polymer and/or non-ionic polymer, used in this invention, is not, per se, critical to the performance of the present invention. Generally the dosage is controlled to be in an amount to flocculate the suspended matter. Those of ordinary skill in the art can readily determine suitable dosage amounts by conventional means. Thus, whilst the exact dosage amount for a particular system can vary widely depending on the nature of the system, the amount of suspended matter and the degree of drainage or retention desired. In general the dosage, based on the dry weight of suspended matter amount, can range:

[0067] for the alumina, from 0.005 to 3% w/w, preferably from 0.01 to 2% w/w

[0068] for the cationic polymer and/or non-ionic polymer combined, from 0.001 to 0.5 weight percent, preferably from 0.01 to 0.3% w/w.

[0069] The alumina and the cationic polymer and/or non-ionic polymer may be contacted with the dispersion in any order. For example, the dispersion may be (i) contacted with the alumina and subsequently with the cationic polymer and/or non-ionic polymer, (ii) contacted with the cationic polymer and/or non-ionic polymer and subsequently with the alumina, (iii) simultaneously contacted with the alumina and the cationic polymer and/or non-ionic polymer. The order of addition of the alumina and the cationic polymer and/or non-ionic polymer may have some influence on the obtained effect. In a preferred embodiment of this invention the alumina is generally added first and the cationic polymer and/or non-ionic polymer added subsequently.

[0070] The method of the present invention can be carried out over a wide pH range, for example at a pH of from 3 to 10. In a preferred aspect, the suspension has a pH of from 4 to 9.

[0071] Paper/Pulps

[0072] The present invention is suitable for use with pulps of both hardwoods, softwoods and non-wood (e.g. straw) or combinations thereof. Pulps of the chemical, mechanical, recycled, semi-chemical or thermomechanical types are suitable for treatment in accordance with the present process.

[0073] The pulp may have a net charge which anionic, cationic or neutral.

[0074] The dispersion of the present invention may be pulp stock of various concentration. The pulp stock may have a concentration of pulp of up to 20 wt. %. The pulp stock may be a thin stock (for example having a concentration of 1-2 wt. %) or a thick stock (for example having a concentration of 3-5 wt. %).

[0075] The present invention is suitable for use in the preparation of a wide range of paper types including newsprint, fine paper and board.

[0076] We have found the present invention to be advantageous in providing useful wet-end papermaking properties, particularly for the retention of fine particulates.

[0077] The invention will now be described, by way of example only, with reference to the accompanying drawings in which:

[0078] FIG. 1 shows a graph;

[0079] FIG. 2 shows a graph;

[0080] FIG. 3 shows a graph; and

[0081] FIG. 4 shows a graph.

[0082] The following preparations and examples are included herein as further description and are illustrative of the present invention.

EXAMPLES

[0083] Flocculation Experiments

[0084] Octasol™ is a cationic colloidal alumina marketed by The Associated Octel Company Limited, UK. A Photometric Dispersion Analyser (PDA 2000, Rank Brother, UK) and Dynamic Drainage Jar (DDJ) were used to examine the effectiveness of different Octasol™ samples at flocculating filler particles, in particular clay, in both the absence and presence of papermaking fibres. The use of Octasol™ in conjunction with a range of different polymers was examined.

[0085] The polymers used were:

TABLE 1

Polymer Product Description			
Polymer Type	Commercial Name	Charge Density	Molecular Weight
Non-ionic Polyacrylamide	Calgon Hydrad 6696EZ	N/A	High
Cationic Polyacrylamide	Allied Colloids Hydrocol 864	High Cationic	High

[0086] The flocculation studies carried out were:

[0087] 1. All Octasol™ samples with clay alone, at dosages of 0.1% to 3.0% w/w on clay, in the absence of fibres. An optimum Octasol™ dosage was determined for the basis of the experiments, and the relationship between Octasol™ particle size, electrophoretic mobility and flocculating ability was examined.

[0088] 2. At the optimum dosage from Step 1, four Pilot Plant Octasol™ samples were used with a non-ionic and cationic polymer, increasing the ratio of polymer to Octasol™ from 0.25:1 to 1:1. Clay was used in the absence of fibres. The order of component addition was also examined, initially by looking at the effect on one Octasol™ sample. Once an optimum ratio of polymer: Octasol™ had been determined a more detailed look at the effect of addition order was carried out.

[0089] 3. At the dosages, ratios and addition orders predefined in Step 2, four Pilot Plant samples were used with the non-ionic and cationic polymers with both clay and fibres. The polymers were the same as those used in Step 2, and detailed in Table 1.

Example 1

Clay Flocculation Induced by Octasol™ and Cationic Polymer Cationic Polymer Dosage

[0090] The Octasol™ dosage was held constant at 0.7% w/w on clay and the cationic polymer dosage varied between 0-0.7% w/w on clay. The effect of the use of the polymer alone at each dosage was also examined. The cationic polymer used was Hydrocol 864, a high molecular weight polyacrylamide (12 million) with a high charge density of about 40% DS.

[0091] FIG. 1 for the cationic polymer shows that although the turbidity of the dual component system is improved over the Octasol™ alone, and at the higher dosages of polymer that there is moderate synergy between the polymer and Octasol™.

[0092] FIG. 2 shows the relative floc sizes of the cationic polymer dual component system using the V_{rms}/V calculations. It can be seen that at the lower polymer dosages of between 0.1-0.4% w/w on clay (ratios 1:4 and 1:2), the calculated floc size from V_{rms}/V is smaller than that when Octasol™ is used alone. As the polymer dosage increases above this, the floc size grows, until at the highest dosage studied where there appears to be floc shrinkage evident.

[0093] Addition Order

[0094] The effect of the addition order was examined at ratios 1:2 for samples PP3, 4 and 6, and at 3:4 for sample PP1, since at these dosages some moderate synergy was observed between the two components. For all four Pilot Plant Octasol™ samples studied, adding Octasol™ after the cationic polymer gave a quicker response than if Octasol™ is added to the clay first, but with little difference in the final turbidity, as seen in Table 2.

[0095] The speed of response in Table 2 was calculated by the increase in DC value of the PDA output between 120 and 130 seconds.

TABLE 2

	Comparison of Addition Order with Octasol™ and Cationic Hydrocol 864							
	Speed of Response (dDC/dt)*				Final Relative Turbidity			
	PP1	PP3	PP4	PP6	PP1	PP3	PP4	PP6
Octasol™ Added First	0.035	0.027	0.011	0.032	0.09	0.11	0.14	0.12
Octasol™ Added Second	0.151	0.195	0.778	0.856	0.05	0.14	0.18	0.19

*dt = 10 Seconds

[0096] Effect of Octasol™ Properties

[0097] Table 3 shows a summary of the final relative turbidity and V_{rms}/V values for when the cationic Hydrocol 864 is used in conjunction with Octasol™. For this data, the polymer was added as the first component and the polymer: Octasol™ ratio was 1:2 with Octasol™ at 0.7% w/w on clay, even for PP1.

TABLE 3

Comparison of Octasol™ and Cationic Hydrocol 864 Induced Clay Flocculation					
	PP1	PP3	PP4	PP6	Hydrocol 864
Mobility ($\mu\text{m.cm/Vs}$)	6.240	6.16	7.750	6.31	
Particle Size (μm)	1.524	1.49	1.491	0.174	
Relative Turbidity	0.220	0.14	0.180	0.190	0.19
V_{rms}/V	0.110	0.03	0.010	0.070	0.04

Example 2

Clay Flocculation Induced by Octasol™ and Non-ionic Polymer Non-ionic Polymer Dosage

[0098] The Octasol™ dosage was held constant at 0.7% w/w on clay and the non-ionic polymer dosage varied between 0-0.7% w/w on clay. The effect of the use of the polymer alone at each dosage was also examined. The non-ionic polymer used was Hydrad 6696EZ, a very high molecular weight polyacrylamide.

[0099] FIG. 3 shows the relative turbidity of the clay suspension with varying non-ionic polymer dosage. As can be seen, the addition of the non-ionic polymer reduced the turbidity below that for the single Octasol™ system with no polymer. There is a little synergistic effect observed between the two components, as the turbidity of the dual component system is only slightly reduced below that of the polymer alone. The best synergy is perhaps seen at polymer: Octasol™ ratio of 1:2.

[0100] FIG. 4 shows the relative floc sizes of the non-ionic polymer dual component systems respectively using the V_{rms}/V calculations. It can be seen that at the lower polymer dosages of between 0.1-0.4% w/w on clay (ratios 1:4 and 1:2) the calculated floc size is smaller than that when Octasol™ is used alone. As the polymer dosage increases above this, the floc size grows, until at the highest dosage studied where the flocs appear to shrink.

[0101] Addition Order

[0102] The effect of the order of addition of the two components was studied at polymer: Octasol™ ratio of 1:2, since at these dosages the greatest synergy between components was observed.

[0103] For all four Pilot Plant Octasol™ samples studied, adding Octasol™ after the non-ionic polymer gave a quicker response than if Octasol™ is added to the clay first, although a slightly higher final relative turbidity was obtained with samples PP4 and PP6, as seen in Table 4.

[0104] The speed of response in Table 4 was calculated by the increase in DC value of the PDA output between 120 and 130 seconds.

TABLE 4

	Speed of Response (dDC/dt)*				Final Relative Turbidity			
	PP1	PP3	PP4	PP6	PP1	PP3	PP4	PP6
Octasol™ Added First	0.029	0.022	0.005	0.031	0.19	0.19	0.20	0.14
Octasol™ Added Second	0.099	0.098	0.755	0.799	0.12	0.13	0.27	0.23

*dt = 10 Seconds

[0105] Effect of Octasol™ Properties

[0106] Table 5 shows a summary of the final relative turbidity and V_{rms}/V values for when the non-ionic Hydrad 6696EZ is used in conjunction with Octasol™. For this data, the polymer was added as the first component and the polymer: Octasol™ ratio was 1:2 with Octasol™ at 0.7% w/w on clay.

TABLE 5

Comparison of Octasol™ and Non-ionic Hydrad 6696EZ Induced Clay Flocculation					
	PP1	PP3	PP4	PP6	Hydrocol 6696EZ
Mobility ($\mu\text{m.cm/Vs}$)	6.240	6.16	7.750	6.31	
Particle Size (μm)	1.524	1.49	1.491	0.174	
Relative Turbidity	0.120	0.13	0.270	0.230	0.32
V_{rms}/V	0.030	0.04	0.050	0.050	0.05

Example 3

Clay Flocculation in the Presence Of Fibres Flocculation Induced by Octasol™ and Polymers

[0107] The four Pilot Plant Octasol™ samples, PP1, PP3, PP4 and PP6, used previously were used at a dosage of 0.7% w/w on clay (0.14% w/w on o.d. fibre) as part of a dual component flocculation system with the non-ionic and cationic polymers, for clay in the presence of fibres.

[0108] Octasol™ and Cationic Polymer

[0109] Cationic Hydrocol 864 polymer was used with Octasol™ in this study. The Octasol™ dosage was fixed at 0.7% w/w on clay, and the polymer at 0.35% w/w on clay for PP3, PP4 and PP6, and at 0.525% w/w on clay for PP1, giving a polymer: Octasol™ ratio of 1:2 (or 3:4 for PP1). In each case, the cationic polymer was added to the pre-mixed clay and fibre suspension as the first component, prior to the addition of Octasol™.

[0110] A summary of the relative turbidities of the dual component Octasol™ and cationic Hydrocol 864 systems can be found in Table 6.

TABLE 6

Comparison of Octasol™ and Cationic Hydrocol 864 Induced Clay Flocculation with Fibres	
Component	Relative Turbidity (τ_p/τ_i)
Hydrocol 864	0.10
Hydrocol 864 with PP1 (ratio 3:4)	0.11
Hydrocol 864 with PP3 (ratio 1:2)	0.15
Hydrocol 864 with PP4 (ratio 1:2)	0.18
Hydrocol 864 with PP6 (ratio 1:2)	0.11

[0111] From Table 6, it can be seen from the very low relative turbidity value that the use of the cationic Hydrocol 864 alone gives very good flocculation of clay in the presence of fibres. The dual component systems with Octasol™ as the second component also give good relative turbidities. However, it seems that the use of Octasol™ slightly impairs the performance of the polymer as the relative turbidity increases. This could be due to cationic charge inundation resulting in a slight re-stabilisation of the clay and fibre suspension.

[0112] Octasol™ and Non-Ionic Polymer

[0113] Non-ionic Hydraid 6696EZ polymer was used with Octasol™ in this study. The Octasol™ dosage was fixed at 0.7% w/w on clay and the polymer at 0.35% w/w on clay, giving a polymer: Octasol™ ratio of 1:2. In each case, the non-ionic polymer was added to the pre-mixed clay and fibre suspension as the first component, prior to the addition of Octasol™.

[0114] A summary of the relative turbidities of the dual component Octasol™ and non-ionic Hydraid 6696EZ systems can be found in Table 7.

TABLE 7

Comparison of Octasol™ and Non-ionic Hydraid 6696EZ Induced Clay Flocculation with Fibres	
Component	Relative Turbidity (τ_p/τ_i)
Hydraid 6696EZ	0.43
Hydraid 6696EZ with PP1 (ratio 1:2)	0.34
Hydraid 6696EZ with PP3 (ratio 1:2)	0.39
Hydraid 6696EZ with PP4 (ratio 1:2)	0.41
Hydraid 6696EZ with PP6 (ratio 1:2)	0.40

[0115] Table 7 shows that the performance of the non-ionic polymer either alone or with Octasol™ is not so effective as that of the cationic polymer alone. However, the combination of Octasol™ with the non-ionic polymer provides a synergy between the components, as the effect on the relative turbidity is greater than for either of the single components. In this case, the non-ionic polymer is able to interact in a positive way with the cationic Octasol™ as there is less repulsion between the two components than with the cationic polymer.

[0116] All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art

without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.

1. A method for flocculating one or more particulate materials present in a dispersion, the method comprising contacting the dispersion with

- (i) fibrous cationic colloidal alumina microparticles; and
- (ii) a cationic polymer and/or a non-ionic polymer.

2. A method according to claim 1 wherein the dispersion is aqueous based.

3. A method according to claim 1 or 2 wherein the dispersion comprises or is components of papermaking stock.

4. A method according to claim 3 wherein the papermaking stock is a pulp of a hardwood or of a softwood, or a combination thereof.

5. A method according to claim 4 wherein the pulp is selected from pulps of the chemical, mechanical, recycled, semi-chemical and thermomechanical types, or mixtures thereof.

6. A method according to any one of the preceding claims wherein the one or more particulate materials are flocculated on a fibrous material.

7. A method according to claim 6 wherein the fibrous material comprises or is fibrous cellulose.

8. A method according to any one of the preceding claims wherein the dispersion is contacted with a composition comprising

- (i) fibrous cationic colloidal alumina microparticles; and
- (ii) a cationic polymer and/or a non-ionic polymer.

9. A method according to any one of the preceding claims wherein the cationic polymer is selected from polyacrylamide, polyethylene imine, polyamines, polycyandiamide formaldehyde polymers, amphoteric polymers, diallyl dimethyl ammonium chloride polymers, diallylaminoalkyl (meth)acrylate polymers, and dialkylaminoalkyl (meth)acrylamide polymers, a copolymer of acrylamide and diallyl dimethyl ammonium chloride, a copolymer of acrylamide and diallylaminoalkyl (meth)acrylates, a copolymer of acrylamide and dialkylaminoalkyl (meth)acrylamides, a polymer of dimethylamine and epichlorohydrin, and natural and semi-synthetic polymers including cationic starch.

10. A method according to any one of the preceding claims wherein the non-ionic polymer is selected from polymers formed from at least one monomer chosen from acrylamide, methacrylamide, and N-tertiary butyl acrylamide.

11. A method according to any one of the preceding claims wherein the charge density of the cationic polymer is no greater than 60%.

12. A method according to any one of the preceding claims wherein the molecular weight of the cationic/non-ionic polymer is no greater than 30,000,000, preferably 500,000 to 30,000,000, more preferably 1,000,000 to 30,000,000, more preferably 5,000,000 to 30,000,000.

13. A method according to any one of the preceding claims wherein the polymer:microparticle ratio is from 10:1 to 1:10, preferably 2:1 to 1:2, more preferably approximately 1:1.

14. A method according to any one the preceding claims wherein the dispersion is contacted with the cationic alumina prior to contact with the cationic polymer and/or the non-ionic polymer.

15. A method according to any one of claims 1 to 13 wherein the dispersion is contacted with the cationic polymer and/or non-ionic polymer prior to contact with the cationic alumina.

16. A method according to any one of claims 1 to 13 wherein the dispersion is simultaneously contacted with the cationic polymer and/or non-ionic polymer and the cationic alumina.

17. A method according to any one of the preceding claims wherein the dispersion has a pH of from 3 to 10.

18. A method for retention and/or drainage of a paper-making stock as defined in any one of the preceding claims.

19. A method according to claim 18 wherein the paper-making stock has a concentration of pulp of up to 20 wt. %.

20. A method according to claim 19 wherein the paper-making stock has a concentration of pulp of 1-2 wt. %.

21. A method according to claim 19 wherein the paper-making stock has a concentration of pulp of 3-5 wt. %.

22. Use of fibrous cationic colloidal alumina microparticles for flocculating one or more particulate materials present in a dispersion characterised by the features of any one of claims 1 to 17.

23. A composition comprising

(i) fibrous cationic colloidal alumina microparticles; and

(ii) a cationic polymer and/or a non-ionic polymer.

24. Paper or a paper product obtained or obtainable using the invention as defined in any one the preceding claims.

25. A flocculated particulate material obtainable by the method according to claim 1 or any claim dependent thereon.

26. A method as substantially hereinbefore described with reference to any one of the Examples.

27. A use as substantially hereinbefore described with reference to any one of the Examples.

28. A composition as substantially hereinbefore described with reference to any one of the Examples.

29. A paper or a paper product as substantially hereinbefore described with reference to any one of the Examples.

30. A flocculated particulate material as substantially hereinbefore described with reference to any one of the Examples.

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