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METHOD OF IMPROVING RETENTION OF FILLERS IN PAPER MAKING WITH ACRYLAMIDE-DIALLYLAMINE COPOLYMER

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This invention, in general, relates to additives useful in the processing of paper. More particularly, this invention is concerned with polymeric compositions which show activity in retention of fillers and fiber fines in paper manufacture.

Paper is manufactured for the most part from wood pulp. A small amount of high grade paper is manufactured from rag pulp. There are five different kinds of wood pulp: mechanical pulp (ground wood), semi-chemical pulp, sufite pulp, sulfate or kraft pulp, and soda pulp. The first is prepared by purely mechanical means, the second by a combination of mechanical and chemical, and the other three by chemical means. The mechanical pulp contains substantially all of the wood except the bark and that lost during storage and transportation. Semi-chemical pulps are partially free of lignin. Chemical pulps, however, are essentially cellulose, the unwanted lignin and other non-cellulosic components of the wood having been dissolved away by the cooking and bleaching treatment. Because of this, chemical pulps are much superior to mechanical and semi-chemical pulps for fine paper making. However, because of the special processing required, they are too expensive to serve as the main source of fiber for the cheaper grades of papers such as newsprint.

If the pulp fibers were the only constituents of a paper sheet, the usefulness of the paper would be very restricted because the sheet would be soft, have a yellowish color, and could not be written or printed upon with ink successfully. If the sheet were thin, it would be transparent to matter printed upon the opposite side. It is necessary, then, to add other substances, such as sizing, coloring agents, and fillers, to the cellulosic fibers to produce paper suited to its many uses.

Many papers, except the absorbent types, filter papers, and most packaging papers, must have a finely ground filler added to them, the purpose of which is to occupy the spaces between the fibers—thus giving a smooth surface, a more brilliant whiteness, improved printability and improved opacity. The fillers are inorganic substances and may be either naturally occurring materials such as talc, agalite, pearl filler, barytes and certain clays such as china clay or artificial fillers such as suitably precipitated calcium carbonate, crown filler (pearl hardening), blanc fixe, and titanium dioxide pigments. Sizing is added to the paper, other than absorbent papers and filter paper, to impart resistance to penetration by liquids. Common sizing agents added to the pulp before it is formed into a sheet are wax emulsions or soaps made by the saponification of rosin with alkali. The sizes are precipitated with alum.

Pulp stock is prepared for formation into paper by two general processes, beating and refining. Mills use either one or the other alone or both together. The most generally used type of beater is that known as the Hollander. Beating the fibers makes the paper stronger, more uniform, more dense, and less porous. It is in the beater that fillers, coloring agents and sizing may be added. The standard practice in making the finer grades of paper, is to follow the beaters with the refiners, the latter being continuous machines.

While the usual practice is to add filler, sizing and color to the beaters, they may be added prior to the Jordan or to a combination of points in the system or subsequent to the beating operation but prior to the refining step, as for example, prior to beating. The order in which the materials are added to the beaters may vary with different mills. Generally, however, the filler is first added to the blended pulp, and after sufficient beating, the sizing and the coloring are added. In some instances, all or part of the sizing and the coloring are added. In some instances, all or part of the sizing is surface applied to the formed, dried sheet, using animal glues, starches, or gelatin as the sizing. Again, alum is most generally added to the beater, but in some mills, this practice is varied, and the pulp may be treated with this chemical during the refining step or even later in the paper processing scheme.

The machines used for the actual formation of the paper sheet are of two general types, the Fourdrinier machine and the cylinder machine. The basic principles of operation are essentially the same for both machines. The sheet is formed on a traveling bronze screen or cylinder, dewatered under rollers, dried by heated rollers and finished by calender rolls. In the Fourdrinier machine, the stock of the foregoing operations is sent to the headbox from which it flows onto a moving, endless bronze wire screen. The pulp fibers remain on the screen while a greater portion of the water, containing unretained fiber fines and unretained filler, drains through. As the Fourdrinier wire moves along, it has a sidewise shaking motion whch serves to orient some of the fibers and give better felting action and more strength to the sheet. While still on the Fourdrinier wire, the paper passes over suction boxes to remove water and under a dandy roll which smooths the top of the sheet. In the cylinder machine, there are several parallel vats into which similar or dissimilar dilute paper stocks are charged. A wire-covered rotating cylinder rotates in each vat. The paper stock is deposited on the turning screen as the water inside the cylinder is removed. As the cylinder revolves further, the paper stock reaches a point where the wet layer comes in contact with and adheres to the moving felt. This felt and paper, after removal of some water, come into contact with the top of the next cylinder and pick up another layer of wet paper. Thus, a composite wet sheet or board is built up and passes through press rolls and onto the drying and smoothing rolls.

In an attempt to improve filler and fines retention in the paper manufacturing operation several attempts have been made to incorporate chemical additives with the paper stock before it reaches either the cylinder vat or the Fourdrinier wire. These additives, for the most part, have not been entirely satisfactory from several operational points of view. One of the chief drawbacks of most chemicals used to improve a fiber and fine retention in the manufacture of paper is that they must possess certain characteristics and properties which are extremely difficult to achieve in any particular chemical. For instance, the particular chemical used should not be affected by other additives normally used in the paper processing operations such as rosin size, alum, sodium aluminate, starch, clays, and the like. Also important for a particular additive to be effective for improving fiber and fine retention is that it must not be affected by variations in pH. Similarly, the ideal additive chemical should not be affected by a particular electro-kinetic charge on the cellulose fibers and fines. The use of a chemical must, of course, be such that it does not have any adverse effects on the finished sheet and it should be relatively safe to handle.

In addition to possessing the above desirable characteristics an additive for improving filler and fines reten-

tion must be capable of acting both upon the filler and fines in the system to efficiently cause such materials to be retained in the finished sheet rather than with one being preferentially acted upon by the additive. Another important characteristic that must be capable of operating on a large variety of stocks.

Also of importance in the selection of fines and filler retention agent is that it must not affect dyestuffs which are frequently used as coloring agents for various types of paper stocks. It also must not interfere with the beneficial effects imparted to paper stocks by coatings which are frequently placed on different types of paper during its manufacture.

Many prior art filler and fiber fines retention aids fail to achieve the above desired objects. In addition, certain of these known retention additives cannot be employed in effective combinations with various fillers or other paper additives. Oftentimes efficiency is low except when gross uneconomical amounts are added. Adverse effects upon the finished paper product are noted when these retention aids cause poor dispersibility of the system additives with resultant localized non-uniform areas. Lastly, many additives fail by promoting filler trapage on the top side of the fiber material.

It, therefore, becomes an object of the invention to provide a new and improved method for improving filler and fines retention in the manufacture of paper by addition of water-soluble polymeric substances during paper processing.

A further object is to provide chemical agents for improving filler and fines retention which are effective at low economical dosages, will not interfere with other additives and substances used in the make-up and manufacture of the paper, and which have no adverse effects on the chemical and physical characteristics of the finished sheet.

Yet another object of the invention is to provide water-soluble polymeric retention additives which when used in combination with alum give especially improved retention effects.

An important object of the invention is to provide chemical additives for improving filler and fine retention in manufactured paper which will operate on a wide variety of paper stocks, are fairly safe to handle and will impart to the finished sheet certain and desirable characteristics which have not heretofore been available when prior attempts have been made to use other chemicals as fines and filler retention aids.

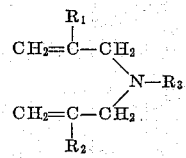
A special object of the invention is to provide versatile high molecular weight completely water-soluble copolymers for use as retention aids which have the additional property of ability to increase drainage properties of the formed paper pulp sheet prior to final processing via drying. The copolymers cause efficient drainage of water from the formed fiber network which has been placed on a foraminous forming surface.

In accordance with the invention it has been discovered that water-soluble copolymeric materials comprising polymerized acrylamide and an allylamine or salt thereof have excellent activity in promoting filler and fiber fines retention in papermaking processes. The copolymers show a retention activity even at addition levels as low as 0.01 pound per ton based on the weight of dry fiber, have unusually good water solubility, and may be used as retention aids for all fiber furnishes including both bleached and unbleached primary or virgin chemical pulps, mechanical pulps, and secondary fibers, that is, fibers previously employed as paper stock.

As broadly outline above, the copolymers of the invention comprise two groups of monomers which are polymerized in the presence of each other in a single step process to give a polymer with the type and amount of recurring units and their respective polar groupings being dependent upon the amount of each monomer employed. The exact molecular configuration, of course, cannot be determined, but is rather considered a statistical average according to the ratio of the monomers employed one to the other with their respective side-groups. The high molecular weight copolymers of the invention are achieved without sacrifice of water solubility necessary in paper pulp filler and fiber fines retention aid work.

The first essential monomeric starting reactant is acrylamide. This monomer is easily obtained by well-known commercial processes such as partial hydrolysis of acrylonitrile. While the amounts of acrylamide in parts by weight which may be employed may be varied over a wide range, for best results, it has been determined that preferred high molecular weight solid materials may be prepared through use of 50–95 parts by weight of acrylamide starting material per 100 parts by weight of copolymer. The most preferred range of acrylamide used is 60 to 90 parts by weight per 100 parts by weight of copolymer. Copolymers synthesized by use of acrylamide in the above recited ranges in combination with monomeric allylamines have exceptional ability in retaining inorganic fillers and fiber fines upon a pulp network. Thus, effective utilization of the above filler additives and paper stock is achieved, and the residual white water which remains after the sheet has been drained and formed will have low amounts of suspended solids. In many cases, subsequent processes for recovery of the suspended solids are not needed, and the white water may be directly reused in the pulp making and processing. If recovery is necessary, the task is made much simpler by the reduction of solids dispersed in the white water.

The other monomeric starting material is a polymerizable diallyl amine, that is, a bis-ethylinically unsaturated compound having the following structural formula:



where R_1 and R_2 are selected from the group consisting of hydrogen and methyl radicals, and R_3 is a member of the class consisting of hydrogen and lower alkyl radicals. Preferably, when R_3 is a lower alkyl radical it contains less than about 4 carbon atoms. The above amine preferably makes up 5–50 parts per 100 parts by weight of the copolymeric compositions which more preferably contain from 10 to 40 parts of the diallyl amine monomer. In the most preferred embodiment then, the copolymer contains from about 60 to about 90 parts of acrylamide and from about 10 to about 40 parts of the cationic allylic monomer. Representative allylic compounds which may be copolymerized with acrylamide include diallylamine, dimethallylamine, diallylmethylamine, dimethallyethylamine, etc. As already mentioned, for effective results any of the above copolymers must be water-soluble in order to act as suitable filler and fines retention aids, and generally have a relatively high molecular weight of at least 10,000 and preferably above 50,000.

In order to prepare the above allylic-acrylamide copolymers it is only necessary to mix the ingredients in the desired proportions and polymerize them by known techniques such as bulk, solution, emulsion, suspensions means etc. The catalyst initiator may be any free radical producing agent. However, it has been found that one particularly preferred polymerization synthesis in such a case is a solution polymerization wherein a redox catalyst system comprising a catalyst initiator and reducing agent is employed in conjunction with a metal activator. Using this scheme, relatively high molecular weight water-soluble viscous materials are produced which have excellent activity in promoting retention of paper pulp fines and fillers.

In a preferred embodiment involving a solution polymerization the allylic amine is first reacted with mineral or organic acids such as hydrochloric, sulfuric, phosphoric,

nitric, formic, acetic, etc., to form salts thereof. To the salt, normally formed in an aqueous solution, is then added acrylamide monomer. The scheme of addition, however, is immaterial. The pH of the monomer mixture generally ranges from 4 to 6 at this stage in the reaction. To the above is then added the catalyst system to initiate the reaction. The polymerization is generally started at ambient temperatures.

During the reaction itself, heat is given off by virtue of the exothermic nature of the polymerization. Temperature rises of 50–100° F. have been noted. Generally, the bulk of the polymerization reaction occurs between 100 and 200° F. Agitation is usually employed during the mixing of monomer ingredients and polymerization step itself.

The reaction mixture then is compounded of aqueous solutions containing about 5 to 80% by weight of monomers, 20% to 95% of water, and 0.001% to about 0.2% of catalyst based on the total weight of reaction mixture. Preferably 0.01 to 0.1% of catalyst is employed. While a redox system of catalyst is preferred, the invention may also include sole use of conventional peroxide oxidizing agents such as potassium persulfate, hydrogen peroxide, and ammonium persulfate.

As noted above, in the preferred embodiment the reaction is initiated by a redox catalytic system additionally containing a metal ion. In a redox system, the catalyst is activated by means of a reducing agent which produces free radicals without the use of heat. One of these reducing agents most commonly used is sodium metabisulfite. Other reducing agents include water-soluble thiosulfates and bisulfites, hydrosulfites and reducing salts such as the sulfates of metals which are capable of existing in more than one valence state. These metals include cobalt, iron, nickel, and copper. The use of a redox initiator system has several advantages, the most important of which is efficient polymerization at lower temperatures. It is therefore not required to decompose the catalyst. The selection of catalyst and reducing agent, should a redox catalyst be used, and the selection of metal activators, for use in the process may be varied according to the choice of the experimenter. Conventional catalysts such as potassium persulfate, ammonium persulfate, etc., used in conjunction with the above reducing agents and metal activators such as ferrous ammonium sulfate work very satisfactory. Use of other metal ions than ferrous ion whose valence state is capable of being varied such as cobalt, iron, nickel, and copper also improve the polymerization scheme. In the most preferred initiator system, ferrous ammonium sulfate, ammonium persulfate, and sodium metabisulfite are employed and when added to the monomer mixture give excellent polymerization products in a minimum of time. In particular, use of ferrous ion obviates the need for nitrogen sparging, which for other systems is normally required to give the most acceptable product. One preferred initiator system contains 50–100 p.p.m. of ferrous ion as ferrous ammonium sulfate, 100 p.p.m. sodium metabisulfite and 100 p.p.m. ammonium persulfate. When a redox catalyst system is employed in conjunction with a metal ion, the concentration of each may range from 0.001 to 0.2% and preferably from 0.01 to 0.1% based on the weight of the reaction mixture.

The following examples are illustrative of representative types of allylamine-acrylamide copolymers and various techniques employed in producing same according to the solution method generally outlined above.

Example I

A monomer solution containing 125 grams of diallylamine was added to an open vessel equipped with an agitator. 125 grams of hydrochloric acid (approximately 37% concentration by weight) was added to the diallylamine solution in order to form the hydrochloride salt thereof. The pH of this solution was approximately 4.5. To the diallyl salt solution was then added 375 grams of acrylamide, also made up in aqueous solution. The respective monomers were thoroughly mixed and sufficient catalyst initiator system, composed of ferrous ammonium sulfate, sodium metabisulfite, and ammonium persulfate, as 1% solutions, were added to give 6, 1, and 1 grams of these reagents respectively. The three reagents were prepared as solutions just prior to their use, since decomposition occurs to some extent in all three solutions. The water content of the reaction mix was adjusted to give a 20% monomer solution. The polymerization reaction proceeded exothermally, starting at ambient temperature (70–95° F.). During the course the reaction appeared to be complete, that is, when heat ceased to be evolved due to the reaction, the copolymer was then diluted to a 5% solution of active copolymer comprising polyacrylamide and polydiallylamine hydrochloride salt. In this example, the ratio of starting monomer acrylamide to starting monomer diallylamine was 75:25.

Example II

A 3-neck flask, equipped with stirring device, thermometer, nitrogen sparger and heating mantle, was set up into which monomer solutions of acrylamide and diallylamine salt were introduced and then thoroughly mixed. Then a vacuum was applied along with heat which was in turn followed by nitrogen sparging. This step was carried out in order to rid the system, both solution and atmosphere above the solution, of air containing oxygen. The catalyst, consisting of a redox system of sodium metabisulfite and ammonium persulfate, was added with continued nitrogen sparging, and the solution was then allowed to polymerize. A 500 gram amount of 10% solution of active chemical prepared with an 85:15 ratio of acrylamide to diallylamine was produced.

Example III

25 pounds of diallylamine was added to 375 pounds of Chicago tap water and placed in a stainless steel reactor (Dopp Kettle). To this was added 25 pounds of a 37% concentration solution of hydrochloric acid producing the diallylamine salt. The pH of this solution at this time was 4.6. 75 pounds of acrylamide was then added to the salt solution and the temperature adjusted within the range of 70–95° F. The initiator system, consisting of 126.3 grams of ferrous ammonium sulfate, 22.7 grams of sodium metabisulfite and 22.7 grams of ammonium persulfate, was added and the reaction allowed to proceed. 30 minutes after a peak temperature of 160° F. was reached, 1,500 pounds of Chicago tap water was added to give a final product containing 5% active copolymer.

In order to produce copolymers of even higher molecular weight and correspondingly proportional excellent retention ability, the special polymerization technique discussed in commonly assigned application, Serial No. 132,562, filed August 21, 1961, may be employed. Broadly speaking, this technique involves preparation of the highly concentrated monomer solution, addition of an inert heat transfer solvent media, which may be referred to as an organic solvent, and subsequent polymerization effected at relatively low temperatures. The polymerization must be carried out under conditions of high agitation and in the presence of an anti-sticking agent, which acts to keep the formed polymer from agglomerating into an unusable mass. The monomers actually copolymerize in a separate stratum within the above system in the presence of a surface active compound acting as the anti-sticking agent. If conditions are followed closely, granules of relatively small size may be obtained which are easily ground into a free-flowing white soluble powder, and are immediately ready for use without further processing.

More specifically, an aqueous solution is prepared containing about 30% to about 80% by weight of monomers, 20% to 70% water, and 0.003% to about 0.2% based on the weight of monomer present of the polymerization

catalyst, such as potassium persulfate. The water solution is then added to or mixed with a water-insoluble, organic, heat transfer medium which preferably is capable of forming an azeotropic mixture with water. The above mixture should contain a minor amount of a surface-active agent which prevents the copolymer from sticking to the agitator or the walls of the vessel. The temperature of the system is raised to a desired point and the mixture is kept in motion by means of an agitator.

Oxygen is removed from the system either by purging with an inert gas such as nitrogen or carbon dioxide, by applying a vacuum or by boiling the mixture. The polymerization is initiated as soon as the oxygen is removed. If an emulsion has formed due to the presence of the surface-active agent, that emulsion breaks at the time polymerization starts and the polymerization is carried out in a separate layer. The organic heat transfer medium substantially surrounds the aqueous medium as the polymerization takes place. Vigorous agitation is employed to continuously shear the polymer layer into particles which vary in diameter, for example, from about 1/16" to about 2" and more often from about 1/4" to 1/2". In a preferred process, the temperature of the mixture is raised to its boiling point or maintained at the boiling point, in the event polymerization was carried out at the boiling point of the mixture. After the polymerization is completed, water is thus removed by azeotropic distillation. The boiling temperature, of course, varies in accordance with the particular organic heat transfer agent in the mixture.

During the boiling off stage, the organic solvent preferably is condensed and returned to the mixture while the water is being trapped and removed. After from 60 to 100% of the water has been eliminated, the granules that have formed are separated from the solvent by filtration and are then washed and air dried.

It has been found that benzene, toluene, xylene, and ethylene dichloride are especially suitable for use in the present process as well as carbon tetrachloride, tetrachloroethylene, and the like. Other comparable organic compounds that form azeotropic mixtures of water, however, could be used without difficulty as long as they do not contain alcohol, aldehyde or ketone groups which would cause undesirable side reactions. The polymerization medium can also contain a non-azeotroping component with boiling point above the distilling temperature. The above materials may be termed organic solvents and are all water insoluble, organic heat exchange materials which are considered inert in the practice of the invention. These organic substances serve as heat transfer media or heat dissipators by suspension of the aqueous monomer phase and subsequently formed copolymeric product.

The catalysts that are employed in the process, include the same conventional peroxidic oxidizing agents as listed above or a redox system. The amounts of catalyst used can also be the same as listed above.

As earlier mentioned, a surface-active agent should be added to the polymerization mixture in order to prevent the polymer from sticking to the walls of the reaction vessel and to the agitator. There are numerous compounds on the market which would perform satisfactorily in that capacity. Materials such as "Ethomid" S–15, O–15, and HT–15, which are ethylene oxide condensates of fatty acid amines, as well as "Arlacel 80" and "Span 80," which are sorbitan mono oleates, will serve adequately as anti-sticking agents as will sorbitan monostearate, sodium dodecyl benzene sulfonate, aluminum stearates, and aluminum oleates. Initially in the process, the presence of the surface active agent may cause the formation of an emulsion. It is essential, however, that the emulsion break and form two separate and distinct layers prior to the polymerization reaction. The amount of surface active agent which is added to the system can vary from about 0.5% to about 7% by weight based on the weight of the heat transfer medium, and preferably will vary from about 2% to 4%.

As was further pointed out above, the heat transfer medium plays an important part in the concentrated solution polymerization method. In particular, the function of the organic liquid is to remove the heat of reaction from the forming polymer.

The removal of dissolved oxygen gas from the reaction mixture is also important. The removal of the oxygen can be accomplished by (1) purging the reaction mixture with an inert gas such as nitrogen or carbon dioxide, (2) boiling the reaction mixture, and (3) applying a partial vacuum to the system. If an inert gas is used to remove the oxygen, it is best applied by passing the gas through a disperser or sparger which is inserted beneath the surface of the reaction mixture.

The water content of the copolymers that are produced by the above method should range from 0 to about 28%. The preferred water content range is from about 5% to about 15%. If the moisture content of the polymer is greater than about 28%, the granules tend to agglomerate.

The following example illustrates how a typical copolymeric retention aid of the invention may be suitably produced by the above high monomer concentration method.

Example IV

To 108.0 grams of water are added 101.25 grams of acrylamide and 34.75 grams of diallylamine which had been previously reacted with sufficient concentrated hydrochloric acid to form the salt thereof. The above ingredients are mixed until complete solubilization is effected. The entire solution is gently agitated and mildly heated at a temperature not greater than 38° C. It is essential that the temperature not exceed the above limit since heating at a higher temperature would effect polymerization prematurely.

In a separate 1000 ml. three-necked flask, equipped with thermometer, Dean and Stark trap, condenser, stirring device and heating mantle attached to a variable transformer, are added 754.0 grams of toluene and 19.6 grams of "Arlacel 80" anti-sticking agent. The reaction flask then is purged with nitrogen at a rate of 960 cc./min. After the inert solvent and anti-sticking agent mixture is purged sufficiently, the above monomeric solution is added to the 1000 cc. reaction flask. The system is put under reduced vacuum (8 inches) and heated to 70° C. After this temperature is reached, the vacuum is shut off and 4.8 grams of a 1% aqueous solution of $Na_2S_2O_5$ is added while the stirring mechanism is running. After a few seconds, 1.2 grams of a 1% aqueous solution of $K_2S_2O_8$ is added. During this addition of redox reagent, the reaction temperature drops two to three degrees C. The redox catalyst is completely added, the vacuum is re-established at an 8" reading, and the reaction mass is reheated to 70° C. When this temperature is again reached the vacuum is shut off and only nitrogen is introduced into the reaction mixture for the duration of the reaction time. Heating is applied in order to maintain the reaction mass at 70° C. until an exotherm occurs. At this time, heat is discontinued and the temperature drops of its own accord to 68° C. After the exothermic reaction has been completed, temperature of the mixture of the polymerization reaction is maintained at about 70° C. for 50–60 minutes. At this time, water is then removed as an azeotropic distillate. Approximately 90% of the total water added was azeotroped off. Filtration from the organic solvent left a white solid granular copolymeric product.

It is understood, of course, that the above discussed methods are only illustrative of typical preferred preparations of the copolymeric retention aids of the invention. The invention in its broader aspects, resides in use of such polymers and is not dependent upon the particu-

lar polymerization technique used. Also, the invention contemplates the use of both allylamine and its salts as starting monomer materials.

EVALUATION OF THE INVENTION

In order to determine the effectiveness of the copolymers of the invention, two procedures were devised. The first, known as the "Phototester Method" involved a measurement of the light absorption of a supernatant liquid remaining after settling of a dispersion of pulp and titania. A blank was run and then compared to samples in which the retention aids of the invention had been previously added. The difference between the percent absorption of the blank sample and the percent absorption of the treated sample gives them a Phototester number. This number is directly related to the ability of the sample tested to act as a retention aid, with retention activity directly proportional to the increase in the Phototester number. The higher the number, then, the greater the retention activity. If, for example, a blank sample gives a 60% absorption and a treated sample a 40% absorption, the difference stated as an absolute number is 20, which then is the Phototester number.

More specifically, this Phototester method is as follows: Bleached sulfite pulp is beaten for 30 minutes and added to the proportioner of a Noble Wood Sheet Machine and the consistency adjusted to give a 0.21% fiber content. To this pulp slurry is added 75 mls. of TiO_2 which had been previously slurried in water to give a 5% suspension, to give an addon of 10% based on the fiber weight. After the titania has been thoroughly dispersed in the pulp for five minutes, 30 ml. of a 2.5% solution of alum is added to give a concentration of 2% alum, based on the fiber weight. The alum is added in order to standardize the system in meeting normal paper mill procedure. The pulp furnish is then removed from the proportioner to a porcelain lined pail and stirred for one hour. Before stirring, the pH had been adjusted as desired with a normal sulfuric acid solution. The pulp furnish, containing the titanium alum is then allowed to settle for one-half hour and the sample of the supernatant liquid is taken and tested in the Phototester machine for light absorbency. The figure obtained, then, corresponds to the percent absorbency of a blank, that is, a pulp treated with titania filler and alum in which no retention aid had been added.

In order to evaluate the retention activity of the polymers of the invention, a 125 ml. sample of pulp containing alum and titanium is added to a 20 ounce jar. The retention aid is then added from a 0.02% solution and the entire mixture swirled briefly. 375 ml. of tap water is added, the jar is capped and inverted five times and allowed to stand for five minutes. The supernatant liquid is then removed and a Phototester measurement taken. In order to avoid aging of solutions which would result in a less meaningful determination, all of the above test solutions of titanium, alum and retention chemicals are freshly made each day. Also, the titanium suspension is never allowed to settle between the time it is made and the time it has been added to the pulp suspension.

The next test method for determining retention activity is known as the "Ash Determination Method." In this method, titania and alum are added to the bleached sulfite pulp as outlined above in the Phototester method. The system is then adjusted to any desired pH. If a blank run is desired, the pulp furnish is then transferred to the head box of a Noble and Wood Sheet Machine where a series of nine sheets are formed continuously, pressed and dried. The white water which has drained into a holding tank is recirculated through the sheet-making machine during the formation of the nine sheets. The sheets are then reduced to ash at 1700° F. for 2 hours and the percent ash remaining is measured. Sheets 3, 5, 7 and 9 are then averaged to give a consistent picture of the percent ash remaining. Of course, the higher the ash total, the greater the retention ability of the additive. The retention aid is added to the pulp furnish containing the titania and alum in any amount as desired, and sheets are made by the same method as in the above blank runs.

Various copolymers were prepared according to the general polymerization techniques outlined above. The ratio of monomers was varied in order to determine those specific polymers giving highest retention activity, as determined by a Phototester determination. Table I below outlines retention testing of various samples in which the composition of the polymer was varied as indicated as well as dosage levels and pH of the pulp furnish.

TABLE I

Composition	pH	Dosage Level, lbs./ton	Phototester No. Average
1. 95% Acrylamide-5% Diallylamine	7.4	1.6	13.5
2. 95% Acrylamide-5% Diallylamine	7.4	0.4	12.5
3. 90% Acrylamide-10% Diallylamine	7.4	1.6	28.3
4. 90% Acrylamide-10% Diallylamine	7.4	0.4	23.0
5. 90% Acrylamide-10% Diallylamine	5.5	1.6	24.3
6. 75% Acrylamide-25% Diallylamine	7.4	1.6	31.5
7. 75% Acrylamide-25% Diallylamine	7.4	0.4	27.0
8. 75% Acrylamide-25% Diallylamine	3.5	1.6	35.5

Table I above illustrates the fact that the monomer ratios of the two components going to make up the copolymers of the invention can be varied over a considerable range with no substantial loss of retention activity.

Next a total of 42 samples of a 5% concentrated solution of a copolymer comprising acrylamide and diallylamine in a 3:1 ratio were tested for retention activity as measured by the Phototester method. Dosages were varied from 0.2 to 3.2 pounds per ton and the pH of the pulp furnish was adjusted at either 4.5, 5.5, or 7.4. Phototester values ranges from 15.8 to 37.5.

Next, a series of samples were synthesized in order to determine whether increase in molecular weight, as determined by viscosity measurements, has a tendency to increase the effectiveness of the polymeric products as retention aids. In this study, samples were prepared in which the molecular weight was varied according to certain manipulative variations of the general polymerization techniques as outlined above. The monomer ratio was kept constant in all cases at 3:1 of acrylamide to diallylamine as well as dosage level of 1.6 lbs./ton and pH of pulp furnish at 5.5.

TABLE II

Viscosity centipoises (5% solids):	Phototester factor
2,700	31.5
11,000	37.0
25,000	38.0

It can be readily seen that the effectiveness of the polymers as retention aids is in direct correlation to their molecular weight, with the most efficient polymers having the highest viscosity. These results become more meaningful when they are converted to percent retention by multiplying each figure by a factor of ten. Thus, use of one of the retention aids of the invention increases the retention of inorganic fillers from 315% to 380% as shown in Table II. Also, it is seen that higher molecular weight products give a substantial increase up to 20% or more in filler retention over the relatively low molecular weight materials although both types show good effectiveness. This type of comparison becomes more striking when speaking in terms of tons of filler which can be utilized by using the retention polymers of the invention. A considerable savings per week or per month becomes quite evident when considered in this manner.

Samples were also prepared and tested in which the copolymer content was varied from 5% concentration in liquid solution to a completely solid active copolymer. In all cases excellent retention activity was noted.

Also, ash determinations of sheets prepared while using the retention aids of the invention showed from 10% to 500% increase in ash content. This was determined by direct comparison between filler retained in the case of a blank sample run, without benefit of retention aid, and filler retained with use of treating agent.

Samples were also made in which the respective monomers of the invention were separately polymerized and tested for their retention activity. In all cases, retention ability was of many magnitudes less. For example, polyacrylamide samples gave Phototester number average results from 0 to 5. Also, polymerized diallylamine salt gave substantially no retention activity.

The retention aids may be added at almost any step in the normal mill process but it is greatly preferred they be added subsequent to the refining step. The most preferred site of addition is at the head box. Another practical application point is at the fan pump where the pulp is simultaneously finally diluted with white water to the proper consistency and pumped to the head box. The retention aids may also be added after the fiber is beaten and before the refining step, although this is a less preferred practice, with the effectiveness of the polymers being somewhat destroyed due to the subsequent agitation and refining steps.

As mentioned above, the polymers of the invention also have activity in improving drainage from the wire surface of the Fourdrinier machine. In many cases, a suitable retention aid shows little or no activity in improving the drainage of white water from the pulp slurry. Oftentimes, the converse is also true, that is, effective drainage aids exhibit poor retention activity. However, in the case of the instant invention, the copolymeric compositions show excellent activity in both fields of paper treatment. Again, the polymers may be added to the fan pump, head box, wire pit, etc., prior to actual formation of the paper sheet. It is preferred that when the materials are to be used for this purpose, they be added after the fibers have been refined. The exact mechanism of the drainage improvement is not known, but it is believed that the fiber fines and foreign matter are agglomerated upon the large fiber particles and thereby a sufficiently strong fiber mat is produced, which still has sufficient porosity to allow the white water to drain therefrom.

The polymers of the invention have found use in increased retention of nearly all types of inorganic fillers and fiber fines. Particularly their retention action is apparent when such fillers as naturally occurring organic materials, talc, agalite, pearl filler, barytes and certain clays such as china clay or artificial fillers such as suitably precipitated calcium carbonate, crown filler (pearl hardening) blanc fixe, and titanium dioxide pigments are added to the pulp slurry. Inorganic coloring pigments and kaolin clays are also efficiently retained upon the fibers by use of the polymeric substances. As discussed above, retention activity of the polymers is somewhat improved through the use of alum, but it is to be understood, of course, that the compositions of the invention show excellent activity even in the absence of alum.

Through use of the copolymers, excellent retention of fiber fines and fillers may be realized in both Fourdrinier and cylinder paper machine systems. Increased filler retention realized from the use of these compounds results in a brighter sheet with better density, opacity, and ash content. Also better sheet formation, smoothness, printability and porosity, and greatly reduced two-sidedness, that is, differences of such properties as color and brightening of the respective sheet sides due to uneven pigment retention, are noted when these copolymers are employed. In addition to the above advantages, use of the retention agent results in cleaner machine operation and a less abrasive system, reduced load to the saveall, and minimal sewer losses due to the decrease in tray and white water solids. A particularly desirable result realized through the use of the copolymers was a decrease in pinholes in the paper sheet with a resultant improved paper product.

The invention is hereby claimed as follows:

1. A method of improving the retention of inorganic filler and fiber fines in the processing of paper which comprises the step of adding to an aqueous filled paper pulp suspension at least a retention improving dosage of an organic water-soluble copolymer formed as the reaction product of 50–95 parts by weight of acrylamide and 5–50 parts by weight of a polymerizable compound selected from the group consisting of diallylamine and salts thereof.

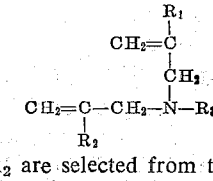
2. A method of improving the retention of inorganic filler and fiber fines in the processing of paper which comprises the step of adding to an aqueous filled paper pulp suspension at least 0.01 pound per ton of fiber of an organic water-soluble polymer formed as the reaction product of 50–95 parts by weight of acrylamide and 5–50 parts by weight of a polymerizable compound selected from the group consisting of diallylamine and salts thereof.

3. The method of claim 2 wherein the filled paper pulp suspension also contains an aluminum salt.

4. The method of claim 3 wherein the aluminum salt is alum.

5. A method of improving the retention of an inorganic filler and fiber fines in the processing of paper which comprises the step of adding to an aqueous filled paper pulp suspension containing alum at least 0.1 pound per ton of fiber of an organic water-soluble copolymer formed as the reaction product of 50.0–95.0 parts by weight of acrylamide and 5.0–50.0 parts by weight of a polymerizable diallyl amine selected from the group consisting of the free base and salt thereof.

6. The method of claim 5 wherein said diallylamine has the following structural formula:



where R_1 and R_2 are selected from the group consisting of hydrogen and methyl radicals and R_3 is a member of a class consisting of hydrogen and lower alkyl radicals.

7. A method of improving the drainage properties of aqueous paper pulp sheet which comprises the steps of treating an aqueous paper pulp suspension with at least 0.01 pound per ton of fiber of an organic water-soluble copolymer formed as the reaction product of 50–95 parts by weight of an acrylamide and 5–50 parts by weight of a polymerizable compound selected from the group consisting of diallylamine and salts thereof; depositing such treated aqueous pulp suspension upon a foraminous forming surface to form a continuous aqueous paper sheet comprising water and a paper fiber network, and draining said water from said fiber network.

8. The method of claim 7 wherein the aqueous paper pulp suspension also contains alum.

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