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ACRYLAMIDE TERPOLYMERS AND THEIR USE IN PAPER MAKING PROCESS

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ABSTRACT OF THE DISCLOSURE

Novel terpolymers which are useful for improving the retention of filler and fiber fines in the processing of paper. The terpolymers are formed by copolymerizing specific quantities of the following three monomers:

(a) acrylamide—85–95 parts by weight (89.5–94.5 preferred);
(b) a polymerizable polycarboxylic acid selected from the group consisting of maleic acid, formic acid, and maleic anhydride—0.3–2.0 parts by weight (0.5–1.5 preferred);
(c) an ethylenically unsaturated water-soluble monomer such as acrylic acid, vinyl acetate, vinyl pyrrolidone, etc.—3–15 parts by weight (5–9 preferred).

The polymers when used as retention aids (a) are unaffected by other additives, (b) are unaffected by changes in pH, (c) are unaffected by electrokinetic charges, (d) are capable of acting on both fiber fines and filler, and (e) are highly effective in retaining fiber fines and filler and thereby increasing the opacity and strength of the paper.

This application is a divisional application of our copending application Ser. No. 398,418, filed Sept. 22, 1964 which in turn was a continuation-in-part of our copending application Ser. No. 205,495 filed June 27, 1962, now abandoned.

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, sulfite 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 transporation. Semi-chemical pulps are partially free of lignin. Chemical pulps, however, are essentially pure cellulose, the unwanted and unstable lignin and other non-cellulosic components of the wood having been dissolved away by the 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 which 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 passed 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 retention 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 possessed by any chemical used as a filler and fines retention additive is that it 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, nor must it 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 wth 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 new water-soluble polymeric materials, which are useful as filler and fiber fines retention aids.

Another object of the invention is to provide a new and improved method for improving filler and fines retention in the manufacture of paper by addition of novel terpolymeric 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.

A special object of the inevntion is to provide water-soluble terpolymeric 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.

Other objects will appear hereinafter.

In accordance with the invention a new class of water-soluble high molecular weight polymeric material has been discovered which has excellent activity in promoting filler and fiber fines retention in papermaking processes. These compositions comprising in chemical combination, polyacrylamide, a polymerized polycarboxylic acid, the monomer of which is either maleic acid, maleic anhydride or fumaric acid and a polymerized ethylenically unsaturated water-soluble monomer, show a retention activity even in addition levels as low as 0.01 pound per ton based on the weight of dry fiber. More preferably, the terpolymeric additives are employed in a level of at least 0.1 pound per ton. The terpolymers of the invention have unusually good water-solubility, notwithstanding the high molecular weights of the products, 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 outlined above, the terpolymers of the invention comprise three groups of monomers which are polymerized in the presence of each other in a single step process to give a terpolymer 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. Extremely high molecular weights and the desired physical characteristic of free-flowing white powder are obtained through a special polymerization technique which will be discussed in more detail hereinafter. The high molecular weight terpolymers 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. It has been determined that the amount of acrylamide which shall be employed to give desired retention results is 85–95 parts by weight.

The most preferred range of acrylamide used is 89.5 to 94.5 parts by weight. Terpolymers synthesized by use of acrylamide in the above recited ranges in specific combination with the other two monomeric substances in weight ranges, which will be discussed further, 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 recovery processes of the suspended solids is 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 next monomeric starting material is a polymerizable polycarboxylic acid which may be chosen from maleic acid, maleic anhydride, or fumaric acid. Again, the amounts of starting polycarboxylic acid monomer

used is important. Excellent retention activity is achieved when from 0.3 to 2.0 parts by weight of the above compounds such as maleic anhydride is employed. The most preferred retention aids comprise those including from 0.5 to 1.5 parts by weight of the polycarboxylic acid monomer. Due to low cost and availability, the most preferred of the above three materials is maleic anhydride which during the polymerization reaction both hydrolyzes and polymerizes to form a plurality of carboxylic acid groups.

The last monomeric reactant to be discussed is a water-soluble ethylenically unsaturated monomer containing polar groups; examples of such monomers are acrylic acid and salts and alkyl esters thereof, vinyl pyrrolidone, vinyl acetate, methacrylamide, vinyl alkyl ethers such as methyl vinyl ether, methacrylic acid and salts and alkyl esters thereof, acrylonitrile, vinyl alcohol, methacrylonitrile, allyl alcohol, allyl amine, etc. By use of the term water-soluble it is intended to include not only those substances which are soluble in all proportions with water, but also to include monomers which may have low solubility, but nevertheless may be dispersed or emulsified in water by suitable techniques. The amount of ethylenically unsaturated monomer employed as a starting material should vary from about three to about fifteen parts by weight. Best results with regard to retention activity and desired physical characeristic of free flowing powder is reached when from five to nine parts by weight of ethylenically unsaturated monomer is employed.

The terpolymers of the invention then, include the following polymeric reactants and their range of starting material weights.

COMPOSITION A

Monomer:	Parts by weight
Acrylamide	85.0–95.0
Polycarboxylic acid monomer	0.3–2.0
Ethylenically unsaturated water-soluble monomer	3.0–15.0

Composition B shows the more preferred general terpolymers of the invention and their respective weight ranges.

COMPOSITION B

Monomer:	Parts by weight
Acrylamide	89.5–94.5
Polycarboxylic acid monomer	0.5–1.5
Ethylenically unsaturated water-soluble monomer	5.0–9.0

The most preferred specific terpolymer of the invention having the range of reactant weights as outlined in Composition B above includes polyacrylamide, maleic anhydride and methacrylic acid.

In order to produce terpolymers of exceedingly high molecular weight, and correspondingly proportionl excellent retention ability, a special polymerization technique was employed. Broadly speaking, this technique involved 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 impractical and unusable mass. 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. The monomers actually terpolymerize in a separate stratum within the above system in the presence of a surface active compound acting as the anti-sticking agent.

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 a 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 terpolymer 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 dioxides, by applying a vacuum or by boiling the mixture. The polymerization is initiated as soon as the oxygen is removed. If an emulsion is formed due to the presence of the surface active agent, the emulsion breaks 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 and after the polymerization is completed, water is 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, tetra chloroethylene, 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 terpolymeric product.

The catalysts that are employed in the process include conventional peroxidic oxidizing agents such as potassium persulfate, hydrogen peroxide, and ammonium persulfate. It is preferred that water-soluble compounds be used for this purpose. The amount of catalyst used in the process can vary from 0.003% to about 0.2% by weight based on the weight of the monomers. A preferred range is from about 0.003% to about 0.05%. Catalyst concentrations above 0.2% will polymerize the aqueous solution containing the three monomers, but the resultant products are inferior to those prepared using amounts of catalyst within the specified ranges. One of the advantages of the subject process, therefore, is that it provides a means of carrying out the polymerization using very small amounts of catalyst.

As was pointed out above 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 the capacity. Materials such as "Ethomid" S–15, O–15, and HT–15, which are ethylene oxide condensates of fatty acid amides, as well as "Arlacel 80" and "Span 80," which are

sorbitan mono oleates, will serve adequately as anti-sticking agent as will sorbitan mono-stearate, 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 about 4% by weight. During the polymerization, the monomer-containing aqueous medium is substantially surrounded by the organic heat transfer medium.

In a preferred embodiment, the polymerization reaction is carried out using a redox type catalytic system. In the method described above, either avoiding or removal of oxygen by other means is needed to permit the catalyst to form free radicals. In a redox system, the catalyst is activated by means of a reducing agent, which in the absence of oxygen immediately produces free radicals without the use of heat. One of the reducing agents most commonly used is sodium metabisulfite. Other suitable agents include water-soluble thiosulfates, bisulfites, hydrosulfites, and reducing salts, such as the sulfates of metal which are capable of existing in more than one valence state. The metals include cobalt, iron, nickel, and copper. The use of a redox initiator system has several advantages, the most important of which is that it is possible to carry out the polymerization at lower temperatures. It is not required to decompose the catalyst.

As has been pointed out, a great many surface active agents can be used in the terpolymerization process. Those compounds mentioned above are illustrative of suitable and readily available products. The amount of surface active agent used in the process can vary from about .5 to 7%, and preferably 2% to 4% by weight based on the weight of the heat transfer medium. Too large a quantity of the surface active agents should be avoided inasmuch as an excess might tend to form stable emulsions or suspensions. The surface active agents function primarily to prevent the forming terpolymer from sticking to either the agitator or walls of the reaction vessel.

The selection of particular catalysts—or activators, should a redox system be employed— for use in the process does not fall within the scope of our invention. Conventional catalysts such as potassium persulfate, and conventional activators, such as sodium, metabisulfite, work very satisfactorily. It is important, however, that the amount of catalyst used in the process vary from 0.003% to about 0.2%, based on the weight of the monomers.

It is preferred to dissolve the catalyst and the activator in separate water solutions prior to adding to the aqueous solutions of the three monomers. The catalyst and activator can be dissolved in the aqueous monomer solution just prior to adding the solution to the organic heat transfer agent. Alternatively, the catalyst can be dissolved in a small amount of water and then be added to the organic heat transfer medium prior to the addition of the monomeric solution. Another satisfactory method would be to dissolve the catalyst and/or activator in water and add this solution to the reaction mixture after the monomeric solution has beetn added to the heat transfer medium.

The water content of the terpolymers that are produced by the above method should range from 0 to about 28%. Our 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.

Several organic relatively water-insoluble heat transfer liquids have been suggested above which can be used in the subject process. It is preferred that those liquids form azeotropic mixtures with water. By azeotropic mixtures, we mean mixtures which on heating will cause water to distill over at temperatures below the normal boiling point of the water at a given pressure. The use of an azeotropic mixture makes it possible to remove water from the terpolymer particles without employing special drying equipment. Apart from the fact that these liquids must not contain reactive groups such as alcohol, aldehyde, and ketone groups, which would cause side reactions, the selection of the particular heat transfer medium is not particularly critical. Benzene is a relatively inexpensive component and it has been found to provide excellent results. For this reason, it is our preferred heat transfer material.

As was 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.

One of the important steps of the polymerization process involves the removal of dissolved oxygen gas from the reaction mixture. 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.

One of the major disadvantages of the prior art methods is that only dilute solutions of monomers could be polymerized without causing a violent reaction or without producing a rubbery, non-flowable material. In the subject process, the total monomer content of the aqueous solution can range from about 30% to about 80% by weight. Primarily because it is possible to work with concentrated solutions of monomer, the formed terpolymers have unusual and highly advantageous properties.

The following examples illustrate typical terpolymers and their method of preparation.

Example I

This example illustrates a typical terpolymer involving terpolymerization of maleic anhydride, methacrylic acid and acrylamide using a redox system of polymerization and a high concentration of monomers via the polymerization technique as described above. Unless otherwise indicated, the percentage figures below are to be taken as percent by weight.

To 108.0 grams of water (12.6%) are added 1.125 grams of maleic anhydride (0.13%), 9.4 grams of methacrylic acid (1.11%), and 10.0 grams of a 50% concentrated aqueous solution of sodium hydroxide (1.17%). The above ingredients are mixed until complete solubilization is effected. 124.425 grams of acrylamide (14.59%) are added to the above mixture and the entire solution was gently agitated and mildly heated at a temperature not greater than 38° C. It is essential that the temperature not exceed above this figure since heating at a higher temperature would effect polymerization prematurely. The pH of the solution is then adjusted with 50% caustic sufficient to raise the pH to 9.0.

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 (67.32%) and 19.6 grams of "Arlacel 80" anti-sticking agent (2.30%). 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 basic 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 (0.56%) while the stirring mechanism is running. After a few seconds, 1.2 grams of a 1% aqueous solution of $K_2S_2O_8$ (0.14%) is added. During this addition of redox reagent, the reaction temperature drops two or three degrees C. The redox catalyst is com-

pletely added, the vacuum is re-established at an 8" reading, and the reaction mass 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 granular product.

Example II

This example was run similar to the procedure outlined in Example I. To a 500 ml. beaker were added 85.5 grams acrylamide, 4.0 grams of methacrylic acid, 0.5 grams of maleic anhydride, and 72 mls. of distilled water. The monomeric solution was stirred and the pH was adjusted from 3.2 to 6.3 with 50% concentrated sodium hydroxide. With gentle stirring 0.8 ml. of a 1% aqueous solution of $K_2S_2O_8$ and 3.2 mls. of a 1% aqueous solution of $Na_2S_2O_5$ were added to the above monomeric solution. In a separate 1000 ml. reaction flask the inert organic solution containing the heat transfer media and anti-sticking agent were prepared. This solvent solution contained 574 grams of toluene and 19.6 grams of Arlacel 80. After heating the inert solvent solution to 71° C. with stirring, the monomeric aqueous solution was added slowly to the reaction flask. The temperature during the addition then dropped to 55° C. whereupon the entire mixture was reheated to 75° C. At this time, an 8" vacuum was applied and a nitrogen layer was put over the reaction surface. The temperature was maintained at 75° C. for 26 minutes, after which time a phase separation was noted. During this time, a vacuum was continuously applied and nitrogen flowed over the surface. After the temperature had dropped about 74° C. the polymerization was considered complete and then the water was removed by azeotropic distillation. 72 mls. of water was removed by this method. The resultant white free-flowing granules were washed and separated by vacuum filtration. These granules could be easily ground to below 40 mesh.

Example III

This example was again run using the general technique outlined in Example I with minor variations in the amounts and ratios of the monomers within the recited limits of the invention, and variations in heat transfer media, and anti-sticking agent.

Again, the aqueous monomeric system was formulated by adding 1.12 grams of maleic anhydride, 9.45 grams of methacrylic acid, and 124.43 grams of acrylamide to 110 mls. of distilled water. The pH was adjusted in this experiment to 9.0 with 50% concentrated sodium hydroxide. In a separate reaction flask, the organic inert solvent system was prepared by adding 0.62 gram of "Arlacel 80" to 683 mls. of toluene. The monomeric aqueous solution was added to the solvent system with stirring, nitrogen continuously run through the system, and vacuum applied to give 22 p.s.i. of actual pressure. Heat was then applied and the temperature raised to 60° C. Heat was momentarily removed, the vacuum was broken and 2.4 mls. of 1% aqueous solution of $Na_2S_2O_5$ solution and 0.6 ml. of a 1% aqueous $K_2S_2O_8$ solution previously diluted to 10 mls. were added to the reaction mixture. The vacuum system was resealed and the temperature adjusted to 60° C. After the temperature was reached, the vacuum was broken slowly over a period of about 30 seconds. Then the temperature of the reaction was held between 59° C. and 61.5° C. The exothermic reaction occurred ten minutes after addition of the catalyst and redox activator. In this run, the duration of the exothermic reaction was 41 minutes. After this time elapsed, 111 mls. of water were distilled off by azeotropic distillation and the final solid white product was separated from the organic heat transfer medium by filtration.

Example IV

In this example, fumaric acid was substituted for maleic anhydride employed in the previous examples.

1.12 grams of fumaric acid, 9.45 grams of methacrylic acid, and 124.43 grams of acrylamide were dissolved in 110 mls. of distilled water and the pH then adjusted to 9.0 with 50% concentrated aqueous sodium hydroxide solution. The organic solvent system was prepared by adding 0.62 gram of "Arlacel 80" to 630 mls. of toluene. The monomeric solution was added to the organic solvent system, with stirring, the reaction flask sealed, and nitrogen introduced for a few seconds through a nitrogen disperser. The vacuum was then applied (22 p.s.i. actual pressure), and heat applied until the temperature reached 70° C. The heating mantle was removed temporarily, the vacuum system broken, and 4.8 mls. of 1% $K_2S_2O_8$, previously diluted to 10 ml. of distilled water, were added. The system was resealed and the temperature adjusted to 70° C., after which time, the vacuum was broken slowly over a period of 30 seconds.

The temperature of the reaction was held between 69° C. and 71.5° C. Twelve minutes after the introduction of the catalyst and redox activator, a phase separation occurred and the exothermic reaction began. This reaction lasted for a total of 18 minutes. After the reaction was completed, 110 mls. of water were distilled off by azeotropic distillation. The solid white terpolymeric product was isolated by filtration.

EVALUATION OF THE INVENTION

In order to determine the effectiveness of the terpolymers 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 terpolymer 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 then 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 30% absorption, the difference stated as an absolute number is 30, which then is the Phototester number. A passable result is generally considered to be 27–28 Phototester units or higher.

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 to 5.5 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 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 terpolymers of the invention, the 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 amount of 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 terpolymers were prepared according to the general polymerization technique outlined in Example I. The ratio of monomers was varied within limits of the invention and respective retention activities determined by a Phototester determination. Table I below outlines preparation and retention testing of various samples in which the composition of the terpolymer was varied as indicated.

TABLE I

Percent Maleic anhydride	Percent methacrylic acid	Percent acrylamide	Phototester No. average
0.56	4.4	95.0	29.7
0.5	7.0	92.5	32.0
0.5	9.0	90.5	28.2
0.75	5.0	94.25	31.0
0.75	8.0	91.25	31.5
0.75	10.0	89.25	31.5
0.83	7.0	92.17	32.7
1.0	5.0	94.0	29.5
1.0	7.0	92.0	31.2
1.0	9.0	90.0	29.6
1.5	5.0	93.5	29.4
1.5	7.0	91.5	30.7
1.5	9.0	89.5	30.3

Table I above illustrates the fact that the monomer ratios of the three components going to make up the terpolymers of the invention can be varied within the above recited range with no substantial loss of retention activity of the respective terpolymers so formed.

A number of terpolymeric substances were synthesized in which the monomer ratios were deliberately varied outside the scope of the invention. In each case, paper retention activities of the produced polymeric chemical retention aids were substantially lower and non-acceptable. The following examples illustrate a few of these preparations wherein terpolymers falling without the scope of the invention were produced.

Example V

This example was run similar to the procedure outlined in Example I, with the exception that the monomer ratio was varied outside the scope of the invention. Specifically, a polymerizable solution was prepared containing 0.11% of maleic anhydride, 0.89% methacrylic acid and 99.0% of acrylamide, the above percentages being based solely on total monomer content. These monomers were terpolymerized and the final product tested for retention activity. This particular product has a Phototester number of 21 which was considered commercially sub-standard in terms of acceptable retention efficiency.

Example VI

Like the above example the monomer ratio of the three monomers was again deliberately adjusted outside the claimed range. In this case, 0.36% of methacrylic acid, 0.04% of maleic anhydride and 99.6% of acrylamide monomers were terpolymerized and the product again tested for retention activity. This particular terpolymer exhibited a Phototester unit number of 20 when employed in the retention test described above. It can readily be seen therefore that the amounts of each monomer comprising the terpolymers of the invention should be maintained within the discovered ranges. Terpolymers having monomer content without such disclosed ranges are decidedly inferior products in terms of their retention activity.

The next study made was to determine whether the temperature and catalyst concentration could be varied without affecting the retention activity of the formed terpolymers. The concentration of catalyst as used in Example I was considered to be standard addition, and respective samples were prepared by varying the catalyst standard addition, as indicated. Also, runs were made involving three separate temperatures with variation of the catalyst concentration at these temperatures. Table II below is an outline of the results of this study.

TABLE II

Polymerization initiation of temperature, ° C.	Redox catalyst concentration	Phototester number average
70	½ std.	32.3
70	1 std.	31.7
70	2 std.	34.0
80	½ std.	33.0
80	1 std.	30.0
80	2 std.	29.4
87.5	½ std.	30.0

Table II above shows that excellent terpolymer additives may be synthesized even though the catalyst concentration and polymerization initiation temperature are considerably varied.

The next study involved varying the specific anti-sticking agent and its percent concentration in toluene as the inert heat-transfer solvent. These variables were also studies at two different pH figures. The results are outlined in Table III below.

TABLE III

Anti-sticking agent	Percent by weight in toluene	pH	Phototester No. average
"Arlacel 80"	0.8	8	29.2
Do	1.6	8	33.6
Do	6.4	8	31.0
Petroleum sulfonate	1.6	8	29.6
Do	0.8	8	31.5
Do	0.4	8	32.2
Do	0.1	9	31.5
Do	0.05	9	31.0

The above figures show that various anti-sticking agents may be employed in synthesizing the terpolymers in the invention with variations in their concentration and that this will cause little or no effect on retention activity. Also, the pH at which the terpolymerization is run may

be changed without changing the effectiveness of the terpolymer retention additives.

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 terpolymeric products as retention aids. In this study, three samples were prepared in which the molecular weight was varied according to certain manipulative variations of the general polymerization technique as outlined above. The monomer ratio was kept constant in all cases and the reactions involved 92.17% acrylamide, 7.0% methacrylic acid, and 0.83% maleic anhydride. In this series, the retention activity was determined according to the ash determination method. Table IV shows results of this work.

TABLE IV

Viscosity centipoises:	Percent ash in Handsheets
390	6.63
715	6.96
1700	7.94

It can be readily seen that the effectiveness of the terpolymers as retention aids is in direct correlation to their molecular weight, with the most efficient samples 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. In other words, higher molecular weight products give a substantial increase up to 10% or more in filler retention. This type of comparison becomes more striking when speaking in terms of tons of filler which can be utilized by using the retention terpolymers of the invention. A considerable savings per week or per month becomes quite evident when considered in this manner.

Field testing was also carried out using the composition of Example I. When compared to prior art, retention additives results were startling. In every case, the terpolymers of the invention showed an improvement in retention activity over commercial additives which had been previously employed. The example below shows one of these typical field runs.

Example VII

In this field trial, a composition of Example I was compared to a cationic which had been previously employed as a retention aid. The particular mill in which the field test was run was a book and bond mill located in the eastern part of the United States. The extended run involved retention of inorganic fillers upon a printing grade furnish. This pulp furnish was composed of 35% bisulfite, 45% soda and 20% deinked stock. 2% titania and 18% clay were added as filler based on the weight of the fiber. 32 pounds of alum additive per ton of fiber lowered the pH to 4.5–4.8.

A 1% aqueous solution of the terpolymer of Example I prepared by dilution for 20 minutes at 67° F. in water was metered into the head box showers just prior to sheet formation. The terpolymer dosage was 0.5 pound per ton of dried fiber. After a period of approximately 1½ hour the ash content of the formed paper sheet as determined by the method generally discussed above nearly doubled as compared to previous ash contents determined when the prior art cationic was employed as a retention aid. Also the weight of a ream of paper composed of 500 25" x 38" sheets, rose from 42 pounds to 50 pounds after the terpolymer was employed. This is evidence of the startling retention of the heavier inorganic fillers by the pulp network when the paper system is treated with a representative terpolymer retention aid of the invention.

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 methacrylic acid gave substantially lower results than any of the terpolymers of the invention. Likewise, the monomers were also copolymerized one with the other and considerable loss in retention activity was noted. In some cases, up to 100% less efficiency in retention activity resulted from the use of various copolymers as compared to the terpolymers of the invention.

Advantage is also realized through the use of the terpolymeric compositions due to their excellent water solubility. For example, typical aqueous terpolymer samples involving a 1% concentration in water may be prepared in a matter of 20 minutes. Prior art compositions involving homopolymers or copolymers of some of the ingredients of the terpolymer invention, often take 2–4 hours or even longer to dissolve in similar concentration in water.

The terpolymer 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 terpolymers being somewhat destroyed due to the subsequent agitation and refining steps.

The terpolymers of the invention have found use in increasing 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 terpolymeric substances. As discussed above, retention activity of the terpolymers 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 terpolymers, 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 terpolymers 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 terpolymers was a decrease in pinholes in the sheet with a resultant improved paper product.

Terpolymers have been above described as comprising in chemical combination, polyacrylamide, a polymerized polycarboxylic acid and a polymerized ethylenically unsaturated monomer. As thus used, this terminology is to be understood as referred to the polymeric chemical combination resulting from polymerization of the respective corresponding monomers in the presence of each other to yield a single terpolymeric compound, rather than a mixture of three separately polymerized monomers.

The invention is hereby claimed as follows:

1. As a paper-pulp processing additive for improving filler and fiber fines retention, an organic water-soluble terpolymer formed as the reaction product of 85.0–95.0 parts by weight of acrylamide, 0.3–2.0 parts by weight of

a polymerizable polycarboxylic acid monomer selected from a group consisting of maleic acid, maleic anhydride, and fumaric acid, and 3–15 parts by weight of an ethylenically unsaturated water-soluble monomer differing from the above monomers.

2. As a paper-pulp processing additive for improving filler and fiber fines retention, an organic water-soluble terpolymer formed as reaction product of 89.5–94.5 parts by weight of acrylamide, 0.5–1.5 parts by weight of maleic anhydride and 5–9 parts by weight of methacrylic acid.

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