

# United States Patent

Varveri et al.

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[54] **POLYAMPHOTERIC POLYMERIC  
RETENTION AIDS**

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162/183, 260/80.3 N

[51] Int. Cl. ....**D21h 3/58**

[58] Field of Search .....162/168, 164; 260/80.3 N

[56] **References Cited**

**UNITED STATES PATENTS**

2,884,058 4/1959 Schuller et al. ....162/168  
2,923,701 2/1960 Schuller et al. ....260/85.5

2,972,560 2/1961 Stilbert et al. ....162/168  
3,147,218 9/1964 Booth et al. ....260/80.3 X  
3,234,076 2/1966 Goldsmith .....162/168

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[57] **ABSTRACT**

The preparation and composition of certain amphoteric polymers, useful as retention aids in the paper industry, is disclosed. The polymers are formed from acrylamide and diallyl quaternary ammonium monomers, in which some of the amide groups are subsequently hydrolyzed to adjust the ratio of quaternary and carboxylic acid groups in the polymer molecule and wherein the diallyl compound undergoes an intramolecular cyclic polymerization. The polymer function as retention aids over wide ranges of alum loading and pH ranges.

**5 Claims, No Drawings**

## POLYAMPHOTERIC POLYMERIC RETENTION AIDS

## BACKGROUND OF THE INVENTION

In papermaking, retention is generally defined as the retaining of inorganic fillers, such as clay and titanium dioxide, as well as cellulosic fines within the paper sheet during manufacture (such as on a Fourdrinier machine). The retention obtained on the wire screen is a function of different mechanisms such as filtration by mechanical entrainment, electrostatic attraction, and bridging between cellulosic fibers and filler. However, since both the cellulose and many common fillers are electronegative, they are mutually repellent and, in the absence of a retention aid the only factor tending to enhance retention is mechanical entrainment.

Generally, retention aids are used because of the high cost of pigments, such as titanium dioxide. The use of the retention aids adds considerably to the amount of such pigments incorporated into the wet web. In addition, the retention aid can appreciably reduce the suspended material in the paper machine white water effluent which reduces the consequential pollution problem and loss of pigment.

Retention aids are commonly used in the manufacture of specialty paper finishes such as bond paper and "publication-type" paper, where high loadings of pigment and/or filler are required. The function of the retention aid is to bind the filler to the cellulosic fibers without mechanically blocking the pores in the paper sheet, thereby not adversely effecting the drainage properties of the wet paper web. This can be best accomplished by producing a microfloc of the filler, through the adsorption of the polymeric retention aid onto the cellulosic fibers which become charged and attract the oppositely charged pigment or filler.

High-speed papermaking machines may run from 1,000 to 2,600 feet per minute, and some machines run at speeds of up to 3,500 feet per minute. Clearly, any adverse effect upon drainage characteristics will result in a reduction in the machine speed.

The prior art has used polyacrylamides as retention aids wherein about 3 to 35 percent of the amide groups have been hydrolyzed to carboxylic acid groups. Such a retention aid could adversely affect drainage properties as it may over floc the pigment. It is essential for alum to be present for such a retention aid to work effectively, and the aid is effective only over a relatively narrow pH range. The retention value can fluctuate as much as 20 percent with small variations of pH or alum loadings.

U.S. Pat. Nos. 2,884,058 and 3,077,430, disclose the use of certain acrylamide copolymers as dry strength agents when used in certain concentrations.

For high-quality paper which is filled with titanium dioxide, rosin is customarily used as a size. Alum is used to set the rosin, i.e., to insolublize and fix the rosin, and also to make the paper system acidic. The alum may function as a link between the anionic pigment and the negatively charged cellulosic fiber, and is also functioning, to a degree, as a flocculant. Generally, the cellulosic pulp, on a dry basis, contains about 9.5 to 2 percent rosin, and has a minimum alum content of about 10-20 pounds per ton. However, paper mills customarily use about 40 pounds of alum per ton of dry pulp in order to insure the desired pH range and rosin sizing. Also commonly used are synthetic sizes, such as "Aqualin," a ketene imine dimer, which are cured at a neutral or alkaline pH; the anionic acrylamide polymers do not function effectively as retention aids in these systems.

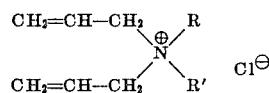
The pH and alum load of paper systems are generally interdependent to a certain degree, although acids such as sulfuric acid may be added to the pulp to reduce the pH to a desired range in the case of low alum loads.

## SUMMARY OF THE INVENTION

This invention provides improvements in the art of papermaking in which the retention of cellulosic fines, fillers, pigments and other chemical additives is aided and improved and

variances in alum load and pH have little or no adverse effect on the retention. In this invention, certain polymers are used which contain quaternary ammonium groupings and amide groupings, and are treated to contain carboxylic acid groupings as well. Thus the polymeric molecules employed contain both positive and negative ionic charges, which are in certain specific ratios as will be discussed hereinafter. These amphoteric polyelectrolytes, which are water soluble, are of value as retention aids because their activity is less affected by variations in pH and the chemical content of the aqueous paper pulp suspension.

The present invention employs certain specific materials which are water-soluble linear amphoteric polymers and which contain, as chain members, units derived from acrylamide monomers and diallyl quaternary ammonium chloride monomers, preferably those of the following general formula:



wherein each of R and R' independently represent an alkyl group of one to 18 carbon atoms in length or a  $\beta$ -propionamido substituent or a betaine substituent. The betaine substituent will generally be a carboxymethyl group or other group capable of forming an internal salt structure in the diallyl quaternary ammonium chloride compound.

The preparation of diallyl methyl carboxymethyl ammonium betaine is described in Example 3 of U.S. Pat. No. 2,935,493. Diallyl  $\beta$ -propionamido carboxymethyl ammonium chloride may also be used as a monomer in the production of the polymers of the present invention. This monomer may be prepared by heating diallylamine at about 60° C. for 5 hours with acrylamide to form diallyl  $\beta$ -propionamido amine and then treating this compound with the sodium salt of chloroacetic acid at 80° C. for 8 hours, whereby a quaternary salt is formed with one positive site and one negative site. The diallyl  $\beta$ -propionamido carboxy methyl ammonium chloride monomer may be considered as providing a betaine unit in the polymer chain, and such a unit, in itself, confers amphoteric properties upon the polymer, since it has both a positive charge and a negative charge site.

Among alkyl groups which may be represented by R and R', may be mentioned, for instance, methyl, ethyl, propyl, isobutyl, hexyl, decyl, dodecyl, and octadecyl. Preferred substituents are methyl and ethyl groups. Mixtures of various diallyl ammonium chloride compounds of the above formula may be used as desired.

At the present time, economic considerations generally dictate the use of more simply constituted monomeric materials, e.g., acrylamide itself, rather than chloroacrylamide, N, N-dimethyl-acrylamide, methacrylamide, or diacetone acrylamide for instance, although these compounds may be used.

The weight ratio of the quaternary ammonium chloride groups and the acrylamide groups can vary from 30/70 to 70/30 with preferred weight ratio being 50:50. At a 50:50 weight ratio of acrylamide: quaternary ammonium compound, in the case of dimethyl diallyl ammonium chloride, for example, the mole ratio of acrylamide to quaternary compound is about 2.27 to 1.0. Molecular weight of the polymer should be at least 10,000; so long as the polymer is water soluble, higher molecular weights are preferred.

After polymerization, some of the acrylamide units are hydrolyzed to carboxylic units. The hydrolysis step will generally only affect the amido groups but if  $\beta$ -propionamido substituents are present upon the quaternary nitrogen atom, they will probably likewise be hydrolyzed. The polymer after hydrolysis may have from 10 quaternary units per 0.1 carboxylic unit up to 10 quaternary units per five carboxylic units. Preferably, however, there are 10 quaternary units per each carboxylic unit in the final polymeric product. At the preferred ratio of 10 quaternary units per 1 carboxylic group,

about 4.3 percent of the amido groups will be hydrolyzed in a 50:50 dimethyldiallyl ammonium chloride: acrylamide copolymer.

In the hydrolysis reaction, it is preferred to use relatively dilute caustic, for instance, less than 20 percent concentration in aqueous solution, with very good mixing at a temperature in the neighborhood of about 60° C. The only effect the temperature variance will have is to modify the rate of hydrolysis. Any alkali metal or ammonium hydroxide or carbonate may be used in the hydrolysis reaction.

Broadly speaking, any diallyl ammonium chloride compound is operable in the present invention, and any ratio of various diallyl ammonium chlorides may be used in polymerization with acrylamide, so long as the ratio of 30/70 to 70/30 by quaternary compound: acrylamide is maintained. It is important that the diallyl ammonium compound be a diallyl ammonium chloride as only the chloride anion will allow the polymerization to proceed to the relatively high molecular weight compounds which are operable in the present invention. The diallyl compound undergoes an intramolecular cyclic polymerization as shown in the structural formulas.

Particularly preferred retention aid polymers are those obtained from polymerizing acrylamide with mixtures of dimethyl diallyl ammonium chloride and diethyl diallyl ammonium chloride. The ratio of the dimethyl diallyl ammonium chloride to the diethyl diallyl ammonium chloride may vary from 99:1 to 1:99, although the most preferred ratio is 95:5 of dimethyl diallyl ammonium chloride: diethyl diallyl ammonium chloride.

The formation of the certain polymeric compounds from acrylamide and diallyl quaternary ammonium compounds is already known, as disclosed in, for instance, U.S. Pat. Nos. 2,923,701 and 3,147,218, the disclosures of which are hereby incorporated by reference. In general, the polymers used in this invention may be made by similar techniques, but utilizing the presently taught ratios of the monomers, chloride anion, and the hydrolysis step, as prescribed herein. Preferably, the reaction is conducted in an aqueous solution using a redox catalyst system, but any method capable of making the unhydrolyzed copolymers desired herein is, of course, satisfactory, so long as the polymers have the required high molecular weight.

In practice, the catalyst may be added to the polymerization reactants over a period of time, and the temperature may be maintained at any convenient point where a set and controllable rate of polymerization is achieved. Such temperatures may vary from say about 20° to about say 90° C., preferably 30° to 75° C., or higher.

The concentration of alkali which can be employed to hydrolyze the cationic copolymer may be selected according to convenience and is within the skill of the art with the expected effects on the hydrolysis rate and the temperature required to achieve the desired hydrolysis in a convenient period of time. When this polymer structure is subjected to hydrolysis conditions, the carboxamido groups are hydrolyzed to carboxyl groups. In this manner, the ratio of cationic quaternary ammonium to anionic carboxylic sites in the molecule may be varied and controlled, as desired, to achieve the most optimum properties.

Polymeric material may be obtained by polymerizing acrylamide, acrylic acid, and a diallyl quaternary ammonium compound in the same ratios as are obtained in the hydrolyzed polymers of the present invention. However, a different product with a lower molecular weight is obtained, which is unsuitable for application as a retention aid. There appears to be a different distribution of the acid monomer in the polymer molecule, and it will readily be seen that hydrolysis is critical in order to obtain the amphoteric polymer which is an effective retention aid.

The polymers of the present invention may be added to the paper pulp at any desired point effective to aid in the retention of fibers and additives in the paper as it is being formed on a paper machine. Generally, the retention aid will be added to a

point proper to the forming surface. It is a particular feature of this invention that the introduction of the polymers described herein into the papermaking pulp will lead to an improved retention of the cellulosic fines and of the various additives especially pigment and fillers, over a wide range of pH and other chemical conditions. Further, there is observed improved retention characteristics as a result of the addition of these polymers over a wide range of alum loading conditions. As is well known, the amount of alum used in the papermaking industry may vary widely, and it is desired to have a retention aid which will yield good retention characteristics over a wide range of alum concentrations. This desired characteristic has been demonstrated by the polymers of the present invention, as shown in connection with the working examples herein. The present invention provides amphoteric polymeric retention aids which may vary no more than 10 percent in retention values across alum load ranges of 1 to 100 pounds of alum per ton of dry pulp, and across pH ranges of 3.5 to 8.0.

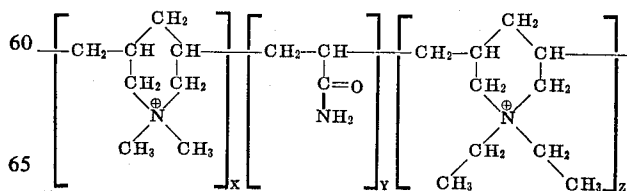
Generally, about one-half pound of retention aid per ton of dry pulp will be added to the paper pulp slurry. A retention aid will seldom be used in amounts of less than 0.1 pound per ton of dry pulp, and in normal practice the retention aid will not be used in amounts higher than 2 pounds per ton of dry pulp for economic reasons, although in some cases more retention aid may be used without adverse effect, for instance, 5 or even 10 pounds per ton of dry pulp. Mixtures of retention aids may be used as desired. The retention aids of the present invention have essentially no detrimental effect on the dry strength of the paper when used in the above concentrations.

Generally, the polymers of our invention may be produced by the following procedure:

A monomer mixture comprising a 50/50 weight ratio of acrylamide to diallyl quaternary ammonium monomers at 20 percent total solids is prepared in aqueous solution. The pH of this monomer solution is adjusted to 6.5 with dilute NaOH solution and then heated to 50° C. and held at this temperature where it is purged with nitrogen gas for a 1-hour period to remove all dissolved oxygen. To this monomer solution a redox polymerization catalyst system is added comprising an aqueous solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{Na}_2\text{S}_2\text{O}_5$  in the following manner:

0.24 percent ammonium persulfate based on the weight of the monomer is added to the monomer mix. Then a dilute solution of sodium metabisulfite is pumped into the monomer solution at such a rate so as to maintain a concentration of  $6.58 \times 10^{-3}$  moles of bisulfite per mole of total monomer per minute. This bisulfite solution initiates and sustains the polymerization reaction at a controlled rate. The polymerization is normally conducted under adiabatic conditions so that the solution exotherms from 50° to about 75° C. within about a 1-hour period.

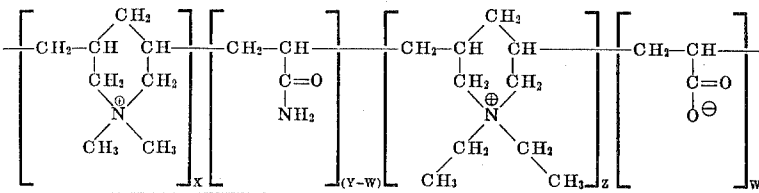
The temperature is then held at about 60° C. for an hour, producing a hyperviscous aqueous solution of a water-soluble polymer of the following representative linear chain; used for illustration purposes only:



wherein  $(X+Z)/Y$  is approximately 1, and  $X/Z$  is approximately 19.

Again by way of illustration, the base polymer is then hydrolyzed by treating the solution with an appropriate amount, which for example is the amount calculated to hydrolyze 4.3 percent of the amide groups, of a potassium hydroxide solution (20 percent solids) at a temperature of about 60° C. for 2 hours. The resultant partially hydrolyzed

polymer has about 10 quaternary units to each carboxylic unit, is water soluble and has the representative structure:



wherein  $(X+Z)/W$  was about 10/1.

The polymeric product may then be recovered as a dry flaked or powdered solid from the viscous solution by solvent precipitation using water miscible organic solvents such as methanol, acetone, etc., or by drum drying or other known techniques. Other substituted diallyl ammonium monomers such as the  $\beta$ -propionamido and betaine monomers previously mentioned may be used with above generalized preparation.

#### EXAMPLE I

Hydrolyzed terpolymer of acrylamide, dimethyl diallyl ammonium chloride, and diethyl diallyl ammonium chloride.

To make 100 lb. of a terpolymer of, by weight, 50 percent acrylamide, 2.5 percent diethyl diallyl ammonium chloride (DEDAAC), and 47.5 percent dimethyl diallyl ammonium chloride (DMDAAC), a charge was prepared comprising 74.8 lb. water, 10 lb. acrylamide, 0.870 lb. DEDAAC, (as 57 percent solution) and 14.3 lb. DMDAAC, (as a 66.5 percent solution). After the addition of small amounts of EDTA (ethylenediamine tetraacetic acid) and sodium salicylate (100 p.p.m.), the pH was adjusted to 6.5, and the charge was purged with nitrogen gas for 1 hour. 11.09 grams of ammonium persulfate in a small amount of water was then added and mixed for 5 minutes. 4.89 grams of sodium bisulfite in 250 ml./H<sub>2</sub>O and a small amount of copper sulfate solution was then pumped into the reactor at a rate between 2 and 2/5 ml./min. until consumed. The reaction completed at about 75° C. Temperature was allowed to recede to 60° C. where it was held for 1 hour. The fully reacted polymer was then hydrolyzed by pumping into it a 20 percent solution of KOH at a rate of 26.5 ml./min. for 30 minutes. It was mixed for 2 additional hours at 60° C., and the resulting polymer solution was drum dried to recover the pure polymer. The polymer was hydrolyzed to the extent of 10 mole percent of the quaternary ammonium groups.

The partially hydrolyzed polymer produced above was used as a retention aid in the laboratory production of a typical bond paper by making 43 lb./3,000 ft.<sup>2</sup> hand sheets using a valley handsheet machine. The retention aid was added to the wet pulp slurry corresponding to a head box addition in an amount equivalent to one-half pound of the retention aid per ton of dry pulp. In this series of laboratory experiments different levels of alum were used to determine the effect of changes in alum loading upon retention.

The results are shown in Table I.

TABLE I

Percent retention of pigment (pH 4.9, adjusted with H <sub>2</sub> SO <sub>4</sub> )	0 lb./ton	40 lb./ton	80 lb./ton
	Alum	Alum	Alum
With retention aid of Example I	82.8	81.5	79.8
Without retention aid	48.6	54.6	55.2

This polymer was also compared to a cationic polymer, "Reten 205," which is believed to be a copolymer of acrylamide (95 percent by weight) and the methosulfate salt of

dimethyl amino ethyl methacrylate quaternized with a methyl group, and also to "Separan PG-2," a slightly anionic polymer

believed to be a homopolymer of acrylamide in which 5 percent of the amide groups are hydrolyzed to carboxylic acid groups. The comparison was made on the retention of TiO<sub>2</sub> in a system using bleached sulfite pulp beaten to a Canadian Standard Freeness of 260 ml. The system contained one percent rosin, 15 percent TiO<sub>2</sub> and various amounts of alum. Handsheets having basis weights of 37.5 pounds were formed after the aid was added and the retention determined. The results are shown in Table II.

TABLE II.—PERCENT RETENTION OF FINES

Polymer	Feed rate,	pH 6.3,	pH 5.5,	pH 4.8,
	lbs./ton dry pulp	10 lbs./alum loading	20 lbs./alum loading	40 lbs./alum loading
Control	0	55.5	61.2	56.0
Example I	0.37	75.2	81.1	81.4
	0.31	74.2	80.6	79.7
	0.275	71.4	78.9	78.2
Separan PG-2	0.5	66.0	78.9	76.9
Reten 205	0.4	73.5	75.0	62.6

#### EXAMPLE II

Hydrolyzed terpolymer of acrylamide, DMDAAC, and diallyl beta-propionamido methyl ammonium chloride.

The system of Example I was followed to produce a polymer of 47.5 percent DMDAAC, 50.0 percent acrylamide, and 2.5 percent of the beta-propionamido adduct. As with Example I, the polymerization reaction was completed at 75° C., it was lowered to 60° C. for 1 hour, and the polymer hydrolyzed to the extent of 10 percent of the number of quaternary ammonium groups by pumping a 20 percent solution of KOH into the product for 30 minutes at 25.9 ml./min.

#### EXAMPLE III

Hydrolyzed terpolymer of 50 percent acrylamide, 2.5 percent carboxymethyl beta-propionamido diallyl ammonium chloride, and 47.5 percent DMDAAC.

Again, a 20 percent monomer batch solution was made and polymerized as in Example I. It was hydrolyzed by introducing a 45 percent KOH solution at a rate of 11.8 ml./min. for 30 minutes.

#### EXAMPLE IV

The three products made in Example I to III were field tested in a paper mill making label paper. The basis weight of this grade was 44 lb./3,000 ft.<sup>2</sup> and the furnish used was a mixture of virgin hardwood and soft wood pulp. This was a rosin-sized, filled sheet. The alum loading in the system was 30–40 lb./ton and gave a white water pH of 4.1 to 4.4.

The filler used was TiO<sub>2</sub> and clay which was fed continuously to the stock immediately prior to the head box. The three products were fed at 0.5 lb. retention aid per ton of finished paper and yielded a 37 percent reduction in the amount of TiO<sub>2</sub> needed to meet a minimum opacity specification. Tests with and without the retention aid showed no adverse effects on mullen, tear, wax pick, or brightness. There was no discernible difference in retention between the three products.

#### EXAMPLE V

One percent hydrolyzed terpolymer of acrylamide, DEDAAC and DMDAAC.

This example was identical to the preparation of example I, except that it was hydrolyzed to one-tenth the extent of Example I, e.g., by pumping a 20 percent KOH solution into the polymer solution at a rate of 2.6 ml./min.

#### EXAMPLE VI

The product made in Example V was field tested in a paper mill making publication grade paper. The furnish used in the paper was 1:1 mix of bleached groundwood and bleached kraft. The filler used was clay and the system pH was 3.9-4.1 adjusted with H<sub>2</sub>SO<sub>4</sub>. There was little or no alum in the system. One pass filler retention increased from 15 to 34 percent with the addition of 0.2 lb./ton, and increase of 56 percent.

#### EXAMPLE VII

Fifty percent hydrolyzed terpolymer of acrylamide, DMDAAC, and DEDAAC.

In this case, a polymer was made consisting of 70 percent acrylamide, 1.5 percent DEDAAC, and 28.5 percent DMDAAC following the general polymerization formula set out above. It was hydrolyzed to the extent of 50 percent of the quaternary ammonium by introducing to the polymer solution a 20 percent KOH solution at a rate of 76 ml./min. for 30 minutes. The batch was then held for 2 hours at 60° C. and drum dried.

#### EXAMPLE VIII

The polymer produced in example VII was used as a retention aid in the laboratory production of a typical bond paper using a valley handsheet machine to make a sheet 42 lb./3,000 sq. ft. The filler used was TiO<sub>2</sub> at 10 percent based on the weight of furnish (bleached sulfite). The retention aid was added to the wet pulp slurry corresponding to a head box addition in an amount equivalent to one-half pound of the retention aid per ton of dry pulp. In this series of laboratory experiments different amounts of alum were used to determine the effect of changes in alum loading upon retention. Results are shown in the following table.

TABLE III

	Percent Retention of TiO <sub>2</sub> (pH 4.7, adjusted with H <sub>2</sub> SO <sub>4</sub> )			
	0 lb./ton alum	20 lb./ton alum	40 lb./ton alum	80 lb./ton alum
With retention aid	62%	75%	88%	86%
Without retention aid	45%	52%	66%	63%

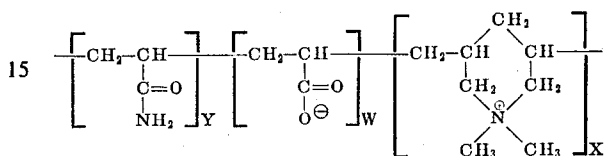
#### EXAMPLE IX

A monomer mixture of 20 percent solids in aqueous solution was formed from the following monomers:

- 60 parts of dimethyl diallyl ammonium chloride
- 40 parts of acrylamide.

The redox polymerization catalyst system set forth in Example I was added to this monomer solution, and polymerization was effected at 59° C. for about 1 hour. The amide groups in

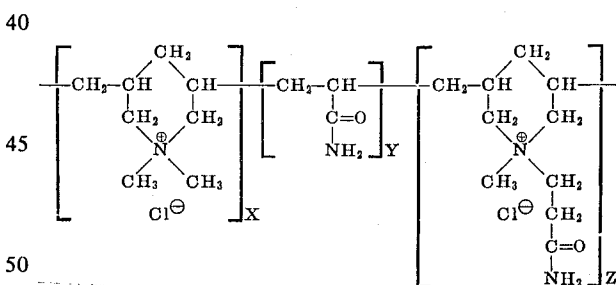
the resultant polymer were hydrolyzed by a 20 percent solution of sodium hydroxide, at a temperature of about 60° C. for 2½ hours. The resultant high molecular weight water soluble amphoteric polymer was used as a retention aid in the production of bond paper, and exhibited good retention and drainage properties with little or no change in these properties caused by varying either pH or alum loading. The hydrolyzed polymer had the representative general structure:



wherein (Y+W)/X was 40/60, and X/W was 10/0.8.

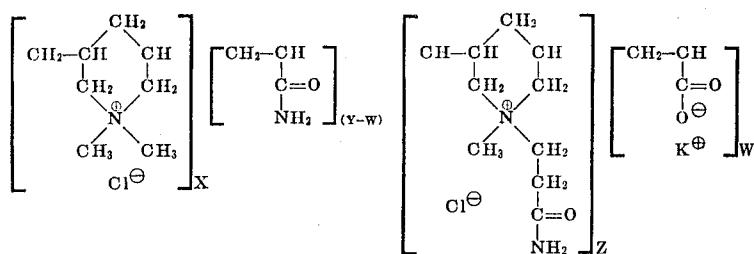
#### EXAMPLE X

Diallyl dimethyl ammonium chloride (38 parts by weight), acrylamide (60 parts by weight), and diallyl methyl beta-propionamido ammonium chloride (2 parts by weight) were dissolved in an aqueous solution at a total solids concentration of 25 percent. To this solution a redox polymerization catalyst composed of an aqueous solution of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was added and allowed to react to completion, the temperature was held at about 60° C. for about an hour. An aqueous solution of a water-soluble polymer was formed which had the representative linear formula:



wherein the ratio (X+Z):Y was 40:60, and the ratio of Z:X was 2:38.

The base polymer was hydrolyzed by treating the same with an appropriate amount of a 15 percent solids potassium hydroxide solution at a temperature of about 60° C. for about 2 hours, and the resulting hydrolyzed polymer had the representative linear formula:



wherein the ratio of (X+Z)/W was 10/1.8.

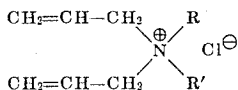
The partially hydrolyzed polymer is useful as a retention aid.

We do not intend to be restricted to the above-described specific copolymers and methods. Our invention may be otherwise practiced within the scope of the following claims.

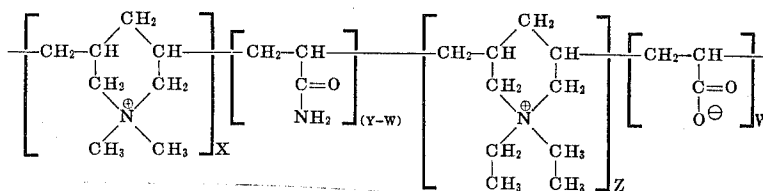
We claim:

1. Method of improving the retention of inorganic filler and cellulosic fines in the production of paper comprising adding to an aqueous paper pulp suspension a retention-improving dosage of about 0.1 to 5 pounds of a copolymer per ton of dry pulp wherein said copolymer is an amphoteric copolymer of (a) acrylamide and (b) diallyl quaternary ammonium compound in a weight ratio of (a) to (b) of from 30:70 to 70:30, in which the amide groups are hydrolyzed to carboxylic acid groups such that the ratio of quaternary ammonium groups to carboxylic groups is from about 10:0.1 to 10:5, and wherein the diallyl quaternary ammonium compound undergoes an intramolecular cyclic polymerization.

2. Method of claim 1 in which the diallyl quaternary ammonium compound is of the general formula:



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wherein R and R' are independently selected from the group consisting of alkyl groups of 1-18 carbon atoms, β-proprionamido and carboxymethyl.

3. The process as claimed in claim 1 wherein the ratio of acrylamide: diallyl quaternary ammonium compound is about 50:50, and wherein the copolymer is hydrolyzed such that the ratio of quaternary ammonium groups to carboxylic groups is about 10:1, and the diallyl quaternary ammonium compound is a mixture comprising about 95 percent dimethyl diallyl ammonium chloride and about 5 percent diethyl diallyl ammonium chloride.

4. The process as claimed in claim 1 wherein the water soluble, amphoteric copolymer has a molecular weight of at least 10,000.

5. In a method of making paper comprising providing an aqueous paper pulp suspension, depositing said aqueous paper pulp suspension on a forming surface to form a continuous aqueous paper sheet containing water and a paper fiber network, and thereafter draining at least a portion of said water from said fiber network, the improvement comprising the step of adding to said aqueous paper pulp suspension, prior to said depositing step, at least 0.1 pounds per ton of dry pulp of a high molecular weight water-soluble polymer of the formula:

where (X+Z)/Y is about 1, X/Z is about 19, and (X+Z)/W is about 10.

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