(54) Title: STRUCTURALLY-MODIFIED POLYMER FLOCCULANTS

(57) Abstract: This invention is directed to structurally-modified water-soluble polymers prepared by initiating polymerization of an aqueous solution of monomers under free radical polymerization conditions to form a polymer solution and adding at least one structural modifier to the polymer solution after at least 30 % polymerization of the monomers has occurred, and to use of the water-soluble cross-linked polymers as flocculating agents.

STRUCTURALLY-MODIFIED POLYMER FLOCCULANTS

TECHNICAL FIELD

This invention is directed to structurally-modified water-soluble polymers prepared by initiating polymerization of an aqueous solution of monomers under free radical polymerization and adding at least one modifier after at least 30% polymerization of the monomers has occurred, and to the use of the polymers as flocculants.

BACKGROUND OF THE INVENTION

Water-soluble polymeric flocculants are commonly used for clarifying suspensions of organic matter of a proteinaceous or cellulosic nature such as those found in sewage and industrial plant treatment effluents or in paper mills.

These suspended materials are hydrophilic in nature and often have specific gravities quite close to the aqueous liquors in which they are suspended, and differ in a marked way with more hydrophobic mineral suspensions in that they are frequently much more difficult to flocculate economically with chemical reagents prior to a physical dewatering step such as filtration, flotation, sedimentation or dewatering. These difficulties are particularly noticeable when higher proportions of suspended matter are present, commonly involving concentrations of 0.5 percent by weight and upwards where the suspensions take on a paste-like consistency and are commonly described as sludges.

It is well known that the clarification or dewatering of sewage and industrial sludges and similar organic suspensions may be aided by chemical reagents,

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added in order to induce a state of coagulation or
flocculation which facilitates the process of
solid/liquid or liquid/liquid separation from water. For
this purpose, lime or salts of iron or aluminum have been
utilized. More recently synthetic polyelectrolytes,
particularly certain cationic and anionic copolymers of
acrylamide, have been found to be of interest.

While strictly mechanical means have been used to
effect solids/liquid separation, modern methods often
rely on mechanical separation techniques that are
augmented by synthetic and natural polymeric materials to
accelerate the rate at which solids can be removed from
water. These processes include the treatment of raw
water with cationic coagulant polymers that settle
suspended inorganic particulates and make the water
usable for industrial or municipal purposes. Other
examples of these processes include the removal of
colored soluble species from paper mill effluent wastes
and the use of polymeric flocculants for the treatment of
industrial water, as sludge conditioners for the
treatment of municipal water systems, as retention and
drainage aids in the manufacture of paper, as chemicals
for recovering useful and valuable substances from white
water in the papermaking process and in emulsion
breaking.

A benchmark test for evaluating the effectiveness of
a flocculant is the so-called drainage test in which the
polymer is added to sludge and mixed so that the polymer
flocculates the sludge. The mixture is then poured
through a belt filter press cloth and the rate at which
water drains is taken as a measure of polymer
performance.

Regarding the mechanism of separation processes,
particles in nature have either a cationic or anionic

charge. Accordingly, these particles often are removed by a water-soluble coagulant or flocculant polymer having a charge opposite to that of the particles. This is referred to as a polyelectrolyte enhanced solids/liquid separation process, wherein a water-soluble or dispersible ionically charged polymer is added to neutralize the charged particles or emulsion droplets to be separated. The dosage of these polymers is critical to the performance of the process. Too little ionically charged polymer, and the suspended particles will not be charge neutralized and will thus still repel each other. Too much polymer, and the polymer will be wasted, or worse, present a problem in and of itself.

Notwithstanding the variety of commercially available polymers that have been found to be capable of flocculating or coagulating sludges, there are various circumstances which tend to limit the usefulness of these reagents. While for certain sludges economical treatments with these known reagents are feasible, more often sludges require very high and cost-ineffective dosages of reagents for successful treatment. Moreover, variations often occur in sludge from any one source. For example, variations in the supply of material to the waste water/sludge/paper furnish process water and/or in the oxidizing conditions that may be involved in the production of these waters lead to a variety of particle types which must be removed. Furthermore, it is not uncommon to encounter sludges that are, for some reason, not amenable to flocculation by any of the known polymeric flocculating agents.

Therefore, there is a need for an improved family of polymers that provide better drainage at lower doses in sludge dewatering. Likewise, there is a continuing need

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for treatments to increase the efficiency of pulp and paper manufacture.

EP 202,780 discloses particulate cross-linked copolymers of acrylamide with at least 5 mole percent dialkylaminoalkyl acrylate for use as flocculants in high-shear applications.

The addition of a cross-linking agent both at the beginning, and during the polymerization process under conditions such that its availability for reaction is substantially constant throughout the process is disclosed in U.S. Patent No. 4,950,725.

EP 374,458 discloses water-soluble branched high molecular weight cationic flocculants formed from monomers polymerized in the presence of chain transfer agents such as isopropanol and branching agents such as methylene bisacrylamide, in which the chain transfer agent is added to prevent cross linking. Cross linking can render the polymer insoluble in water.

Addition of chain transfer agent at the conclusion of polymerization of a DADMAC/acrylamide copolymer to produce a linear higher molecular weight copolymer is disclosed in EP 363,024.

U.S. Patent No. 4,913,775 discloses use of substantially linear cationic polymers such as acrylamide/dimethylaminoethyl acrylate methyl chloride quaternary salt copolymers and bentonite as additives in pulp or paper manufacture.

U.S. Patent No. 5,393,381 discloses use of a branched cationic polyacrylamide powder such as an acrylamide/dimethylaminoethyl acrylate quaternary salt copolymer and bentonite for paper or cardboard manufacture.

SUMMARY OF THE INVENTION

We have discovered that the late stage addition to a
polymerization reaction of a structural modifier as
described herein results in formation of a more
effective, structurally-modified flocculant. When the
structural modifier is a chain-transfer agent, the
resulting water-soluble polymers typically have a faster
rate of solubilization, higher reduced specific
viscosities and are more active than unmodified analogs.
This is applicable to cationic, anionic, or nonionic
polymers, synthesized using water-in-oil emulsion,
dispersion, or gel polymerization techniques.

Accordingly, in its principal aspect, this invention
is directed to a water-soluble polymer prepared by
initiating polymerization of an aqueous solution of
monomers under free radical polymerization conditions to
form a polymer solution and adding at least one
structural modifier to the polymer solution after at
least 30% polymerization of the monomers has occurred.

DETAILED DESCRIPTION OF THE INVENTION

Definitions of Terms

As used herein, the following abbreviations and
terms shall have the following meanings.

"AcAm" for acrylamide.

"DADMAC" for diallyldimethylammonium chloride.

"DMAEA" for dimethylaminoethyl acrylate.

"DMAEM" for dimethylaminoethyl methacrylate.

"DMAEA•BCQ" for dimethylaminoethyl acrylate, benzyl
chloride quaternary salt.

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"DMAEA•MCQ" for dimethylaminoethyl acrylate, methyl chloride quaternary salt.

"EDTA•4Na$^+$" for ethylenediaminetetraacetic acid, tetrasodium salt.

"Alfonic$^®$ 1412-60" is a ethoxylated linear alcohol (60% ethylene oxide), available from Vista Chemical Co., Houston, TX.

"Span 80" for sorbitan monooleate available from ICI Specialty Chemicals, Wilmington, DE.

"Triton$^®$ N-101" for nonylphenoxy polyethoxy ethanol, available from Rohm and Haas Co., Philadelphia, PA.

"Tween 61" for POE (4) sorbitan monostearate, available from ICI Specialty Chemicals, Wilmington, DE.

"AIBN" for 2,2'-azobis(isobutyronitrile), available from E. I. duPont Nemours & Co. Inc.; Wilmington, DE.

"AIVN" for 2,2'-azobis(2,4-dimethylvaleronitrile), available from E. I. duPont Nemours & Co. Inc.; Wilmington, DE.

"POE" for polyoxyethylene.

"RSV" stands for Reduced Specific Viscosity. Within a series of polymer homologs which are substantially linear and well solvated, "reduced specific viscosity (RSV)" measurements for dilute polymer solutions are an indication of polymer chain length and average molecular weight according to Paul J. Flory, in "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY., © 1953, Chapter VII, "Determination of Molecular Weights", pp. 266-316. The RSV is measured at a given polymer concentration and temperature and calculated as follows:

$$RSV = \frac{[(\eta/\eta_o)-1]}{c}$$

η = viscosity of polymer solution

η_o = viscosity of solvent at the same temperature

c = concentration of polymer in solution.

The units of concentration "c" are (grams/100 ml or g/deciliter). Therefore, the units of RSV are dl/g. In this patent application, a 1.0 molar sodium nitrate solution is used for measuring RSV, unless specified. The polymer concentration in this solvent is 0.045 g/dl. The RSV is measured at 30 °C. The viscosities η and η_o are measured using a Cannon Ubbelohde semimicro dilution viscometer, size 75. The viscometer is mounted in a perfectly vertical position in a constant temperature bath adjusted to 30 ± 0.02 °C. The error inherent in the calculation of RSV is about 2 dl/grams. When two polymer homologs within a series have similar RSV's that is an indication that they have similar molecular weights.

"IV" stands for intrinsic viscosity, which is RSV extrapolated to the limit of infinite dilution, infinite dilution being when the concentration of polymer is equal to zero.

"Based on formula" means the amount of reagent added based on the total formula weight.

"Based on polymer active" and "based on monomer" mean the amount of a reagent added based on the level of vinylic monomer in the formula, or the level of polymer formed after polymerization, assuming 100% conversion.

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"Raw water" means water from natural geographical sources including rivers, lakes, well water, rain water, and the like.

"Process water" means water used in a process such as a manufacturing process (paper machine), steel production, chemical production processes, refinery processes, food production processes (i.e., sugar process), and the like.

"Waste water" means water from a manufacturing process, municipal waste or other waters which are required to be treated prior to discharge to a receiving stream, lake or other water way.

"Papermaking process" means a method of making paper products from pulp comprising forming an aqueous cellulosic papermaking furnish, draining the furnish to form a sheet and drying the sheet. The steps of forming the papermaking furnish, draining and drying may be carried out in any conventional manner generally known to those skilled in the art. Conventional coagulants, conventional flocculants, microparticles, alum, cationic starch or a combination thereof may be utilized as adjuncts with the structurally-modified water-soluble polymer of this invention, though it must be emphasized that no adjunct is required for effective retention and drainage activity.

"Monomer" means a polymerizable allylic, vinylic or acrylic compound. The monomer may be anionic, cationic or nonionic. Vinyl monomers are preferred, acrylic monomers are more preferred.

Representative non-ionic, water-soluble monomers include acrylamide, methacrylamide, *N,N*-dimethylacrylamide, *N,N*-diethylacrylamide, *N*-isopropylacrylamide, *N*-vinylformamide,

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N-vinylmethylacetamide, *N*-vinyl pyrrolidone, hydroxyethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, *N-t-*butylacrylamide, *N*-methylolacrylamide, and the like.

Representative anionic monomers include acrylic acid, and it's salts, including, but not limited to sodium acrylate, and ammonium acrylate, methacrylic acid, and it's salts, including, but not limited to sodium methacrylate, and ammonium methacrylate, 2-acrylamido-2-methylpropanesulfonic acid (AMPS), the sodium salt of AMPS, sodium vinyl sulfonate, styrene sulfonate, maleic acid, and it's salts, including, but not limited to the sodium salt, and ammonium salt, sulfonate itaconate, sulfopropyl acrylate or methacrylate or other water-soluble forms of these or other polymerisable carboxylic or sulphonic acids. Sulfomethylated acrylamide, allyl sulfonate, sodium vinyl sulfonate, itaconic acid, acrylamidomethylbutanoic acid, fumaric acid, vinylphosphonic acid, vinylsulfonic acid, allylphosphonic acid, sulfomethyalted acryamide, phosphonomethylated acrylamide, and the like.

Representative cationic monomers include dialkylaminoalkyl acrylates and methacrylates and their quaternary or acid salts, including, but not limited to, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethyaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric

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acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dialkylaminoalkylacrylamides or methacrylamides and their quaternary or acid salts such as acrylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate, diallyldiethylammonium chloride and diallyldimethyl ammonium chloride. Alkyl groups are generally C_{1-4} alkyl.

"Structural modifier" means an agent that is added to the aqueous polymer solution to control the polymer structure and solubility characteristics. The structural modifier is selected from the group consisting of cross-linking agents and chain transfer agents.

"Chain transfer agent" means any molecule, used in free-radical polymerization, which will react with a polymer radical forming a dead polymer and a new radical. In particular, adding a chain transfer agent to a polymerizing mixture results in a chain-breaking and a concommitant decrease in the size of the polymerizing chain. Thus, adding a chain transfer agent limits the molecular weight of the polymer being prepared. Representative chain transfer agents include alcohols such as methanol, ethanol, 1-propanol, 2-propanol, butyl alcohol, and glycerol, and the like, sulfur compounds such as alkylthiols, thioureas, sulfites, and disulfides, carboxylic acids such as formic and malic acid, and their salts and phosphites such as sodium hypophosphite, and

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combinations thereof. *See* Berger et al., "*Transfer Constants to Monomer, Polymer, Catalyst, Solvent, and Additive in Free Radical Polymerization,*" Section II, pp. 81-151, in "*Polymer Handbook,*" edited by J. Brandrup and E. H. Immergut, 3d edition, John Wiley & Sons, New York (1989) and George Odian, *Principles of Polymerization,* second edition, John Wiley & Sons, New York (1981). A preferred alcohol is 2-propanol. Preferred sulfur compounds include ethanethiol, thiourea, and sodium bisulfite. Preferred carboxylic acids include formic acid and its salts. More preferred chain-transfer agents are sodium hypophosphite and sodium formate.

"Cross-linking agent" or "branching agent" means a multifunctional monomer that when added to polymerizing monomer or monomers results in "cross-linked" polymers in which a branch or branches from one polymer molecule become attached to other polymer molecules. Preferred cross-linkers are polyethylenically unsaturated monomers. Representative preferred cross-linking agents include N,N-methylenebisacrylamide, N,N-methylenebismethacrylamide, triallylamine, triallyl ammonium salts, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, polyethylene glycol diacrylate, triethylene glycol dimethylacrylate, polyethylene glycol dimethacrylate, N-vinylacrylamide, N-methylallylacrylamide , glycidyl acrylate, acrolein, glyoxal and vinyltrialkoxysilanes such as vinyltrimethoxysilane (VTMS), vinyltriethoxysilane, vinyltris(β-methoxyethoxy)silane, vinyltriacetoxysilane, allyltrimethoxysilane, allyltriacetoxysilane, vinylmethyldimethoxysilane, vinyldimethoxyethoxysilane, vinylmethyldiacetoxysilane, vinyldimethylacetoxysilane, vinylisobutyldimethoxysilane, vinyltriisopropoxysilane, vinyltri-n-butoxysilane, vinyltrisecbutoxysilane,

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vinyltrihexyloxysilane, vinylmethoxydihexyloxysilane,
vinyldimethoxyoctyloxysilane,
vinylmethoxydioctyloxysilane, vinyltrioctyloxysilane,
vinylmethoxydilauryloxysilane,
vinyldimethoxylauryloxysilane,
vinylmethoxydioleyoxysilane, and
vinyldimethoxyoleyloxysilane. A more preferred
vinylalkoxysilane monomer is vinyltrimethoxysilane.

Preferred Embodiments

The water-soluble modified polymers prepared as
describe herein may be cationic, anionic or non-ionic.
They may be emulsion polymers, dispersion polymers, or
gel polymers.

"Emulsion polymer" and "latex polymer" mean a water-
in-oil polymer emulsion comprising a cationic, anionic or
nonionic polymer according to this invention \in the
aqueous phase, a hydrocarbon oil for the oil phase and a
water-in-oil emulsifying agent. Inverse emulsion
polymers are hydrocarbon continuous with the water-
soluble polymers dispersed within the hydrocarbon matrix.
The inverse emulsion polymers are then "inverted" or
activated for use by releasing the polymer from the
particles using shear, dilution, and, generally, another
surfactant. See U.S. Pat. No. 3,734,873, incorporated
herein by reference. Representative preparations of high
molecular weight inverse emulsion polymers are described
U. S. Patent nos. 2,982,749; 3,284,393; and 3,734,873.
See also, "Mechanism, Kinetics and Modeling of the
Inverse-Microsuspension Homopolymerization of
Acrylamide," Hunkeler, et al., Polymer (1989), 30(1),
127-42; and "Mechanism, Kinetics and Modeling of Inverse-
Microsuspension Polymerization: 2. Copolymerization of

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Acrylamide with Quaternary Ammonium Cationic Monomers,"
Hunkeler et al., Polymer (1991), 32(14), 2626-40.

The aqueous phase is prepared by mixing together in
water one or more water-soluble monomers, and any
polymerization additives such as inorganic salts,
chelants, pH buffers, and the like.

The oil phase is prepared by mixing together an
inert hydrocarbon liquid with one or more oil soluble
surfactants. The surfactant mixture should have a low
HLB, to ensure the formation of an oil continuous
emulsion. Appropriate surfactants for water-in-oil
emulsion polymerizations, which are commercially
available, are compiled in the North American Edition of
McCutcheon's Emulsifiers & Detergents. The oil phase may
need to be heated to ensure the formation of a
homogeneous oil solution.

The oil phase is then charged into a reactor
equipped with a mixer, a thermocouple, a nitrogen purge
tube, and a condenser. The aqueous phase is added to the
reactor containing the oil phase with vigorous stirring
to form an emulsion. The resulting emulsion is heated to
the desired temperature, purged with nitrogen, and a
free-radical initiator is added. The reaction mixture is
stirred for several hours under a nitrogen atmosphere at
the desired temperature. Upon completion of the
reaction, the water-in-oil emulsion polymer is cooled to
room temperature, where any desired post-polymerization
additives, such as antioxidants, or a high HLB surfactant
(as described in U.S. Patent 3,734,873) may be added.

The resulting emulsion polymer is a free-flowing
liquid. An aqueous solution of the water-in-oil emulsion
polymer can be generated by adding a desired amount of
the emulsion polymer to water with vigorous mixing in the

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presence of a high-HLB surfactant (as described in U.S. Patent 3,734,873).

"Dispersion polymer" means a dispersion of fine particles of polymer in an aqueous salt solution which is prepared by polymerizing monomers with stirring in an aqueous salt solution in which the resulting polymer is insoluble. See U.S. Pat. nos. 5,708,071; 4,929,655; 5,006,590; 5,597,859; 5,597,858 and European Patent nos. 657,478 and 630,909.

In a typical procedure for preparing a dispersion polymer, an aqueous solution containing one or more inorganic or hydrophobic salts, one or more water-soluble monomers, any polymerization additives such as processing aids, chelants, pH buffers and a water-soluble stabilizer polymer is charged to a reactor equipped with a mixer, a thermocouple, a nitrogen purging tube, and a water condenser. The monomer solution is mixed vigorously, heated to the desired temperature, and then a water-soluble initiator is added. The solution is purged with nitrogen while maintaining temperature and mixing for several hours. After this time, the mixture is cooled to room temperature, and any post-polymerization additives are charged to the reactor. Water continuous dispersions of water-soluble polymers are free flowing liquids with product viscosities generally 100-10,000 cP, measured at low shear.

In a typical procedure for preparing gel polymers, an aqueous solution containing one or more water-soluble monomers and any additional polymerization additives such as chelants, pH buffers, and the like, is prepared. This mixture is charged to a reactor equipped with a mixer, a thermocouple, a nitrogen purging tube and a water condenser. The solution is mixed vigorously, heated to the desired temperature, and then one or more water-

soluble free radical polymerization initiators are added.
The solution is purged with nitrogen while maintaining
temperature and mixing for several hours. Typically, the
viscosity of the solution increases during this period.
After the polymerization is complete, the reactor
contents are cooled to room temperature and then
transferred to storage. Gel polymer viscosities vary
widely, and are dependent upon the concentration and
molecular weight of the active polymer component.

The polymerization reactions described herein are
initiated by any means which results in generation of a
suitable free-radical. Thermally derived radicals, in
which the radical species results from thermal, homolytic
dissociation of an azo, peroxide, hydroperoxide and
perester compound are preferred. Especially preferred
initiators are azo compounds including 2,2'-azobis(2-
amidinopropane) dihydrochloride, 2,2'-azobis[2-(2-
imidazolin-2-yl)propane] dihydrochloride, 2,2'-
azobis(isobutyronitrile) (AIBN), 2,2'-azobis(2,4-
dimethylvaleronitrile) (AIVN), and the like.

The polymerization conditions utilized herein are
selected such that the resulting water-soluble
structurally-modified polymer has a molecular weight of 2
million to 30 million and an intrinsic viscosity above 1,
more preferably above 6 and still more preferably 15 to
30 dl/g. The reduced specific viscosity of the water-
soluble structurally-modified polymer is generally above
3, preferably above 12 and frequently above 24 dl/g.

The structural modifiers are added to the reaction
mixture after the start of polymerization of the monomers
and prior to completion of polymerization of the
monomers. They may be added all at once as a single
treatment, or in portions. The level of modifier added
to the aqueous polymer solution depends on the efficiency

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of the structural modifier, the polymer concentration, and the degree of polymerization at which it is added.

The degree of polymerization of monomers is determined by the change in the reaction density for water-in-oil emulsion polymerization, calorimeterically by measuring the heat of reaction, by quantitative infrared spectroscopy, or chromatographically, by measuring the level of unreacted monomer.

When a chain-transfer agent is the structural modifying agent, the chain-transfer agent may be added all at once as a single treatment, in portions, or in a manner such that the rate of addition parallels polymer conversion. In one embodiment, addition may be as a single treatment added after about 30%, preferably after about 50% polymerization of the monomers. The level of chain-transfer agent added is generally between from about 1 to about 30,000 ppm, preferably from about 25 to about 10,000 ppm and more preferably from about 50 to about 2,000 ppm based on monomer. When the chain-transfer agent is sodium hypophosphite, the level added is generally from about 2 to about 2000 ppm, preferably from about 100 to about 1000 ppm.

When the structural modifier is a cross-linking agent, the cross-linking agent is added after about 30%, preferably after about 50% polymerization of the monomers. The level of cross-linking agent is generally from about 0.1 to about 500 ppm, preferably from about 1 to about 50 ppm based on monomer. When the cross-linking agent is methylenebisacrylamide, the level is generally from about 0.5 to about 50 ppm, preferably from about 1 to about 10 ppm based on monomer.

When the cross-linker is a vinyltrialkoxysilane, the level of cross-linker is generally from about 0.1 to about 30,000 ppm, preferably from about 0.5 to about

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15,000 ppm, more preferably from about 1 to about 3,000
ppm based on monomer. The vinyltrialkoxysilane may be
added all at once as a single treatment, or in portions
after the polymerization of the monomers has started,
preferably after about 30 percent of the monomers have
polymerized.

When the structural modifier is a combination of a
cross-linker and a chain transfer agent, the amounts of
each may vary widely based on the chain-transfer constant
"efficiency" of the chain-transfer agent, the
multiplicity and "efficiency" of the cross-linking agent,
and the point during the polymerization where it is
added. For example from about 1,000 to about 5,000 ppm
(based on monomer) of a moderate chain transfer agent
such as isopropyl alcohol may be suitable while much
lower amounts, typically from about 100 to about 500 ppm,
of more effective chain transfer agents such as
mercaptoethanol are useful. Representative combinations
of cross-linkers and chain transfer agents contain from
about 1 to about 30,000 ppm, preferably from about 25 to
about 10,000 and more preferably from about 300 to about
1500 ppm (based on monomer) of chain transfer agent and
from about 1 to about 500, preferably from about 2 to
about 100 and more preferably from about 5 to about 50
ppm (based on monomer) of cross-linker. A preferred
combination of cross-linker and chain transfer agent is
methylenebisacrylamide and formic acid and its salts,
preferably sodium formate.

Where the structural modifier is a cross-linking
agent, polymers formed by the addition of a cross-linking
agent to the polymerization generally between 30% and 99%
conversion, preferably between 50 and 90% conversion, and
frequently between 65 and 85% conversion, are more active
than the unmodified polymers which are substantially

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linear, cross-linked, water-insoluble particles disclosed
in US 4,950,725 and EP 202,780 and the highly branched,
water-soluble polymers disclosed in US 5,945,494.

The polymers modified with a cross-linking agent
after the start of polymerization differ from the
particulate polymer flocculants disclosed in US 4,950,725
and EP 202,780 that are swellable, but, insoluble in
water. These particles are formed either through the
addition of a water-soluble cross-linking agent, or a
mixture of different cross-linking reagents with
different reactivities, usually polyethylenically
unsaturated monomers at the front-end, or alternatively
both at the beginning of the process and at or near the
end of the process such that the availability of the
cross-linker is substantially constant throughout the
reaction or by cross-linking preformed water-soluble
polymers. Polymers modified with a cross-linking agent
as described herein are not particulate in aqueous
solution.

The polymers of this invention also differ from
polymers disclosed in US 5,945,494, which are water-
soluble, highly branched species. Essential to the
formation of these polymers is the inclusion of a
molecular weight modifying, or chain-transfer agent in
combination with high levels of a branching agent (4 to
80 ppm, based on initial molar content) to form highly-
branched, water-soluble polymers. As stated in US
5,945,494 column 5, lines 35-38, in the absence of a
chain-transfer agent, the incorporation of even extremely
small amounts of branching agent, e.g. 5 parts per
million may cause crosslinking, rendering the polymer
insoluble in water. The combination of a branching agent
and a molecular weight modifying agent included in the
aqueous monomer solution at the start of reaction as

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disclosed in US 5,945,494, will yield highly branched polymers with polymer chains of limited molecular weight.

It is believed that polymers modified with a cross-linking agent after the start of polymerization described herein contain a mixture of linear high molecular weight polymer formed during the initial part of the reaction, and long-chain branched polymer formed during the latter part of the reaction. For aqueous solutions made-up from polymers modified using late addition of a cross-linking agent, it is possible that water-soluble, non-particulate, aggregates of several entangled polymer chains exist. Macromolecular entanglements have been proposed for high molecular weight polymers, formed by free-radical polymerization methods (Gardner, et. al., J. Applied Polymer Science, 22 881-882, (1978); A. Wan, Polymer Preprints, Am. Chem. Soc., Division of Polymer Chemistry, 37(2), 655, (1996).

In a preferred aspect of this invention, the structurally-modified water-soluble polymer is selected from the group consisting of emulsion polymers, dispersion polymers and gel polymers.

In another preferred aspect, the monomers are selected from acrylamide or methacrylamide and one or more monomers selected from the group consisting of diallyldimethylammonium chloride, dimethylaminoethyl acrylate methyl chloride quaternary salt, acrylamidopropyltrimethylammonium chloride, dimethylaminoethyl methacrylate methyl chloride quaternary salt, methacrylamidopropyltrimethylammonium chloride, acrylic acid, sodium acrylate, ammonium acrylate, methacrylic acid, sodium methacrylate, and ammonium methacrylate.

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In another preferred aspect, the structural modifier is selected from the group consisting of cross-linking agents, chain transfer agents and mixtures thereof.

In another preferred aspect, the chain transfer agents are selected from the group consisting of alcohols, sulfur compounds, carboxylic acids or salts thereof, phosphites, and combinations thereof.

In another preferred aspect, the chain transfer agents are selected from sodium formate and sodium hypophosphite.

In another preferred aspect, the cross-linking agent is selected from the group consisting of N,N-methylenebisacrylamide, N,N-methylenebismethacrylamide, triallylamine, triallyl ammonium salts, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, N-vinyl acrylamide, N-methyl allylacrylamide, vinyltrimethoxysilane, and combinations thereof.

In another preferred aspect, the cross-linking agent is vinyltrimethoxysilane.

In another preferred aspect, the cross-linking agent is methylenebisacrylamide.

In another preferred aspect, the monomers are acrylamide and dimethylaminoethylacrylate benzyl chloride quaternary salt and the structural modifier is vinyltrimethoxysilane.

In another preferred aspect, the monomers are acrylamide and diallyldimethylammonium chloride and the structural modifier is vinyltrimethoxysilane.

In another preferred aspect, the monomers are acrylamide and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is methylenebisacrylamide.

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In another preferred aspect, the monomers are acrylamide and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is sodium formate.

In another preferred aspect, the monomers are acrylamide and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is sodium hypophosphite.

In another preferred aspect, the monomers are acrylamide and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is a combination of sodium formate and methylenebisacrylamide.

In another preferred aspect, the monomers are acrylamide, dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is methylenebisacrylamide.

In another preferred aspect, the monomers are acrylamide, dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is sodium formate.

In another preferred aspect, the monomers are acrylamide, dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier isa combination of methylenebisacrylamide and sodium formate.

In another preferred aspect, the monomers are acrylamide, dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is vinyltrimethoxysilane.

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In another preferred aspect, the monomers are acrylamide and acrylic acid or a salt thereof and the structural modifier is sodium hypophosphite.

In another aspect, this invention is directed to a method of preparing a structurally-modified water-soluble polymer comprising initiating polymerization of an aqueous solution of monomers under free radical polymerization conditions to form a polymer solution and adding at least one structural modifier to the polymer solution after at least 30% polymerization of the monomers has occurred.

In another aspect, this invention is directed to a method of flocculating an aqueous suspension of organic matter comprising adding to the suspension an effective flocculating amount of the structurally-modified water-soluble polymer prepared by initiating polymerization of an aqueous solution of monomers under free radical polymerization conditions to form a polymer solution and adding at least one structural modifier to the polymer solution after at least 30% polymerization of the monomers has occurred.

In another aspect, this invention is directed to a method of clarifying waste water comprising adding to the waste water an effective flocculating amount of a structurally-modified water-soluble polymer prepared by initiating polymerization of an aqueous solution of monomers under free radical polymerization conditions to form a polymer solution and adding at least one structural modifier to the polymer solution after at least 30% polymerization of the monomers has occurred.

The effective flocculating amount of the structurally-modified water-soluble polymer depends on the characteristics of the water being treated and can be readily determined by one of ordinary skill in the art.

Polymer should be dosed at a sufficient level to cause
flocculation of the dispersed material and cause improved
settling. Typical dosages are from about 10 to 1,000
ppm, preferably from about 15 to about 400 ppm and more
preferably from about 20 to about 200 ppm based on
polymer actives.

In another aspect, this invention is directed to a
method of increasing retention and drainage in a
papermaking furnish comprising adding to the furnish an
effective amount of a structurally-modified water-soluble
polymer prepared by initiating polymerization of an
aqueous solution of monomers under free radical
polymerization conditions to form a polymer solution and
adding at least one structural modifier to the polymer
solution after at least 30% polymerization of the
monomers has occurred.

The effective amount of the structurally-modified
water-soluble polymer depends on the characteristics of
the particular papermaking furnish and can be readily
determined by one of ordinary skill in the papermaking
art. Typical dosages are from about 0.01 to about 6,
preferably from about 0.1 to about 4 and more preferably
from about 0.1 to about 2 pounds polymer actives/ton
solids in the furnish.

The structurally-modified water-soluble polymer of
this invention may also be used in combination with a
coagulant as part of a dual polymer treatment program.
The retention and drainage properties of the furnish may
also be improved by addition of a microparticle is
described in United States Pat. Nos. 4,753,710 and
4,913,775 incorporated herein by reference.

"Microparticles" means highly charged materials that
improve flocculation when used together with natural and
synthetic macromolecules. Microparticles are used in

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combination with other wet end additives to improve
retention and drainage on the paper machine.
Microparticles encompass a broad set of chemistries
including polysilicate microgel, structured colloidal
silicas, colloidal alumina, polymers including copolymers
of acrylic acid and acrylamide and and naphthalene
sulfonate/formaldehyde condensate polymers, bentonite and
mineral clays such as montmorillonite, saponite and
smectite types and colloidal silica in its many forms
including modified colloidal silicic acids such as those
described in PCT/US98/19339.

Representative copolymers of acrylic acid and
acrylamide useful as microparticles include Nalco® 8677
PLUS, available from Nalco Chemical Company, Naperville,
IL, USA. Other copolymers of acrylic acid and acrylamide
are described in U.S. Patent No. 5,098,520, incorporated
herein by reference.

"Bentonites" include any of the materials
commercially referred to as bentonites or as bentonite-
type clays, i.e., anionic swelling clays such as
sepialite, attapulgite and montmorillonite. In addition,
the bentonites described in U.S. Patent No. 4,305,781 are
suitable. A preferred bentonite is a hydrated suspension
of powdered bentonite in water. Powdered bentonite is
available as Nalbrite™, from Nalco Chemical Company.

Representative dispersed silicas have an average
particle size of from about 1 to about 100 nanometers
(nm), preferably from about 2 to about 25 nm, and more
preferably from about 2 to about 15 nm. This dispersed
silica, may be in the form of colloidal, silicic acid,
silica sols, fumed silica, agglomerated silicic acid,
silica gels, precipitated silicas, and all materials
described in Patent Cooperation Treaty Patent Application
No. PCT/US98/19339, so long as the particle size or

ultimate particle size is within the above ranges.
Dispersed colloidal silica in water with a typical
particle size of 4 nm is available as Nalco® 8671, from
Nalco Chemical Company. Another type of inorganic
colloid used as a microparticle is a borosilicate in
water; available as Nalco® 8692, from Nalco Chemical
Company. Other types of colloidal silica and modified
colloidal silicas are commercially available from E.I.
DuPont de Nemours and Co., Wilmington, DE under the
tradename Ludox®, from Akzo Nobel, Surte, Sweden (BMA or
NP Series), from Vinings Industries Inc., Atlanta, GA and
from Nissan Chemical Industries, Ltd., Tokyo, Japan.

Representative naphthalene sulfonate/formaldehyde
condensate polymers include Nalco® 8678 from Nalco
Chemical Company.

The amount of microparticle added is from about 0.05
to about 10, preferably from about 0.1 to about 9 and
more preferably about 0.2 to about 6 pounds
microparticle/ton.

"Pounds microparticle/ton" means pounds of actual
microparticle per 2000 pounds of solids present in
slurry. The abbreviation for pounds of actual
microparticle per 2000 pounds of solids present in slurry
is "lbs microparticle/ton".

The microparticle is added to the papermaking
furnish either before or after the structurally-modified
polymer is added to the furnish. The choice of whether
to add the microparticle before or after the polymer can
be made by a person of ordinary skill in the art based on
the requirements and specifications of the papermaking
furnish.

Optionally, a coagulant is added to the furnish
prior to the addition of the structurally-modified water-
soluble polymer. Preferred coagulants are water-soluble

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cationic polymers such as epichlorohydrin-dimethylamine or polydiallyldimethylammonium chloride, alum, polyaluminum chlorides or cationic starch.

In another aspect, this invention is directed to a method of increasing retention and drainage in a papermaking furnish comprising adding to the furnish a microparticle and an effective amount of a structurally-modified water-soluble polymer prepared by initiating polymerization of an aqueous solution of monomers under free radical polymerization conditions to form a polymer solution and adding at least one structural modifier to the polymer solution after at least 30% polymerization of the monomers has occurred.

In another aspect, this invention is directed to a method of increasing retention and drainage in a papermaking furnish comprising adding to the furnish a microparticle, a coagulant and an effective amount of a structurally-modified water-soluble polymer prepared by initiating polymerization of an aqueous solution of monomers under free radical polymerization conditions to form a polymer solution and adding at least one structural modifier to the polymer solution after at least 30% polymerization of the monomers has occurred.

In another aspect, this invention is directed to a method of flocculating an aqueous coal refuse slurry comprising adding an effective amount of a structurally-modified water-soluble polymer prepared by initiating polymerization of an aqueous solution of monomers under free radical polymerization conditions to form a polymer solution and adding at least one structural modifier to the polymer solution after at least 30% polymerization of the monomers has occurred.

The foregoing may be better understood by reference to the following examples which are presented for

purposes of illustration and are not intended to limit
the scope of the invention. Examples 1-10 illustrate the
embodiment of the invention which is late addition of
cross linker; Examples 11-14, 25 and 26 illustrate the
embodiment of the invention which is late addition of
chain transfer agent; and Examples 15-23 illustrate the
embodiment of the invention which is late addition of
both cross-linker and chain transfer agent.

POLYMERS MODIFIED BY LATE ADDITION OF CROSS LINKING AGENTS

Example 1

Polymer 1, a control polymer of 15% polymer solids,
90/10 mole percent AcAm/DMAEA·BCQ dispersion is
synthesized in the following manner:

To a 1500 ml reaction flask fitted with a mechanical
stirrer, thermocouple, condenser, nitrogen purge tube and
addition port is added 213 g of a 49.6% aqueous solution
of acrylamide (Nalco Chemical Company, Naperville, IL),
56.6 g of dimethylaminoethylacrylate benzyl chloride
quaternary salt (70.9% aqueous solution, Nalco Chemical
Company, Naperville, IL), 9 g of glycerin, 59 g of the
copolymer of dimethylaminoethylacrylate benzyl chloride
quaternary salt and diallyldimethylammonium chloride (15%
aqueous solution, Nalco Chemical Company, Naperville,
IL), 0.4 g of ethylenediaminetetraacetic acid,
tetrasodium salt, 157 g of ammonium sulfate and 424 g of
deionized water. The mixture is then heated to 48 °C
while stirring at 900 rpm. After reaching 48 °C, 1.2 g
of a 1.0% aqueous solution of 2,2'-azobis(2-
amidinopropane) dihydrochloride (V-50, Wako Chemicals,
Dallas, TX) is added to the reaction mixture, the system
is purged with nitrogen and the temperature is maintained

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at 48 °C. Two hours after initiation, 3.8 g of a 1.0%
aqueous solution of 2,2'-azobis(2-amidinopropane)
dihydrochloride is added to the reaction and at three
hours after initiation 6.0 g of
dimethylaminoethylacrylate benzyl chloride quaternary
salt and at four hours 4 g of a 10% aqueous solution of
2,2'-azobis(2-amidinopropane) dihydrochloride is added.
At six hours the reaction is cooled to ambient
temperature and 55.0 g of sodium sulfate, 10.0 g sodium
thiosulfate, and 10.0 g acetic acid are added. The
resulting product is a smooth milky white dispersion with
a bulk viscosity of 30 cP (centipoise) and a reduced
specific viscosity of 17.8 dl/g (0.045% polymer in 0.125
N NaNO$_3$ solution at 30 °C).

Example 2

Polymer 2, a vinyltrimethoxysilane modified 15%
polymer solids, 90/10 mole percent AcAm/DMAEA·BCQ
dispersion polymer is synthesized using the general
procedure described in Example 1. The standard method is
modified by adding 0.25 g vinyltrimethoxysilane (Huls
America, Inc., Bristol, PA) to the reaction mixture at
3.5 hours after initiation (approximately 88%
conversion). No further modifications are made. The
reduced specific viscosity of the product is 18.3 dl/g
(0.045% polymer in 0.125 N NaNO$_3$ solution at 30°C).

Example 3

Polymer 3, a vinyltrimethoxysilane modified 15%
polymer solids, 90/10 mole percent AcAm/DMAEA·BCQ
dispersion is synthesized using the general procedure
described in Example 1. The standard method is modified
by addition of 0.10 g vinyltrimethoxysilane (Huls
America, Inc. Bristol, PA) to the reaction mixture at 3

hours after initiation (approximately 86% conversion).
No further modifications are made. The resulting product
is a smooth milky white dispersion has a bulk viscosity
of 30 cP and a reduced specific viscosity of 16 dl/g
(0.045% polymer in 0.125 N NaNO$_3$ solution at 30 °C).

Example 4

    Polymer 4, a VTMS modified 15% solids, 90/10 mole
percent AcAm/DMAEA·MCQ is synthesized using the following
procedure.

    To a 1500 ml resin flask equipped with a stirrer,
temperature controller, nitrogen sparge tube and water
condenser is added 335.2 g of deionized water, 230.3 g of
a 48.6% aqueous solution of acrylamide (Nalco Chemical
Co., Naperville, IL), 43.6g of dimethlyaminoethylacrylate
methyl chloride quaternary salt (DMAEA·MCQ, 80%, NCF
Manufacturing, Riceboro, GA), 50.0 g of a 15% solution of
poly(dimethlaminoethylmethacrylate methyl chloride
quaternary salt, Nalco Chemical Co., Naperville, IL), 5.0
g of adipic acid, 13.5 g of glycerol, 0.42 g of EDTA·4Na$^+$
and 302.0 g ammonium sulfate. The mixture is heated to
48 °C and 1.0 g of a 1% solution of V-50 is added. The
resulting solution is sparged with nitrogen at the rate
of 1000 ml/min. After 15 minutes, polymerization begins
and the solution becomes viscous. Over the next four
hours, the temperature is maintained at 48 °C. After 3.0
hours of polymerization, an additional 2.0 g of a 1%
solution of V-50 is added to the reaction mixture. After
3.5 hours of polymerization (approximately 80%
conversion), 0.25 g of vinyltrimethoxysilane is added to
the reaction mixture. At four hours after initiation,
4.0 g of a 10% solution of V-50 is added to the
dispersion and the reaction is allowed to continue for
another 4 hours. After this time, the dispersion is

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cooled to room temperature, and 5.0 g of adipic acid and
10.0 g of sodium thiosulfate is added. The polymer
product has a Brookfield viscosity of 150 cP (#3 spindle,
12 rpm) and a reduced specific viscosity of 18 dl/g at
450 ppm in 1 N NaNO₃.

Example 5

Polymer 5, a 21% polymer solids, 70/30 mole percent
acrylamide/diallyldimethyl ammonium chloride VTMS-
modified dispersion polymer was synthesized in the
following manner.

To a 1500 ml reaction flask fitted with a mechanical
stirrer, thermocouple, condenser, nitrogen purge tube,
and addition port is added 28.0 g of a 49.4% aqueous
solution of acrylamide (Nalco Chemical Company,
Naperville, IL), 175.0 g of a 63% aqueous solution of
diallyldimethyl ammonium chloride (Nalco Chemical
Company, Naperville, IL), 44.0 g of a 15% aqueous
solution of a homopolymer of dimethylaminoethyl acrylate
methyl chloride quaternary salt (Nalco Chemical Company,
Naperville, IL), 0.66 g of sodium formate, 0.44 g of
ethylenediaminetetraacetic acid, tetra sodium salt, 220.0
g of ammonium sulfate, 44.0 g sodium sulfate, 0.20 g
polysilane antifoam (Nalco Chemical Company, Naperville,
IL), and 332.0 g of deionized water. The resulting
mixture is heated to 42 °C and is stirred at 700 rpm.
Upon reaching 42 °C, 5.0 g of a 10.0% aqueous solution of
2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride
(VA-044, Wako Chemicals, Dallas, TX) is added to the
reaction mixture and a nitrogen purge started. Forty-
five minutes after initiator addition, 194.7 g of a 49.4%
aqueous solution of acrylamide is added to the reaction
mixture over a period of 6 hours. At 4.5 hours after
initiator addition (~80% acrylamide conversion based on

total monomer), 0.26 g of vinyltrimethoxysilane (Huls America, Inc., Bristol, PA) is added to the reaction. At 8 hours after the initiator addition, the reaction mixture is cooled to ambient temperature. The product is a smooth milky white dispersion with a bulk viscosity of 520 cP and a reduced specific viscosity of 4.5 dl/g (0.045% solution of the polymer in 1.0 N aqueous sodium nitrate at 30 °C).

Example 6

    Polymer 6, a vinyltrimethoxy silane-modified, 21% polymer solids, 70/30 mole percent acrylamide/diallyldimethyl ammonium chloride dispersion polymer is synthesized following the procedure described in Example 5, except that the vinyltrimethoxysilane is added to the reaction 5.5 hours after initiator addition (~90% acrylamide conversion based on total monomer). The product is a smooth milky white dispersion with a bulk viscosity of 460 cp and a reduced specific viscosity of 5.1dl/g (0.045% solution of the polymer in 1.0 N aqueous sodium nitrate at 30 °C).

    The polymers synthesized by the methods of Example 1-6 are summarized in Table 1.

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Table 1

Polymer Modified by Late Addition of VTMS

(VTMS levels in ppm based on polymer actives in product)

Polymer	Modified	Form	[VTMS] (ppm)	RSV (dl/g)
1	no	hydrophobic dispersion	None	18
2	yes	hydrophobic dispersion	1667	18
3	yes	hydrophobic dispersion	667	16
4	yes	hydrophilic dispersion	1667	18
5	yes	hydrophilic dispersion	1250	4.5
6	yes	hydrophilic dispersion	1250	5.1
7[1]	no	hydrophilic dispersion	None	18
8[2]	no	hydrophilic dispersion	None	4.5

[1]Commercially available 90/10 mole percent AcAm/DMAEA·MCQ copolymer (Nalco Chemical Company, Naperville, IL).

[2]Commercially available 70/30 mole percent AcAm/DADMAC copolymer (Nalco Chemical Company, Naperville, IL).

Example 7

Three experimental techniques are utilized to assess the utility of the structurally-modified polymers in papermaking applications. These techniques are detailed below. For the first two techniques, a synthetic alkaline paper furnish is utilized.

The alkaline furnish has a pH of 8.1 and is composed of 80 weight percent cellulosic fiber and 20 weight percent filler diluted to an overall consistency of 0.5% by weight using synthetic formulation water. The cellulosic fiber consists of 60% by weight bleached hardwood kraft and 40% by weight bleached softwood kraft. The filler is a commercial ground calcium carbonate provided in dry form. The formulation water contains 200 ppm calcium hardness (added as $CaCl_2$), 152 ppm magnesium

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hardness (added as MgSO$_4$), and 110 ppm bicarbonate alkalinity (added as NaHCO$_3$).

Britt Jar Test

The Britt Jar Test uses a Britt CF Dynamic Drainage Jar developed by K. W. Britt of New York University, which generally consists of an upper chamber of about 1 liter capacity and a bottom drainage chamber, the chambers being separated by a support screen and a drainage screen (typically 200 mesh or 76 μm opening). Below the drainage chamber is a flexible tube extending downward equipped with a clamp for closure. The upper chamber is provided with a 2-inch, 3-blade propeller to create controlled shear conditions in the upper chamber. The test is performed according to the following sequence:

Time (seconds)	Action
0	Commence shear via mixing; add synthetic furnish.
10	Add starch (usually 10 lb/t).
20	Add flocculant to be tested.
30	Open the tube clamp to commence drainage.
60	Stop draining and measure turbidity of filtrate.

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Where the beneficial effect of microparticles on polymer performance is evaluated, the following sequence is used:

Time (seconds)	Agitator Speed (rpm)	Action
0	750	Commence shear via mixing; add synthetic furnish.
10	750	Add cationic starch (usually 10 lb/t).
20	2000	Add flocculant to be tested.
50	750	Reduce the shear via mixing speed.
60	750	Add microparticle.
70	750	Open the tube clamp to commence drainage.
100	750	Stop draining.

The starch used is Solvitose N, a cationic potato starch, commercially available from Nalco Chemical Company, Naperville, IL. The material drained from the Britt Jar (the "filtrate") is collected and diluted with water to provide a turbidity which can be measured conveniently. The turbidity of such diluted filtrate is then determined in Nephelometric or Formazine Turbidity Units (NTU or FTU). The turbidity of the filtrate is inversely proportional to the papermaking retention performance; the lower the turbidity value (or higher the turbidity reduction), the higher is the retention of filler and/or fines. Therefore the lower the turbidity, the more efficient the flocculant. The turbidity values are determined using a Hach Turbidimeter.

Filler retention for the synthetic alkaline furnish is also determined by gravimetric analysis (500 - 550 $^\circ$C) of the filtrate collected.

Focused Beam Reflectance Measurement (FBRM)

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The size of flocs formed (evaluated by determining changes in the mean chord length) for the synthetic alkaline furnish are measured *in-situ* using a Focused Beam Reflectance (FBRM) instrument to measure peak mean chord length. The FBRM employed in the following examples is described in U.S. Patent No. 4,871,251 and Alfano, et al., Nordic Pulp and Paper Research Journal, 13, (2), 159 (1998), and generally consists of a laser source, optics to deliver the incident light to and retrieve the scattered light from the furnish, a photodiode, and signal analysis hardware. Commercial instruments (Model # M100 or M500) are available from Lasentec™, Redmond, Washington.

The experiment consists of taking 300 ml of the desired paper furnish and placing this in the appropriate mixing beaker. Shear is provided to the furnish via a variable speed motor and propeller. The propeller is set at a fixed distance from the probe window to ensure slurry movement across the window. The change in mean chord length of the the furnish relates to papermaking retention performance; the greater the change induced by the treatment, the higher the retention value. Therefore a larger mean chord length number means that the flocculant is more efficient. A typical dosing sequence is shown below.

Time (seconds)	Action
0	Commence mixing. Record baseline floc size.
30	Add cationic starch. Record floc size change.
45	Add flocculant to be tested. Record floc size change.
90	Terminate experiment.

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Dissolved Air Flotation Test (DAF)

Samples of dissolved air flotation (DAF) influent are obtained from a Southern United States newsprint deinking mill. Typical jar tests are used to monitor polymer performance. Samples of the deinking influent are stirred at 200 rpm (fast mix) for 3 minutes. A coagulant (alum) is added at the beginning of fast mix and the flocculant during the last 40 seconds of the fast mix. This is followed by a slow mix at 25 rpm for 2 minutes. The samples are allowed to settle for 5 minutes and an aliquot of the upper liquid layer is removed. The turbidity of these aliquots is determined with a HACH DR2000 at 450 nm. The lower the turbidity, the more efficient the flocculant.

The Britt Jar test described above is utilized to obtain the results of Tables 2-4. In all examples, a greater turbidity reduction resulted from use of VTMS-modified dispersion polymer flocculants than with the equivalent dispersion polymer flocculants which are not modified.

Table 2

Polymer Retention Performance Comparison for Modified
versus
Unmodified Dispersion Polymers at 750 rpm (low shear)

	Performance[2]	
Dosage[1]	Polymer 7	Polymer 4
0.3	69.2	71.5
0.6	78.3	83.2
0.9	82.6	86.9

[1]pound active per ton solids.

[2]measured in terms of percent turbidity reduction.

Table 3

Polymer Retention Performance for Modified versus
Unmodified
Dispersion Polymers at 1250 rpm (medium shear)

Dosage[1]	Performance[2]			
	Polymer 1	Polymer 2	Polymer 7	Polymer 4
0.60	57.1	59.4	57.1	59.4
0.90	62.9	64.7	59.7	62.5
1.20	63.7	72.1	62.3	69.5

[1]pound active per ton solids.

[2]measured in terms of percent turbidity reduction.

Table 4

Polymer Retention Performance for Modified versus
Unmodified
Dispersion Polymers at 1500 rpm (high shear)

Dosage[1]	Performance[2]				
	Polymer 1	Polymer 2	Polymer 3	Polymer 7	Polymer 4
0.60	-	-	-	50.4	53.3
0.90	52.6	60.6	-	-	-
1.20	54.2	-	55.3	55.6	63.4
1.80	-	-	67.5	55.6	64.3
2.10	65.1	67.8	71.1	-	-

[1]Pound active per ton solids.
[2]Measured in terms of percent turbidity reduction.

The Dissolved Air Flotation test (DAF) is utilized
to obtain the results of Table 5. In the tests, the VTMS
modified dispersion polymer flocculant provided greater

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turbidity reduction than the equivalent unmodified
polymer flocculant.

Table 5

Clarification of DAF Influent using Modified and
Unmodified Polymers (performance in terms of percent
turbidity reduction for a polymer dose of 1.6 ppm)

Polymer 8	Polymer 5	Polymer 6
69.23	70.9	71.4

Table 6

Clarification of DAF Influent using Unmodified and
Modified polymers

	Performance[2]		
Polymer Dose[1] (ppm)	Polymer 8	Polymer 5	Polymer 6
0.8	67.89	69.23	68.56
1.6	76.59	78.93	77.26

[1]In the presence of 150 ppm alum.
[2]Measured in terms of percent turbidity reduction.

The foregoing results demonstrates that a modified
polymer shows improved performance over that of an
unmodified polymer having comparable solution properties.

Example 8

AcAm/DMAEA•MCQ (9:1) inverse emulsion polymers
modified with MBA at different conversions are
synthesized in the following manner:

An aqueous monomer phase is made-up by stirring
together 364.37 g of a 49.6% aqueous solution of

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acrylamide (AcAm, Nalco Chemical Co., Naperville, IL),
178.33 g of water, 9.00 g of adipic acid, 27.00 g of
NaCl, and 0.80 g of a 50% aqueous solution of NaOH. The
components are stirred until dissolved. To the resulting
solution is added 67.90 g of a 80.3% solution of
dimethylaminoethylacrylate methyl chloride quaternary
salt (DMAEA•MCQ, CPS Chemical Co.; Old Bridge, NJ) and
0.09 g of EDTA•4Na$^+$ (ethylenediamine tetraacetic acid,
tetra sodium salt, Van Waters & Rogers, Geismar, LA).
The pH of the resulting mixture is 3.9.

An oil phase is prepared by heating a mixture of
234.29 g of paraffinic oil (Isopar M, Exxon, Houston,
TX), 13.50 g of Span-80 and 4.50 g of Tween-61 until the
surfactants dissolve (54-57 °C). The oil phase is
charged into a 2 L reactor and heated to 45 °C. With
vigorous stirring (900 rpm, 10 mm rod with a teflon
paddle at the base and 6-blade turbine mounted 3-inches
from the bottom), the monomer phase is added over 2
minutes. The resulting mixture is stirred for 30
minutes.

To the water-in-oil emulsion is added 0.200 g of
AIBN and 0.027 g of AIVN. The polymerization is carried
out under a N$_2$ atmosphere at 45°C for 4 hours, then 70°C
for one hour. The percent conversion is estimated by
density change. A density of 0.9855 g/ml is measured for
the starting emulsion, and a density of 1.0217 g/ml for
the final emulsion. At different densities of the
emulsion (related to percent monomer conversion), 4.72 g
of a 200 ppm solution of methylene bisacrylamide (4 ppm
based on monomer, MBA, Aldrich Chemical Company,
Milwaukee, WI) is added to the reaction mixture.
Polymers prepared using the foregoing procedure are shown
in Table 7. Polymer 14 is representative of those
polymers disclosed in EP 202,780. For these emulsion

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polymers synthesized at 26 percent actives, the highest
reduced specific viscosity is obtained for polymers where
MBA is added at 75-85% conversion.

Table 7

Representative 90/10 mole % AcAm/DMAEA·MCQ Copolymers
Modified Using MBA, Prepared According to the Method of
Example 8

Polymer	[MBA], ppm	Added at % Conversion	RSV, (dl/g)
9	0	NA	27.0 ± 2.8
10	4	75-85	31.9 ± 1.4
11	4	65	26.3
12	4	46	22.0
13	4	17	16.0
14[1]	4	0	13.0

[1]Polymer synthesized as described in EP 202,780.

Table 8

Reduced Specific Viscosity of Modified Polymers (90/10
mole % AcAm/DMAEA·MCQ)

Polymer	MBA Concentration (ppm)	Added At % Conversion	RSV, (dl/g)
9	0	NA	26.8
10	4	82	31.0
14[1]	4	0	13.0
15[1]	2	0	19.3
16[1]	6	0	9.4

[1]Polymer synthesized as described in EP 202,780.

Table 8 illustrates that when the cross-linking
agent is present at the beginning of polymerization, the
resulting polymers show a drop in reduced specific
viscosity even at very low MBA concentrations. In
contrast to the polymers disclosed in EP 202,780, the
polymers modified as described herein have a greater
viscosity, which is advantageous for a flocculant.

Example 9
        Polymers modified with MBA according to the
procedure described in Example 8 are compared to polymers
conventionally cross-linked. It is known to those
skilled in the art that conventionally, the cross-linker
is added at the beginning of the polymerization. We have
discovered that when the cross-linker is added is of
critical importance to the flocculating ability of the
resultant polymer. Tables 8-15 illustrate the surprising
superiority of polymer 10, modified by late addition of
cross-linker over polymer 14 that is conventionally
cross-linked and polymer 9 that is unmodified. Tables 9,
10, 12, 13, 15 and 16 contain results of Britt Jar tests,
and Tables 11 and 14 contain results of FBRM tests.

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Table 9

Retention Performance for Modified and Unmodified Polymers

Dose[1]	Performance[2]		
	Polymer 9	Polymer 10	Polymer 14
0.14	58.6%	59.8%	NA
0.28	69.1%	78.1%	71.9%
0.56	84.3%	87.2%	82.9%

[1]Pounds active per ton of slurry solids

[2]Percent turbidity reduction indicative of total retention; synthetic alkaline furnish.

Table 10

Retention Performance for Modified and Unmodified Polymers

Dose[1]	Performance[2]	
	Polymer 9	Polymer 10
0.25	55.9%	68.8%
1.00	87.5%	95.1%
2.00	87.6%	99.9%

[1]Pounds active per ton of slurry solids.

[2]Percent increase in filler retention; synthetic alkaline furnish.

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Table 11

Flocculation Performance of Modified and Unmodified Polymers Determined using FBRM

	Performance[2]	
Dose[1]	Polymer 9	Polymer 10
0.25	36.0	32.1
0.50	44.1	35.5
1.00	45.2	46.0
2.00	46.2	57.2

[1]Pounds active per ton of slurry solids.

[2]Change in peak mean chord length; synthetic alkaline furnish.

Table 12

Retention Performance for Modified and Unmodified Polymers

	% Turbidity Reduction[1]	
Polymer	0.5 lb/t	1. 0 lb/t
14	51.9	66.3
13	54.3	71.4
12	56	70.8
11	66	79.2
10	62	78.7
9	60.3	78

[1]Furnish from a southern paper mill.

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Table 13

Retention Performance for Modified and Unmodified

Polymers

Dose[1]	Performance[2]	
	Polymer 9	Polymer 10
1.0	18.9%	20.4%
2.0	36.5%	40.2%
4.0	55.0%	64.1%

[1]Pounds active per ton of slurry solids.

[2]Percent turbidity reduction; at a midwestern paper
mill.

Table 14

Flocculation Performance of Modified and Unmodified

Polymers Determined using FBRM

(Model M100)

Dose[1]	Performance[2]	
	Polymer 9	Polymer 10
0.25	48.5	58.7
0.50	60.0	69.5
1.00	73.5	94.4

[1]Pounds active per ton of slurry solids.

[2]Change in peak mean chord length; furnish from a
midwestern paper mill.

The data in the above tables clearly show that the
structurally-modified polymers are more efficient and
effective retention aids than the linear controls for
synthetic alkaline furnish and mill furnishes.

Example 10

        The following two Britt Jar test experiments
demonstrate that the polymers of this invention modified
by late addition of cross-linkers have better retention
performance than conventional treatments when used
together with bentonite in a microparticle program on a
synthetic alkaline furnish. The results are detailed in
Tables 15 and 16.

Table 15

Performance of Modified and Unmodified Polymers in
Conjunction with Microparticles

Polymer[1]	Bentonite dose (pounds active per ton of slurry solids)	Retention, %
9	1.0	81.5
10	1.0	87.5
17[2]	1.0	78.1

    [1]Treated at 1.5 pounds active per ton of slurry
solids; synthetic alkaline furnish.
    [2]Cationic flocculant FO 4198, available from SNF, St.
Etienne, France. (cationic, branched dry polymer
described in US 5,393,381).

    Table 16 shows the results for a
polymer/microparticle combination, where the
microparticle is either bentonite or borosilicate,
available from Nalco Chemical Co. of Naperville, IL under
the tradename UltraXol®. For the sake of clarity,
modified polymers of this invention are offset to the
right in the first column, for comparison to conventional
treatments which are offset to the left.

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Table 16

Performance of Modified and Unmodified Polymers in
conjunction with Microparticles

Polymer/Dose[1]	Microparticle /Dose[1]	Retention, %
9/0.5	bentonite/3.0	72.8
9/1.0	bentonite/1.0	77.1
9/1.0	bentonite/3.0	86.4
10/0.5	bentonite/3.0	79.8
10/1.0	bentonite/1.0	88.0
10/1.0	bentonite/3.0	95.1
14/0.5	bentonite/3.0	63.3
14/1.0	bentonite/3.0	80.4
10/0.5	borosilicate/1.0	79.5
10/1.0	borosilicate/1.0	93.9

[1]Pounds active per ton of slurry solids; synthetic
alkaline furnish.

Table 16 demonstrates that the modified polymers of
this invention (Polymer 10) performs better than the
commercially available flocculant (Polymer 9) in a
microparticle program of bentonite or borosilicate.
Polymers synthesized with cross-linking agent added
upfront (Polymer 14) also show inferior performance to
the modified polymer of this invention.

CHAIN TRANSFER AGENT MODIFIED POLYMERS

Example 11

An AcAm/DMAEA•MCQ (90:10) copolymer lattice modified
by late addition of sodium formate at high conversion
(Polymer 18), is synthesized in the following manner.

An aqueous monomer phase is made-up by stirring
together 484.12 g of a 49.4% aqueous solution of
acrylamide (Nalco Chemical Co., Naperville, IL), 20.25 g
of water, 9.00 g of adipic acid, 27.00 g of NaCl, and
0.27 g of a 50% aqueous solution of NaOH. The components
are stirred until dissolved. To the resulting solution
is added 90.30 g of a 80.2% solution of
dimethylaminoethylacrylate methyl chloride quaternary
salt (DMAEA•MCQ, CPS Chemical Co.; Old Bridge, NJ) and
0.18 g of EDTA•4Na$^+$ (Van Waters & Rogers, Geismar, LA).
The pH of the resulting mixture is 3.8.

An oil phase is prepared by heating a mixture of
243.00 g of paraffinic oil (Isopar M, Exxon, Houston,
TX), 8.92 g of Span-80 and 13.58 g of Tween-61 until the
surfactants dissolve (54-57 °C). The oil phase is
charged into a 2 L reactor and heated to 45 °C. With
vigorous stirring (900 rpm, 10 mm rod with a teflon
paddle at the base and 6-blade turbine mounted 3-inches
from the bottom), the monomer phase is added over 2
minutes. The resulting mixture is stirred for 30
minutes.

To the water-in-oil dispersion is added 0.200 g of
AIBN and 0.027g of AIVN. The polymerization is carried
out under a N$_2$ atmosphere at 45 °C for 4 hours, then 70 °C
for one hour. At a conversion of 80% (estimated by
density change), 8.29 g of a 38% solution of sodium
formate (2000 ppm based on monomer, Van Waters & Rogers,
Geismar, LA) is added to the reaction mixture. The
resulting polymer has an RSV of 30.9 dl/g (1M NaNO$_3$, 450

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ppm, 30°C). An unmodified polymer polymerized without
late addition of sodium formate (Polymer 19, Table 17) is
synthesized in a similar manner. These polymers are
characterized in Table 17.

Table 17

Representative Cationic AcAm/DMAEA·MCQ Copolymers
Modified Using Sodium Formate
(prepared according to the method of Example 11)

Polymer	Mole % DMAEA·MCQ	Sodium formate		RSV (dl/g)
		ppm	Added at (% Conversion)	
18	10	2000	82	30.9
19	10	0	—	17.8

To those skilled in the art, formic acid or metal
salts thereof, are known as efficient chain transfer
agents to limit the molecular weight and viscosity of
acrylamide based polymers (for example, U.S. Patent No.
4,307,215). It has also been reported (4,307,215 at
col.1, line 54) that addition of chain transfer agent
after polymerization has no effect on molecular weight.
However, as shown in Tables 17, 19 and 22, we have found
that adding chain transfer agents at different
polymerization stages gives polymers with increased
reduced specific viscosity over unmodified analogs.
Tables 18 and 20 illustrate that the modified polymers
are superior to the unmodified control polymers in paper
retention tests.

Table 18

Retention Performance for Modified and Unmodified
Polymers

Dose[1]	Performance[2]	
	Polymer 19	Polymer 18
0.25	61.4%	71.6%
0.50	72.2%	86.6%
1.00	85.2%	93.5%

[1]Pounds active per ton of slurry solids.

[2]Percent turbidity reduction; synthetic alkaline
furnish.

Example 12

An AcAm/DMAEA•MCQ (90:10) copolymer lattice modified
by late addition of sodium hypophosphite at high
conversion (Polymer 20), is synthesized in the following
manner.

An aqueous monomer phase is made-up by stirring
together 281.96 g of acrylamide (Mitsubishi, Japan),
194.00 g of water, 9.00 g of adipic acid, 27.00 g of
NaCl, and 0.27 g of a 50% aqueous solution of NaOH. The
resulting mixture is stirred for 10 minutes. To the
resulting suspension is added 107.54 g of a 79.4 %
solution of dimethylaminoethylacrylate methyl chloride
quaternary salt (DMAEA•MCQ, CPS Chemical Co.; Old Bridge,
NJ) and 0.18 g of EDTA•4Na[+] (Van Waters & Rogers, Geismar,
LA). A solution is obtained by heating the suspension to
35 °C while stirring for about 10 minutes. The pH of the
resulting mixture is 3.8.

An oil phase is prepared by heating a mixture of
252.00 g of paraffinic oil (Isopar M, Exxon, Houston,
TX), 15.79 g of Span-80 and 11.21 g of Tween-61 until the

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surfactants dissolve (54-57 °C). The oil phase is charged into a 2 L reactor and heated to 42 °C. With vigorous stirring (900 rpm, 10 mm rod with a teflon paddle at the base and 6-blade turbine mounted 3-inches from the bottom), the monomer phase is added over 2 minutes. The resulting mixture is stirred for 30 minutes.

To the water-in-oil emulsion is added 0.200 g of AIBN and 0.027 g of AIVN. The polymerization is carried out under a N_2 atmosphere at 42 °C for 2 hours. The reaction mixture is then cooled to 35 °C, 0.85 g of a 10% aqueous solution of 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044, Wako Chemical Co.) is added, and the reaction continued for 19 hours. At a conversion of 75 % (estimated by density change, 100 minutes), 1.84 g of a 20 % solution of sodium hypophosphite monohydrate (1000 ppm based on monomer, J. T. Baker, Phillipsburg, NJ) is added to the reaction mixture. The resulting polymer has an RSV of 27.7 dl/g (1M NaNO$_3$, 450 ppm, 30 °C).

An unmodified polymer polymerized without late addition of sodium hypophosphite (Polymer 21) is synthesized in a similar manner, except, VA-044 is omitted from the formulation and polymerization is performed using a 42-50 °C temperature gradient over 2.5 hours, then at 70 °C for 1 hour. Polymer 21 has an RSV of 13.6 dl/g (1M NaNO$_3$, 450 ppm, 30°C).

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Table 19

Representative Cationic AcAm/DMAEA•MCQ Latex Copolymers

Modified Using Sodium Hypophosphite

(prepared according to the method of Example 12)

Polymer	Mole % DMAEA·MCQ	Modification			RSV (dl/g)
		Chain Transfer Agent	Level (ppm)	Added at % conversion	
20	10	Sodium hypopho sphite	1,000	75	27.7
21	10	---	---	---	13.6

Table 20

FBRM Measurement of Polymers 9, 20 and 21 using the

Dosing Sequence in Table 21

(Lasentec M500)

	Performance[2]		
Dose[1]	Polymer 9	Polymer 21	Polymer 20
0.25	4.2 (± 0.3)	1.6 (±1.2)	5.8 (± 1.8)
0.50	7.7 (± 0.7)	3.8 (± 0.9)	10.0 (± 1.3)
1.00	13.3 (±1.4)	7.8 (± 2.0)	15.8 (± 2.0)

[1]Pounds active per ton of slurry solids.

[2]Change in peak mean chord length; synthetic alkaline furnish

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Table 21

Dosing Sequence for Table 20

Time (seconds)	Action
0	Commence mixing. Record baseline floc size.
20	Add flocculant to be tested. Record floc size change.
60	Terminate experiment.

Example 13

An AcAm/sodium acrylate (70:30) copolymer lattice
modified by late addition of sodium hypophosphite at high
conversion (Polymer 22), is synthesized in the following
manner.

An aqueous monomer phase is made-up as follows. A
50% aqueous solution of NaOH (92.0 g) is added dropwise
to a cold solution of acrylamide (376.8 g of a 50.8 %
aqueous solution), 166.5 g of water, and 83.0 g of
glacial acrylic acid until a solution pH of 8.3 is
obtained. A 2 % solution of EDTA•4Na$^+$ (Van Waters &
Rogers, Geismar, LA) is added to the resulting mixture.

An oil phase is prepared by heating a mixture of
252.8 g of paraffinic oil (Escaid-110), 12.2 g of Span-80
and 7.3 g of Tween-61 until the surfactants dissolved
(54-57 °C). The oil phase is charged into a 2 L reactor
and heated to 45 °C. With vigorous stirring (900 rpm, 10
mm rod with a teflon paddle at the base and 6-blade
turbine mounted 3-inches from the bottom), the monomer
phase is added over 2 minutes. The resulting mixture is
stirred for 30 minutes.

To the water-in-oil emulsion is added 0.51 g of
AIBN. The polymerization is carried out under a N$_2$
atmosphere at 45 °C for 4 hours, then at 70 °C for 1
hour. At a conversion of 70 % (estimated by density
change, 90 minutes), 4.0 g of a 0.5 % solution of sodium

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hypophosphite monohydrate (67 ppm based on monomer, J. T. Baker, Phillipsburg, NJ) is added to the reaction mixture. The resulting polymer has an RSV of 50.7 dl/g (1M NaNO$_3$, 450 ppm, 30°C).

An unmodified polymer polymerized without late addition of sodium hypophosphite (Polymer 23) is synthesized in a similar manner.

Table 22

Representative Anionic AcAm/Sodium Acrylate Latex
Copolymers
Modified Using Chain-Transfer Agents
(prepared according to the method of Example 13)

Polymer	Mole % Sodium acrylate	Modification			RSV (dl/g)
		Chain transfer agent	Level (ppm)	Added at % conversion	
22	30	Sodium hypophosphite	67	70	50.7
23	30	---	---	---	20.0

Example 14

An aqueous dispersion of acrylamide/acrylic acid copolymer (70/30 mole %), that contains sodium formate (CTA) in the initial monomer phase and is modified by late addition of sodium hypophosphite at high conversion (Polymer 24), is synthesized in the following manner.

A monomer reaction solution is prepared by combining 334.6 g deionized water, 65.0 g sodium sulfate, 85.0 g ammonium sulfate, 1.4 g sodium formate, 326.3 g of a 48.9 % aqueous solution of acrylamide, 0.40 g of the tetrasodium salt of ethylene diamine tetracetic acid, 69.3 g acrylic acid, 13.5 g of a 50 % aqueous solution of sodium hydroxide, and 100.0 g of a 12 % aqueous solution of poly(acrylamidomethylpropanesulfonic acid/methacrylic

acid) copolymer (Nalco Chemical Company, Naperville, IL).
The pH of the resulting mixture is 4.0. The monomer
reaction solution is heated to 35 °C with thorough mixing.
To the homogenous monomer reaction solution is added 1.0
g of a 1 % aqueous solution of VA-044 (2,2'-Azobis (*N*,*N*'-
dimethyleneisobutyramidine)dihydrochloride), Wako
Chemicals USA, Inc.; Richmond, VA). The polymerization
is carried out under N_2 atmosphere at 35 °C with thorough
mixing. After a total reaction time of 4 hours, 1.0 g of
a 1 % aqueous solution of VA-044 is added to the reaction
mixture. At a monomer conversion of 80 %, 0.57 g of a 10
% aqueous solution of sodium hypophosphite monohydrate
(250 ppm based on monomer) is added to the reaction
mixture. After a total reaction time of 8 hours, 2.0 g
of a 10 % aqueous solution of VA-044 is added, and the
reaction continued for another 4 hours (for a total
reaction time of 12 hours). The product of this reaction
is a milky white liquid having a RSV of 30 dl/g (1 M
$NaNO_3$, 450 ppm, 30 °C).

An unmodified polymer polymerized without late
addition of sodium hypophosphite (Polymer 25) is
synthesized in a similar manner. The unmodified polymer
has a RSV of 34 dl/g (1 M $NaNO_3$, 450 ppm, 30 °C).

Table 23

Representative Anionic Acrylamide/Acrylic Acid Dispersion
Polymers Modified Using Chain-Transfer Agents
(prepared according to the method of Example 14)

Polymer	Mole % Acrylic acid	Chain transfer agent	Level (ppm BOM)	Added at % conversion	RSV (dL/g)
24	30	Sodium hypophosphite	250	80	30
25	30	---	---	---	34

Table 24

Retention and Drainage Performance of Polymers 24 and 25

Dose[1]	% Turbidity Reduction[2]	
	Polymer 24	Polymer 25
0.25	69.6	59.2
0.5	78.0	69.3
1.00	83.7	78.5

[1]Pounds polymer active per ton of slurry solids.

[2]Britt Jar testing, synthetic alkaline furnish.

POLYMERS MODIFIED WITH COMBINATIONS OF CROSSLINKER &
CHAIN TRANSFER AGENTS

Example 15

An AcAm/DMAEA•MCQ (90:10) copolymer lattice modified
with a chain-transfer and cross-linking agent added
during polymerization (Polymer 26) is synthesized as
follows.

An aqueous monomer phase is made-up by stirring
together 364.37 g of a 49.6% aqueous solution of
acrylamide (Nalco Chemical Co., Naperville, IL), 175.20 g

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of water, 9.00 g of adipic acid, 27.00 g of NaCl, and
0.80 g of a 50% aqueous solution of NaOH until the
components are in solution. To the resulting solution is
added 67.90 g of a 80.3% solution of
dimethylaminoethylacrylate methyl chloride quaternary
salt (DMAEA•MCQ, CPS Chemical Co.; Old Bridge, NJ) and
0.09 g of EDTA•4Na $^+$ (Van Waters & Rogers, Geismar, LA).
The pH of the resulting mixture is 3.8.

An oil phase is prepared by heating a mixture of
234.29 g of paraffinic oil (Isopar M, Exxon, Houston,
TX), 13.5 g of Span-80 and 4.5 g of Tween-61 until the
surfactants dissolve (54-57 °C). The oil phase is
charged into a 2 L reactor. With vigorous stirring (900
rpm, 10 mm rod with a teflon paddle at the base and 6-
blade turbine mounted 3-inches from the bottom), the
monomer phase is added over 2 minutes. The resulting
mixture is stirred for 30 minutes and heated to 45 °C.

To the water-in-oil emulsion is added 0.200 g of
AIBN and 0.027 g of AIVN. The polymerization is carried
out under a N_2 atmosphere at 45 °C for 4 hours, then 70 °C
for one hour. A solution of 0.0059 g methylene
bisacrylamide (25 ppm, Aldrich Chemical Company,
Milwaukee, WI) and 0.1882 g sodium formate (800 ppm, Van
Waters & Rogers, Geismar, LA) in 5.87 g water is added to
the reaction mixture at a constant rate from 54-80%
monomer conversion. The resulting polymer has a RSV of
22.7 dl/g (1M $NaNO_3$, 450 ppm, 30°C).

Example 16

An AcAm/DMAEA•MCQ (1:1) copolymer lattice modified
with a chain-transfer and cross-linking agent added
during polymerization (Polymer 27) is synthesized in the
following manner.

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An aqueous monomer phase is made-up by stirring
together 130.1 lb of a 49.5% aqueous solution of
acrylamide (Nalco Chemical Co., Naperville, IL), 180.6 lb
of water, 8.0 lb of adipic acid, 24.0 lb of NaCl, and 0.7
lb of a 50% aqueous solution of NaOH until the components
are in solution. To the resulting solution is added
219.5 lb of a 80.0% solution of
dimethylaminoethylacrylate methyl chloride quaternary
salt (DMAEA•MCQ, CPS Chemical Co.; Old Bridge, NJ) and
0.2 lb of EDTA•4Na$^+$ (Van Waters & Rogers, Geismar, LA).
The pH of the resulting mixture is 3.8.

An oil phase is prepared by heating a mixture of
208.0 lb of paraffinic oil (Escaid 110, Exxon, Houston,
TX), 7.2 lb of Span-80 and 15.2 lb of Tween-61 until the
surfactants dissolved (54-57 °C) in a 100-gal reactor. A
water-in-oil dispersion is made by adding the monomer
phase to the oil phase and stirring for 30 minutes. To
the water-in-oil dispersion is added 0.26 lb of AIBN and
0.04 lb of AIVN. The polymerization is carried out under
a N_2 atmosphere at 42 °C. A solution of 0.006 lb
methylene bisacrylamide (25 ppm, Aldrich Chemical
Company, Milwaukee, WI) and 0.192 lb sodium formate (800
ppm, Van Waters & Rogers, Geismar, LA) in 6.00 lb water
is added to the reaction mixture at a constant rate from
11-82% monomer conversion. When the reaction appeared
complete, the reaction mixture is heated at 75 °C for 1
hour. After cooling 14.4 lb of Alfonic® 1412-60 is added to
the dispersed polymer. Polymer 27 has a RSV of 8.8 dl/g
(IM $NaNO_3$, 450 ppm, 30°C).

Polymer 28 (Table 25) is synthesized in a similar
manner.

Table 25

Representative Cationic AcAm/DMAEA.MCQ Copolymers
Modified Using Combinations of Chain Transfer Agent and
Cross-linking Agent

Polymer	Mole % DMAEA.MCQ	[MBA] ppm	[NaF] ppm	Added at (% Conversion)	RSV (dl/g)
26	10	25	800	54-82	22.7
27	50	25	800	11-82	8.8
28	50	25	800	6-49	6.2
29[1]	50	0	0	—	21.0

[1]50:50 mole percent AcAm/DMAEA•MCQ latex copolymer
(Nalco Chemical Co., Naperville, IL).

Example 17

    To further demonstrate the superiority of the
modified polymers, they are compared to polymers prepared
according to the procedure of EP 374,458 as follows.

    The three 10 mole % cationic copolymers of DMAEA•MCQ
with acrylamide (Polymers 30, 31 and 32) shown in Table
26 are synthesized according to the procedure outlined in
EP 374,458 at page 6, line 53, example 5B. The polymers
contain varying amounts of a branching (or cross-linking)
and chain transfer agents.

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Table 26
Representative Polymers Prepared as Described in EP
374,458

Polymer	Chain transfer agent (1.5% Isopropanol) %	Branching or Cross-linking agent (Methylene bisacrylamide), ppm	Solubility Quotient, %
30	3	8	33
31	9	8	36
32	18	8	52.5

The retention performance of Polymers 31 and 32,
representative of the polymers described in EP 374,458,
is compared to a modified polymer of this invention in
Table 27 (Polymer 10). The results are presented in
Table 27.

Table 27
Comparative Retention Performance of Modified and
Unmodified Polymers

Dose[1]	Polymeric Treatments		
	Polymer 31	Polymer 32	Polymer 10
0.50	62.9%	59.9%	87.2%
1.00	73.7%	68.6%	93.3%

[1]Pounds active per ton of slurry solids, synthetic
alkaline furnish.
[2]Percent turbidity reduction.

As shown in Table 27, as a flocculant alone, the
polymers of EP 374,458 show significantly inferior
retention performance to the modified polymers of this
invention. The retention performance of the polymers of
EP 374,458 and a representative modified polymer of this

invention in conjunction with bentonite in a
microparticle program is shown in Table 28. This data
shows the superiority of modified polymers of this
invention over those disclosed in EP 374,458.

Table 28

Comparative Britt Jar Retention Performance (Turbidity
reduction) of Modified and Unmodified Polymers

Polymer Treatment/Dose[1]	Bentonite dose[1]	Retention, %
10/1.0	1.0	88.0
31/1.0	1.0	61.6
32/1.0	1.0	57.8
10/1.0	3.0	95.1
31/1.0	3.0	65.1
32/1.0	3.0	63.5

[1]Pounds active per ton of slurry solids.

Example 18

Polymer 33, a polymer of ~20% polymer solids,
65/25/10 mole percent AcAm/DMAEA•BCQ/DMAEA•MCQ dispersion
is synthesized in the following manner.

A 1500 ml reaction flask is fitted with a mechanical
stirrer, thermocouple, condenser, nitrogen purge tube,
and addition port. To this reactor is added 139 g of a
49.4% aqueous solution of acrylamide (Nalco Chemical Co.,
Naperville, IL), 134 g of dimethylaminoethylacrylate
benzyl chloride quaternary salt (71.5% aqueous solution,
Nalco Chemical Co., Naperville, IL), 36 g of
dimethylaminoethylacrylate methyl chloride quaternary
salt (80% aqueous solution, NCF Manufacturing, Riceboro,

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GA), 10 g of glycerin, 56 g of the copolymer of
dimethylaminoethylacrylate benzyl chloride quaternary
salt and diallyldimethylammonium chloride (15% aqueous
solution, Nalco Chemical Co., Naperville, IL), 10 g of
the homopolymer of dimethylaminoethylacrylate methyl
chloride quaternary salt (15% aqueous solution, Nalco
Chemical Co., Naperville, IL), 0.25 g of
ethylenediaminetetraacetic acid, tetra sodium salt, 152 g
of ammonium sulfate and 380 g of deionized water. The
mixture is then heated to 48 °C while stirring at 700
rpm. After reaching 48 °C, 2.0 g of a 1.0% aqueous
solution of 2,2'-azobis(2-amidinopropane) dihydrochloride
(V-50, Wako Chemicals of Dallas, TX) is added to the
reaction mixture and the temperature is maintained at 48
°C throughout the reaction. Forty five minutes into the
reaction (~10% monomer conversion) 2.5 g of a 10% aqueous
solution of sodium formate is added to the reaction. Two
hours after initiation 3.0 g of a 1.0% aqueous solution
of 2,2'-azobis(2-amidinopropane) dihydrochloride is added
to the reaction, and at four hours 4.0 g of a 10% aqueous
solution of 2,2'-azobis(2-amidinopropane) dihydrochloride
is added. At eight hours the reaction is returned to
ambient temperature and 59.9 g of sodium sulfate, and
11.9 g acetic acid are added. The resulting product is a
smooth milky white dispersion with a bulk viscosity of
100 cP having a RSV of 10.2 dl/g (0.125 N NaNO$_3$ solution
at 0.045% polymer).

Example 19

Polymer 34 is prepared according to the procedure of
Example 18, except that MBA is added instead of sodium
formate. At ~80% monomer conversion, 2.0 g of a 0.1%
aqueous methylene bisacrylamide solution is added. The
resulting product is a smooth milky white dispersion

having a bulk viscosity of 100 cP and a RSV of 9.5 dl/g
(0.045% polymer in 0.125 N NaNO$_3$ solution).

Example 20

     Polymer 35 is prepared according to the procedure of
Example 19, except sodium formate (2.5 g of 10% aqueous
solution) is added to the monomer (0% conversion), and no
methylene bisacrylamide is added. The resulting product
is a smooth milky white dispersion having a bulk
viscosity of 100 cP and a RSV of 12.1 dl/g (0.045%
polymer in 0.125 N NaNO$_3$ solution).

Example 21

     Polymer 36 is prepared according to the procedure of
Example 20, except that 2.0 g of a 0.1% aqueous solution
of methylene bisacrylamide is added at ~80% conversion.
The resulting product is a smooth milky white dispersion
having a bulk viscosity of 100 cP and a RSV of 12.0 dl/g
(0.045% polymer in 0.125 N NaNO$_3$ solution).

Example 22

     A 10/90 mole % DMAEA•MCQ/AcAm dispersion polymer
with methylenebisacrylamide and sodium formate added late
in the polymerization (polymer 37) is prepared according
to the method of Example 4, except that the amount of
deionized water in the formula is reduced by 10.0 g, and
instead of vinyltrimethoxysilane, a solution containing
0.0015 g of methylenebisacrylamide, 0.075 g sodium
formate and 9.9235 g of deionized water is fed to the
polymerization over 90 minutes, beginning at 1.5 hours
after initiation. The resulting polymer product has a
Brookfield viscosity of 300 cP (#3 spindle, 12 rpm) and a
RSV of 18.5 dl/g at 450 ppm in 1 M NaNO$_3$.

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Table 29

Cationic Dispersion Polymers Modified with Cross-linking
agent and Chain Transfer Agents

Polymer	AcAm (mole %)	DMAEA·MCQ (mole %)	DMAEA· BCQ (mole %)	Na formate (ppm)	Na formate added at	MBA (ppm)	MBA added at	RSV (dl/g)
37	90	10	-	500	1.5-3 hours	10	1.5-3 hours	18.5
33	65	10	25	1275	~10%	0	NA	10.2
34	65	10	25	1275	~10%	10	~80 %	9.5
38	65	10	25	500	6-41%	10	6-41%	16.2
35	65	10	25	1000	0	0	NA	12.1
36	65	10	25	1000	0	10	~80 %	12
39[1]	65	10	25	0	NA	0	NA	18
40[2]	65	20	15	0	NA	0	NA	18
41	65	20	15	1275	~10%	10	t=3 hr	16.3

[1]Available from Nalco Chemical Company, Naperville, IL.

[2]Available from Derypol, S.A., Barcelona Spain.

Table 30

Retention Performance of Modified and Unmodified Polymers
(in terms of percent turbidity reduction)

Dosage lbs/ton	Polymer 7	Polymer 37
0.3	66.3	70.9
0.6	78.5	81
1	88.8	89.5

Example 23

High Shear Test for Dewatering

To illustrate that polymers prepared according to the procedure of Example 17 are less efficient than the structurally-modified polymers disclosed herein, some comparative testing is done as follows.

The polymer at the desired concentration is added to 200 ml of sludge from a Midwestern municipal facility and mixed using the Britt Jar impeller at 1200 rpm for 1 or 2 seconds depending on the sludge. The conditioned sludge is then poured through a belt filter press filter medium. The amount of water drained in 10 seconds is taken as a measure of the polymer performance, and a larger amount of drainage indicates better dewatering capabilities.

The sludge dewatering performance of the modified polymers are compared to their unmodified counterparts in Tables 31-34. For each example, higher drainage is obtained with the polymers modified according to the procedures described herein than with the equivalent unmodified polymer.

Table 31

Ten Second Free Drainage

Dose, (ppm)	Drainage, (ml)	
	Polymer 29	Polymer 28
29	40	
36	46	
43	50	
51	44	72
58		94
65		108
72		112

Table 32

Ten Second Free Drainage Results

Dose, (ppm)	Drainage, (ml)			
	Polymer 39	Polymer 33	Polymer 34	Polymer 38
48		68		
58	68	78		74
68	72	80	86	86
77	80	84	90	82
86	80		98	
95			96	

66

Table 33

Ten Seconds Free Drainage Results

Dose, (ppm)	Drainage, (ml)	
	Polymer 39	Polymer 36
113	52	58
122	54	72
131	66	74
140	60	74

Table 34

Ten Seconds Free Drainage Results

Dose (ppm)	Drainage, (ml)	
	Polymer 39	Polymer 36
39	34	
49	54	
59	48	78
68		86
77		88

Example 24

Procedure for Coal Refuse Slurry Laboratory Cylinder
Settling Test

Comparative flocculation performance of an
acrylamide/acrylic acid copolymer (70:30 mole %) modified
by late addition of sodium hypophosphite (Polymer 24) and
the corresponding unmodified polymer (Polymer 25) in a
mining applications is done as follows.

A 5-gallon sample of coal refuse slurry is stirred
constantly to ensure that the slurry is well dispersed.
The slurry is then transferred to 500-ml graduated

cylinders. Masking tape is placed on each of the 500-ml
cylinders adjacent to the cylinder graduation marks. The
initial level of the coal refuse slurry at time equal to
zero (which is at the 500-ml mark of the graduated
cylinder) is marked on the masking tape. Prior to each
test the 500 ml-cylinder containing the coal refuse
slurry is inverted several times to disperse any settled
solids. The cylinder is then quickly dosed with the
desired amount of a 0.12 % polymer actives solution
(flocculant) and inverted 4 times. The cylinder is then
returned to the upright position and a timer is started.
The position of the solids interface is monitored as a
function of time (in seconds) by marking the level of the
solids interface on the masking tape at the appropriate
time interval. When the rate of descent of the solid
interface begins to slow down the marking of the masking
tape is ended. The settling rate (in inches/minute) of
the coal refuse slurry for the free-fall region is
calculated by dividing the distance of the solid
interface from the initial level (in inches) by the
elapsed time (in seconds). A faster settling rate
indicates better performance

Table 35

Flocculation Performance of Polymers 24 and 25 in Mining
Application

| Dose (ml)[1] | Settling Rate (in/min) | |
	Polymer 24	Polymer 25
7	5.4	2.6
9	8.1	4.2
11	10.5	
13		7.0

[1]ml of a 0.12 % polymer actives dispersion.

Example 25

A 22.7% polymer solids, 70/30-mole percent
acrylamide/acrylic dispersion polymer (Polymer 42) is
synthesized in the following manner.

To a 1500 ml reaction flask fitted with a mechanical
stirrer, thermocouple, condenser, nitrogen purge tube,
addition port and heating tape is added a solution
prepared by combining 356.6 g of deionized water, 64 g
sodium sulfate, 84 g ammonium sulfate, 2.8 g sodium
formate, 85.0 g of a 16 % aqueous solution of
poly(acrylamidomethylpropanesulfonic acid/methacrylic
acid) copolymer (Nalco Chemical Company, Naperville, IL)
329.6 g of a 48.4 % aqueous solution of acrylamide (Nalco
Chemical Company, Naperville, IL), 0.40 g of the
tetrasodium salt of ethylene diamine tetracetic acid,
69.3 g acrylic acid (Rohm and Haas Texas, Inc., Deer
Park, TX), and 4.0 g of a 50 % aqueous solution of sodium
hydroxide. The pH of the resulting mixture is 3.6. The
monomer reaction solution is heated to 35 °C with thorough
mixing. To the homogenous monomer reaction solution is
added 1.0 g of a 1 % aqueous solution of VA-044 (2,2′-
Azobis (N, N′-dimethyleneisobutyramidine)
dihydrochloride), Wako Chemicals USA, Inc., Richmond,
VA). The polymerization is carried out under N_2
atmosphere at 35 °C with thorough mixing. After a total
reaction time of 6 hours, 2.0 g of a 1 % aqueous solution
of VA-044 is added to the reaction mixture. The reaction
mixture is kept at 35 °C overnight. The next day, 2.0 g
of a 10 % aqueous solution of VA-044 is added, and the
reaction temperature is maintained for another 2 hours
before the reaction mixture is cooled and removed from
the reactor. The product of this reaction is a milky

white liquid (700 cP., RSV of 33.7 dl/g (1 M NaNO$_3$, 450
ppm, 30 °C).

Example 26

A 22.7% polymer solids, 70/30 mole percent
acrylamide/acrylic acid dispersion polymer modified with
sodium formate (Polymer 43) is synthesized according to
the procedure of Example 25. After a total 7 hours of
reaction time (~ 81% conversion), 2.8 g of sodium formate
is added to the reaction mixture. The polymerization is
then continued and finished as described in Example 25.
The product of this reaction is a milky white liquid (570
cP., RSV of 30.8 dl/g in 1 M NaNO$_3$, 450 ppm, 30 °C).

Table 36

Flocculation Performance of Modified and Unmodified
Anionic Dispersion Polymers

Dose[1]	Performance[2]	
	Polymer 42	Polymer 43
0.25	44	56
0.50	59	63
1.0	69	81
1.5	73	95

[1]Pounds polymer actives per ton of slurry solids.
[2]Change in peak mean chord length; synthetic alkaline
furnish.

70

CLAIMS

1.   A structurally-modified water-soluble polymer prepared by initiating polymerization of an aqueous solution of monomers under free radical polymerization conditions to form a polymer solution and adding at least one structural modifier to the polymer solution after at least 30% polymerization of the monomers has occurred.

2.   The structurally-modified water-soluble polymer according to claim 1 selected from the group consisting of emulsion polymers, dispersion polymers and gel polymers.

3.   The structurally-modified water-soluble polymer of claim 1 wherein the monomers are selected from acrylamide or methacrylamide and one or more monomers selected from the group consisting of diallyldimethylammonium chloride, dimethylaminoethyl acrylate methyl chloride quaternary salt, acrylamidopropyltrimethylammonium chloride, dimethylaminoethyl methacrylate methyl chloride quaternary salt, methacrylamidopropyltrimethylammonium chloride, acrylic acid, sodium acrylate, ammonium acrylate, methacrylic acid, sodium methacrylate, and ammonium methacrylate.

4.   The structurally-modified water-soluble polymer of claim 1 wherein the structural modifier is selected from the group consisting of cross-linking agents, chain transfer agents and mixtures thereof.

5.   The structurally-modified water-soluble polymer of claim 4 wherein the chain transfer agents are selected from the group consisting of alcohols, sulfur compounds, carboxylic acids or salts thereof, phosphites, and combinations thereof.

6.   The structurally-modified water-soluble polymer of claim 5 wherein the chain transfer agents are selected from sodium formate and sodium hypophosphite.

7.   The structurally-modified water-soluble polymer of claim 4 wherein the cross-linking agent is selected from the group consisting of *N,N*-methylenebisacrylamide, *N,N*-methylenebismethacrylamide, triallylamine, triallyl ammonium salts, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, *N*-vinylacrylamide, *N*-methylallylacrylamide, vinyltrimethoxysilane, and combinations thereof.

8.   The structurally-modified water-soluble polymer of claim 7 wherein the cross-linking agent is vinyltrimethoxysilane.

9.   The structurally-modified water-soluble polymer of claim 7 wherein the cross-linking agent is methylenebisacrylamide.

10.   The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide and dimethylaminoethylacrylate benzyl chloride quaternary salt and the structural modifier is vinyltrimethoxysilane.

11.   The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide and diallyldimethylammonium chloride and the structural modifier is vinyltrimethoxysilane.

12.   The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is methylenebisacrylamide.

13.   The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide and

dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is sodium formate.

14. The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is sodium hypophosphite.

15. The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is a combination of sodium formate and methylenebisacrylamide.

16. The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide, dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is methylenebisacrylamide.

17. The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide, dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is sodium formate.

18. The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide, dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylacrylate methyl chloride quaternary salt and the structural modifier is a combination of methylenebisacrylamide and sodium formate.

19. The structurally-modified water-soluble polymer of claim 1 wherein the monomers are acrylamide, dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylacrylate methyl chloride

quaternary salt and the structural modifier is
vinyltrimethoxysilane.

20. The structurally-modified water-soluble polymer
of claim 1 wherein the monomers are acrylamide and
acrylic acid or a salt thereof and the structural
modifier is sodium hypophosphite.

21. A method of preparing a structurally-modified
water-soluble polymer comprising initiating
polymerization of an aqueous solution of monomers under
free radical polymerization conditions to form a polymer
solution and adding at least one structural modifier to
the polymer solution after at least 30% polymerization of
the monomers has occurred.

22. A method of flocculating an aqueous suspension
of organic matter comprising adding to the suspension an
effective flocculating amount of the structurally-
modified polymer of claim 1.

23. A method of clarifying waste water comprising
adding an effective flocculating amount of the
structurally-modified water-soluble polymer of claim 1 to
the waste water.

24. A method of increasing retention and drainage
in a papermaking furnish comprising adding an effective
amount of the structurally-modified water-soluble polymer
of claim 1 to the furnish.

25. The method of claim 24 further comprising adding
a microparticle to the furnish.

26. The method of claim 25 further comprising adding
a coagulant to the furnish.

27. A method of flocculating an aqueous coal refuse
slurry comprising adding an effective amount of the
structurally-modified water-soluble polymer of claim 1 to
the slurry

INTERNATIONAL SEARCH REPORT	International application No.
	PCT/US01/10867

A. CLASSIFICATION OF SUBJECT MATTER .

IPC(7)   : C08F 265/10; C08J 3/24
US CL   : 525/244, 313, 329.4, 329.7, 329.8, 329.9
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

   U.S. :   525/244, 313, 329.4, 329.7, 329.8, 329.9

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

   BRS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,557,061 A (HAMANN) 19 January 1971	1, 2, 4, 7-13, 15, 16, 18, 19 and 21-27
A	US 4,753,710 A (LANGLEY et al.) 28 June 1988	1-27
A	US 5,594,494 A (NEFF et al.) 31 August 1999	1-27

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 JULY 2001	**2 6 JUL 2001**

Name and mailing address of the ISA/US	Authorized officer
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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 3
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

   It is unclear which monomers or combination of monomers are being recited as being requisite in the claimed polymer.

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
                        ☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1)) (July 1998) ★