United States Patent Office 3,734,820
Patented May 22, 1973

3,734,820

CATIONIC DEXTRAN GRAFT COPOLYMERS AS DRY STRENGTH ADDITIVES FOR PAPER

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No Drawing. Filed Sept. 22, 1971, Ser. No. 182,898
Int. Cl. D21h 3/20
U.S. Cl. 162—168 10 Claims

ABSTRACT OF THE DISCLOSURE

Paper products exhibiting markedly improved dry strength properties are produced by adding to the aqueous cellulose dispersion, prior to sheet formation, novel, cationic graft copolymers of certain polymerizable acrylic and/or diallylic quaternary ammonium monomers and acrylamide grafted onto a dextran substrate.

BACKGROUND OF THE INVENTION

The present invention is directed to novel, cationic graft copolymers of certain polymerizable acrylic and/or diallylic quaternary ammonium monomers and acrylamide grafted onto a dextran substrate and their use as dry strength additives. Paper products prepared using these graft copolymers as dry strength additives exhibit markedly improved properties. These dextran graft copolymers are incorporated into the paper product during the paper making process, preferably by adding them to the aqueous cellulosic pulp dispersion.

It is a well-accepted fact that it is desirable in many applications to have paper products with good dry strength. In addition, it is well known that the paper industry has a strong movement underway to reduce the basis weight of paper, especially that of publication grade paper. Reduced basis weight in paper would correspondingly reduce mailing cost. Dry strength aids are needed for lighter weight paper because as the basis weight is lowered and the pigment loadings are increased to maintain opacity, the dry strength of the paper decreases. By using dry strength additives to maintain the strength of the lower basis weight paper, the production costs are reduced since less pulp and power are needed to make an equivalent sheet.

In the past, natural polymers such as guar and locust bean gums and the native and modified starches have been the most commonly used dry strength additives. The performance of these natural polymers is difficult to control and hence somewhat inconsistent. In addition, the uses of starches involves lengthy preparation procedures and starches are not well retained by the fibers without the use of additional costly additives. However, because of their low cost and availability, these compounds have heretofore been used despite their disadvantages.

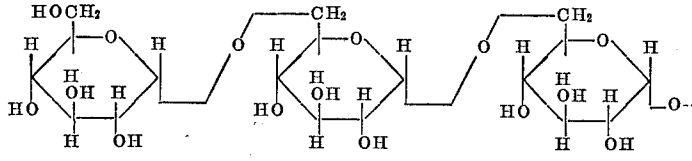
More recently, several synthetic dry strength resins have appeared in the market. These compounds are basically modified polyacrylamides or modified cationic starch derivatives. These compounds, while somewhat effective under normal conditions, do not maintain paper strength at lower basis weight and they do not function well in alkaline media. The requirement of functioning well in an alkaline system is important since there is a desire in the paper industry to change from the present acid (pH 3.5 to 5.5) system of paper making to neutral or alkaline (pH 7 to 9.0) system. The acid system is detrimental to machine parts and results in a paper sheet that becomes brittle and yellow with age. Another advantage of an alkaline system is that an inexpensive pigment, such as calcium carbonate, can be used instead of the more expensive titanium dioxides and aluminum oxides.

Therefore, it is an object of this invention to produce a dry strength additive which works well in low basis weight paper, gives consistent performance, and performs well in both alkaline and acidic systems.

SUMMARY OF THE INVENTION

We have found that paper products have superior dry strength properties when they contain from 0.1 to 5.0 percent by weight based on the dry weight of the paper of our novel, cationic dextran graft copolymers.

The dextran useful in our invention is a naturally-occurring polymer having a molecular weight between 20,000 and 50,000,000 or higher. The general structure is illustrated below.

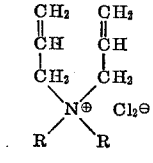


The graft copolymers of our invention have two basic components, (1) a dextran substrate and (2) an acrylic or diallylic polymerizable quaternary ammonium monomer. The graft copolymers consist of from 5 to 97.5 percent by weight of the dextran substrate and the remaining percentage being derived from one or more of the polymerizable quaternary ammonium monomers.

The preferred polymers of our invention have an additional component comprising acrylamide or the equivalent methacrylamide. The preferred compounds are graft copolymers of (1) a dextran substrate, (2) acrylamide and (3) one or more acrylic or diallylic polymerizable quaternary ammonium monomers. These polymers consist of from 5 to 97.5 percent by weight of the dextran substrate and the remaining percentage being derived from acrylamide and the polymerizable quaternary ammonium monomer. The acrylamide should be at least 5 percent but no more than 75 percent of the remainder. Therefore, the preferred polymers consist of 5 to 97.5 percent by weight of the dextran substrate, from about 0.125 to about 71 percent by weight acrylamide and the remainder the quaternary ammonium monomer.

As mentioned above, the useful-cationic monomers are the acrylic and diallylic quaternary ammonium monomers. These monomers are well reported in the literature and are known to readily undergo free radical polymerization. They may be illustrated by the following formulas.

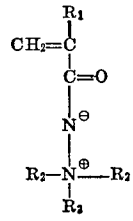
The diallylic quaternary ammonium compounds which are useful in our invention are the di lower alkyl diallyl quaternary ammonium chlorides. They are represented by the formula:



where R is H or an alkyl group of 1 to 4 carbon atoms. The preparation and use of this class of compounds is illustrated in Butler, U.S. Pat. 3,288,770, Boothe, U.S.

Pat. 3,461,163 and 3,472,740, Schuller et al., U.S. Pat. 2,923,701 and Booth et al., U.S. Pat. 3,147,218.

The useful acrylic aminimides are represented by the formula:

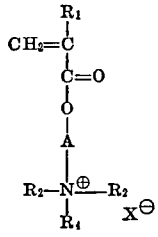


where R_1 is H or CH_3; R_2 is a lower alkyl group of 1 to 4 carbon atoms, preferably CH_3; R_3 is an alkyl group of 1 to 4 carbon atoms or a mono or dihydroxy alkyl group of 1 to 4 carbon atoms, preferably R_3 is $—CH_3$,

$$—CH_2—\underset{OH}{CH}—CH_3 \text{ or } —CH_2—\underset{OH}{CH}—CH_2—OH$$

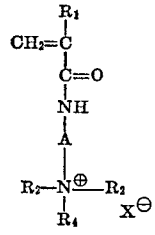
For example, see U.S. Pats. 3,485,806 and 3,527,802.

The useful acryloxyalkyl quaternary ammonium compounds are represented by the formula:

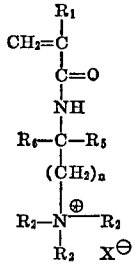


wnere R_1 is H or CH_3; R_2 is a lower alkyl group of 1 to 4 carbon atoms; R_4 is H or a lower alkyl group of 1 to 4 carbon atoms; X is an anion selected from chlorine, bromine, and methyl sulfate; A is an alkyl group of 1 to 6 carbon atoms or a hydroxy alkyl group of 1 to 4 carbon atoms. The preferred compounds of this structure are dimethylaminoethyl methacrylate, 2 - hydroxy - 3-methacryloxy propyltrimethyl ammonium chloride, and 2-methacryloxyethyltrimethyl ammonium methyl sulfate.

The useful acrylamidoalkyl quaternary ammonium compounds are represented by the formula:



where R_1, R_2; R_4, X and A are as defined above. A particularly useful group of acrylamidoalkyl quaternary ammonium monomers are represented by the formula:



where R_1, R_2, and X are as defined above; R_5 is H or a linear or branched alkyl group of up to 5 carbon atoms and R_6 is phenyl or a linear or branched alkyl group of up to 5 carbon atoms and where n is 1 or 2.

For additional useful acrylic and diallylic polymerizable quaternary ammonium monomers, see the article entitled "Cationic Quaternary Polyelectrolytes—A Literature Review" by M. F. Hoover, J. Macromolecular Sci.-Chem., vol. 4, No. 6, 1327–1417 (1970).

There are many well-known methods of grafting various monomers onto carbohydrate-type substrates as is realized by one skilled in the art. The method ultimately chosen is not important so long as it yields a graft polymer onto the dextran. The method which we used is the ceric salt redox system. It is known that certain ceric salts form a redox system when coupled with certain reducing agents such as alcohol, aldehydes, or amines. The reaction proceeds by a single electron transfer step, resulting in cerous ion and a partially oxidized reducing agent in free radical form; the free radical being formed on the dextran substrate backbone. If a monomer is present, polymerization will occur. However, since the free radical is on the substrate backbone, only graft polymers will be formed without contamination of other polymers. Using this method, we have prepared various graft copolymers with dextran. However, the same copolymers may be prepared using any other of the well known grafting techniques. Examples 1 to 9 below illustrate the preparation of some of the dextran graft copolymers of our invention.

EXAMPLE 1

A dextran graft copolymer of dimethyldiallyl ammonium chloride (DMDAAC) and acrylamide (AM) having a weight percentage of 40 percent dextran, 30 percent DMDAAC and 30 percent AM was prepared as follows. The reagents used were 20 grams of dextran having an average molecular weight of about 50 million, 22 grams of a 68.1 percent DMDAAC solution, 15 grams of acrylamide, 450 grams water, and 5 milliliters of a 0.1 normal ceric ammonium nitrate solution in one normal nitric acid. Into a one liter, four-necked flask equipped with purge tube, thermometer, stirrer and condenser was added the dextran and 400 grams of water. The dextran solution was purged with nitrogen for one hour at 30° C. At the same time, the acrylamide was dissolved in 50 grams of water in a beaker and purged with nitrogen. After the purging, a nitrogen blanket was kept over the flask and the DMDAAC was added and the mixture stirred for ten minutes. Then the acrylamide was added and the reaction mixture stirred for another ten minute interval. The ceric catalyst solution was then added and the reaction mixture stirred for three hours at 30° C. The resulting polymer was precipitated from isopropanol and oven dried for twenty-four hours and evaluated as a dry strength additive.

EXAMPLE 2

A 40 percent dextran, 60 percent acrylamide graft copolymer was prepared in the following manner. Into a 500 milliliter flask equipped with a purge tube, thermometer, stirrer and condenser was added 120 grams of water and 5 grams of dextran having an average molecular weight of about 50 million. This dextran solution was purged with nitrogen for two hours at 30° C. while being stirred. Then 7.5 grams of acrylamide dissolved in 25 milliliters of water was added and the reaction mixture stirred for five minutes. Five milliliters of the ceric catalyst solution was then added. The catalyst solution was 0.1 normal ceric ammonium nitrate in one normal nitric acid. The mixture was then stirred for two hours at 30° C. The polymer was then precipitated from acetone and dried under vacuum for twenty-four hours.

EXAMPLE 3

A 38.4 percent dextran, 30.8 percent acrylamide, 30.8 percent DMDAAC graft copolymer was prepared as follows. Into a 500 milliliter flask equipped with a purge tube, thermometer, stirrer and condenser was added 5 grams of dextran having an average molecular weight of about 50 million and 100 milliliters of water. This dextran solution was purged with nitrogen for one hour at

30° C. while being stirred. Then 4 grams of acrylamide dissolved in 25 milliliters of water and 5.5 grams of a 68.1 percent DMDAAC solution were added. The mixture was stirred for five minutes and then 5 milliliters of the ceric catalyst solution was added (same as in Example 1 above). The mixture was then stirred for three hours at 30° C. The resulting polymer was precipitated from isopropanol and dried.

EXAMPLE 4

A 40 percent dextran, 60 percent 2-hydroxy-3-methacryloxy propyl trimethyl ammonium chloride graft copolymer was prepared in the following manner. Into a 500 milliliter flask equipped with a purge tube, thermometer, stirrer and condenser was added 5 grams of dextran having an average molecular weight of about 50 million and 100 milliliters of water. This dextran solution was purged with nitrogen for one hour at 30° C. while being stirred. Then 7.5 grams of cationic monomer dissolved in 25 milliliters of water was added and the mixture stirred for five minutes. Five milliliters of the ceric catalyst solution was added (same as in Example I above). The mixture was then stirred for three hours at 30° C. The resulting polymer was precipitated from acetone and dried.

EXAMPLE 5

A 20 percent dextran, 40 percent acrylamide, 40 percent DMDAAC graft copolymer was prepared in the following manner. Into a one liter, four-necked flask equipped with purge tube, thermometer, stirrer and condenser was added 10 grams of dextran haivng an average molecular weight of about 50 million and 391 grams of water. The dextran solution was purged with nitrogen for one hour at 30° C. while being stirred. At the same time, 20 grams of acrylamide was dissolved in 50 milliliters of water in a beaker. After the dextran solution was purged, 29.2 grams of a 68.1 percent DMDAAC solution was added and the reaction mixture stirred for five minutes. Then the acrylamide solution was added and the reaction mixture stirred for an additional five minutes. Five milliliters of the ceric catalyst solution (same as in Example 1 above) was added and the reaction mixture stirred at 30° C. for three hours. The resulting polymer was precipitated from isopropanol and dried.

EXAMPLE 6

A 20 percent dextran, 60 percent acrylamide, 20 percent DMDAAC graft copolymer was prepared in the following manner. Into a one liter, four-necked flask equipped with purge tube, thermometer, stirrer and condenser was added 16 grams of dextran having an average molecular weight of about 50 million and 385.4 milliliters of water. The dextran solution was purged with nitrogen for one hour at 30° C. After the dextran slurry was purged, 14.6 grams of a 68.1 percent DMDAAC solution was added and the reaction mixture stirred for five minutes. Then 30 grams of acrylamide dissolved in 50 milliliters of water was added and the reaction mixture stirred for another five minutes. Five milliliters of the ceric catalyst (same as in Example 1) was added and the reaction mixture stirred for three hours at 30° C. The resulting polymer was diluted to about 3 percent solids with water and then precipitated from an alcohol-ether mixture and dried under vacuum.

EXAMPLE 7

A 40 percent dextran, 30 percent acrylamide, 30 percent DMDAAC graft polymer was prepared in the following manner. The dextran used had a molecular weight of about 20,000. Into a one liter, four-necked flask equipped with purge tube, thermometer, stirrer and condenser was added 20 grams of dextran and 390 milliliters of water. The resulting solution was purged with nitrogen for one hour at 30° C. After the purge, 24 grams of a 62.5 percent DMDAAC solution was added and the reaction mixture stirred for five minutes. Then 15 grams of acrylamide predissolved in 50 milliliters of water was added and the reaction mixture stirred for another five minutes. Five milliliters of the ceric catalyst solution (same as in Example 1) was added and the reaction mixture stirred for three hours at 30° C. The resulting polymer was precipitated from acetone and dried.

EXAMPLE 8

A 40 percent dextran, 30 percent acrylamide, 30 percent DMDAAC graft copolymer was prepared using the same procedure as Example 7. However, the dextran used in this example had a molecular weight of about 273,000.

EXAMPLE 9

A 40 percent dextran, 30 percent acrylamide, 30 percent 1,1-dimethyl-1-(2-hydroxy propyl) amine methacrylamide graft copolymer was prepared as follows. Into a one liter flask equipped with a purge tube, thermometer, stirrer and condenser was added 20 grams of dextran and 400 milliliters of water. This dextran solution was purged with nitrogen for one hour at 30° C. Then 15 grams of the aminimide dissolved in 25 mililliters of water was added and the mixture stirred for 15 minutes. Then 15 grams of acrylamide dissolved in 25 milliliters of water was added and the mixture stirred for an additional five minutes. After this, 5 milliliters of the ceric catalyst soluiton was added (same as in Example 1) and the reaction mixture stirred for three hours at 30° C. The resulting polymer was precipitated from acetone and oven dried.

We have prepared many additional graft copolymers using various other monomers, various weight ratios of dextran to monomer, and various weight ratios of the different comonomers. The graft copolymers of our invention consist of from 5 to 97.5 percent by weight of the dextran substrate and the remaining percentage being one or more of the monomers mentioned above.

The dextran graft copolymers of our invention were evaluated for their dry strength in alkaline media and also in acidic media. The polymers were also evaluated at various feed rates ranging from 0.25 percent to about 1 percent by weight based on the weight of the dry pulp.

The polymers were evaluated by preparing a series of hand sheets on a Noble Wood machine using the various additives. The hand sheets were then conditioned at 50 percent RH for a minimum of twenty-four hours at 70° F. and then tested for burst and tensile strength. The strength values were reported as a percent increase over the control. The control was a hand sheet prepared under similar conditions except no dry strength additives were employed.

The pulp stock used in preparing the hand sheets was bleached, hardwood sulfite pulp. The freeness was 650 cc. Schopper Reigler. When using acid medium, 2 percent alum was also employed. However, when using alkaline medium, no additional additives other than the dry strength compound were used. The hand sheets prepared had a sheet weight of about three grams per sheet, which is approximately equivalent to forty-five pounds per 3,000 ft.^{2} The dry strength compounds were added at the headbox and mixed there for three minutes. When running under acid media, the headbox and sheet mold pH was adjusted to 4.5 with 0.5 NH_2SO_4. When running under alkaline conditions, they were left unadjusted, which was a pH of from 7 to 9. During the preparation, there was no white water circulation. The sheets were dried for five minutes at 230° F. before conditioning and evaluating. The burst strength was tested by a Mullen Tester according to TAPPI standard test procedure T403. The tensile strength was tested by a TMI instrument in accordance with TAPPI standard test procedure T404.

The following tables illustrate the results of hand sheets prepared using some of the graft copolymers of our invention.

Table 1 illustrates the effectiveness of the graft copolymers compared to dextran alone and a physical mixture of dextran and polymer. In the tables, the compositions of the copolymers are given in weight percentages. The percent feed rate for Table 1 was 1 percent by weight based on weight of the dry pulp and the results are for alkaline pH.

TABLE 1

Sample Number	Composition	Percent increase Burst	Tensile
1	Dextran	8	1
2	Mixture of 60% dextran and 40% of a 50/50 acrylamide/DMDAAC copolymer.	6	−0.3
3	40% dextran/30% acrylamide/30% DMDAAC graft polymer.	61.8	21.1
4	40% dextran/60% 2-hydroxy-3-methacrylyloxy propyl trimethyl ammonium chloride graft polymer.	19.1	6.9

Table 2 illustrates the results of various feed rates for a 40 percent dextran/30 percent acrylamide/30 percent DMDAAC graft copolymer. In addition, this table illustrates that our graft copolymers are effective in acidic and alkaline systems.

TABLE 2

Percent feed rate	Alkaline, percent increase Burst	Tensile	Acid, percent increase Burst	Tensile
1	60.9	28.8	----	----
0.5	48.4	23.6	----	----
0.25	19.5	18.0	----	----
0.125	17.9	19.2	----	----
1	43.1	38.0	39.9	12.8
0.5	----	----	28.7	9.9
0.25	----	----	9.4	0.0

As can be seen from the above tables, the compounds of our invention are effective dry strength additives in both acid and alkaline media and at various feed rates.

The paper of the present invention generally is prepared by forming an aqueous suspension of paper making cellulosic fibers, adding to said suspension a dry strength additive and any other desirable additive, sheeting the fibers to form a cellulosic web and heating the web until dry to form the paper.

The dry strength additives of the present invention may be added to the cellulosic pulp suspension in amounts ranging from 0.1 to 5.0 percent by weight based on the dry weight of the cellulosic fibers. Below 0.1 percent, no appreciable effect on the paper is noticeable and the use of concentrations in the neighborhood of 5 percent is generally an overtreatment. The preferred range is from 0.2 to 1.0 percent.

The exact pH and concentration at which the dry strength additives of our invention will be utilized in the paper making process will vary from instance to instance. It will depend largely on the type of cellulosic fiber being employed, the other common paper making additives being used, and the properties desired of the final product. Accordingly, in each instance, the optimum condition can easily be found by simply laboratory trials. However, the dry strength additives of our invention are effective within the pH range of about 3.5 to 9 and in the concentration range mentioned above.

The polymers of our invention may be added at any convenient point in the paper making process so long as they are added after the fan pump.. In addition, they may be added as a dry powder or an aqueous solution. The use of an aqueous solution is preferred since it insures a more uniform mixture of the additive and paper fibers.

The temperature at which the sheets is dried and the duration of the drying are not critical. The additives are substantially non-thermosetting and hence need not be subjected to any critical drying conditions. Therefore, the invention contemplates that the paper will be produced by drying on rolls in the normal range of 190–250° F.

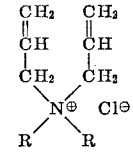
The dry strength additives of our invention are also compatible with most of the other commonly employed materials used in the paper formation. For example, they are compatible with rosin and the other common sizing agents, alum, the pigments such as clay, $CaCO_3$ and TiO_2, and the basically used dyes.

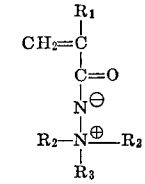
We claim:

1. A graft copolymer comprising from 5 to 97.5 percent by weight of a dextran substrate and the remainder derived from one or more polymerizable acrylic or diallylic quaternary ammonium monomers.

2. A graft copolymer comprising from 5 to 97.5 percent by weight of a dextran substrate, from 0.125 to 71 percent by weight acrylamide and the remainder derived from one or more polymerizable acrylic or diallylic quaternary ammonium monomers.

3. A graft copolymer as in claim 2 wherein the polymerizable acrylic or diallylic quaternary ammonium monomers are selected from the group having the formulae:





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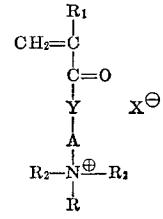
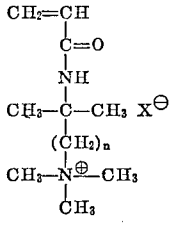


(III)

where R is hydrogen or an alkyl group of 1 to 4 carbon atoms; R_1 is H or CH_3; R_2 is selected from alkyl groups of 1 to 4 carbon atoms; R_3 is selected from alkyl groups of 1 to 4 carbon atoms, mono-hydroxy-alkyl groups of 1 to 4 carbon atoms, and dihydroxy alkyl groups of 1 to 4 carbon atoms; Y is —O— or —NH—; A is an alkyl group of 1 to 6 carbon atoms or a hydroxyalkyl group of 1 to 4 carbon atoms and X^- is an anion selected from chlorine, bromine, and methyl sulfate.

4. A graft copolymer as in claim 2 wherein the polymerizable quaternary ammonium monomer is dimethyl diallyl ammonium chloride.

5. A graft copolymer as in claim 2 wherein the polymerizable quaternary ammonium monomer has the formula:

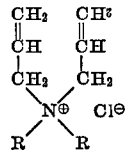


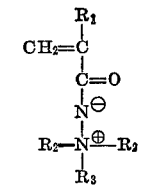
where n is 1 or 2 and X^- is an anion selected from chlorine, bromine, and methyl sulfate.

6. An improved process for making paper having dry strength comprising forming an aqueous suspension of paper making cellulosic fibers, adding to said suspension a dry strength additive, sheeting the fibers to form a web and heating the web until dry to form the paper, wherein the improvement comprises adding an effective amount as the dry strength additive a graft copolymer comprising from 5 to 97.5 percent by weight of a dextran substrate and the remaider derived from one or more polymerizable acrylic or diallylic quaternary ammonium monomers.

7. An improved process for making paper having dry strength comprising forming an aqueous suspension of paper making cellulosic fibers, adding to said suspension a dry strength additive, sheeting the fibers to form a web and heating the web until dry to form the paper, wherein the improvement comprises adding an effective amount as the dry strength additive a graft copolymer comprising from 5 to 97.5 percent by weight of a dextran substrate, from 0.125 to 71 percent by weight acrylamide and the remainder derived from one or more polymerizable acrylic or diallylic quaternary ammonium monomers.

8. An improved process as in claim 7 wherein the polymerizable quaternary monomers are selected from the group having the formulae:





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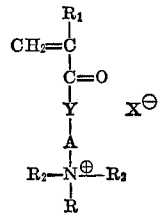
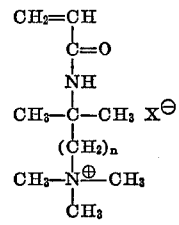


(III)

where R is hydrogen or an alkyl group of 1 to 4 carbon atoms; R_1 is H or CH_3; R_2 is selected from alkyl groups of 1 to 4 carbon atoms; R_3 is selected from alkyl groups of 1 to 4 carbon atoms, mono-hydroxy-alkyl groups of 1 to 4 carbon atoms, and dihydroxy alkyl groups of 1 to 4 carbon atoms; Y is —O— or —NH—; A is an alkyl group of 1 to 6 carbon atoms or a hydroxyalkyl group of 1 to 4 carbon atoms and X^- is an anion selected from chlorine, bromine, and methyl sulfate.

9. An improved process as in claim 7 wherein the polymerizable quaternary ammonium monomer is dimethyl diallyl ammonium chloride.

10. An improved process as in claim 7 wherein the polymerizable quaternary ammonium monomer has the formula:



where *n* is 1 or 2 and X^- is an anion selected from chlorine, bromine, and methyl sulfate.

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U.S. Cl. X.R.

162—175; 260—17.4