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2,884,057

**PAPER OF IMPROVED DRY STRENGTH AND  
METHOD OF MAKING SAME**

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The present invention relates to cellulosic webs of improved dry strength. The invention relates to such webs and particularly to paper comprising cellulosic fibers having uniformly adsorbed thereon a small but effective amount of a normally water-soluble linear polymer containing quaternary ammonium groups as agent imparting the dry strength referred to. The invention includes paper, paper board, and other webs composed of fibers carrying in addition to the dry strength agent rosin and other sizing agents, hydrophobic organic impregnating agents, wet strength agents, fillers, dyes, and pigments. The invention further includes methods for manufacturing various types of cellulosic webs described.

The novel strengthened cellulosic webs of the present invention are suitable for special use as bank note, bond, ledger and book paper; map, blueprint and graph paper; newsprint paper; wrapping paper and bag paper; paper toweling; saturating papers; cardboard, hardboard, and insulating board; other formed, pressed webs; and shaped articles of the type formed from papier-mâché.

By "dry strength" is meant the strength of the cellulosic web in its normally dry condition, and paper which has a dry strength about 10% in excess of its normal strength as the result of resin treatment is generally regarded as possessing a materially improved dry strength.

The invention is based chiefly upon our discovery that cellulosic webs composed of cellulosic fibers having uniformly adsorbed thereon a small amount of a normally water-soluble high molecular weight linear chain polymer carrying quaternary ammonium groups as more particularly hereinafter described possess materially increased dry strength. That is, we have found that when cellulosic fibers are slurried with an aqueous suspension containing a polymer of the type mentioned, the polymer is rapidly adsorbed by the fibers and that when the thus treated fibers thus carrying a uniformly adsorbed amount of the polymer are made into a web and the web is dried, the resulting web possesses materially greater dry strength than that possessed by corresponding webs composed of cellulosic fibers having adsorbed thereon none of the polymers referred to.

The strengthening agents employed in the present invention are synthetic, hydrophilic, cationic linear chain polymers or macromolecules containing quaternary ammonium groups. The chains may be polyalkane chains containing only carbon atoms, polyazaalkane chains containing carbon and nitrogen atoms, polyoxaalkane chains containing carbon and oxygen atoms, or polythiaalkane chains containing carbon and sulfur atoms. Moreover, chains may be composed of a variety of atoms including carbon, nitrogen, sulfur, and oxygen atoms or may be

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composed wholly of carbon atoms. Further, the chains may carry a variety of substituents, as will be more fully disclosed. The strengthening agents themselves are cationic polyelectrolytes which have the capacity of substantially depositing themselves on cellulosic fibers in aqueous suspension and, when so deposited, increase the dry strength of paper made therefrom. The deposition is irreversible in that the resin is not removed during the steps to which the fibers are normally subsequently subjected in their manufacture into paper.

It is a feature of the invention that useful results are obtained in the case of inherently water-soluble polymers when each polymeric macromolecule contains a surprisingly small proportion of quaternary ammonium group, proportions being in the range of one such group for every 1,000 linear chain atoms. As a result, it appears that in such cases it is sufficient if each macromolecule contains even one quaternary ammonium group. On the other hand, distinct strengthening effects have been observed when there are present as many as 500 quaternary ammonium groups for each 1,000 atoms of the chain.

The strengthening agents are normally water-soluble; that is, they are water-soluble in the form employed. When adsorbed on cellulose fibers, however, they appear to become insoluble and are not removed to any significant extent by ordinary washing.

In numerous instances a significant strengthening effect is noted when the fibers have adsorbed thereon as little as 0.01%, based on their dry weight, of the strengthening agent and may carry as much as 5%-10% or more. A near maximum improvement in strength takes place when the fibers carry roughly 1%-3% of the material, larger amounts acting to improve the dry strength still further, but not in proportion to the amount added.

The mechanism by which these agents act is not known, but evidently they strengthen or supplement the normal gelatinous fiber-to-fiber bonding or cementation which takes place when the fibers are sheeted from aqueous suspension and the sheets thus formed are dried.

From the foregoing it will be seen that the strengthened cellulosic webs of the present invention consist essentially of interfelted cellulosic fibers having uniformly adsorbed thereon from 0.01% to 10%, based on their weight, and preferably about 1% to 3% of a long chain normally water-soluble linear polymer carrying quaternary ammonium groups. In addition, the web may contain a normally effective amount of any of the common sizing materials, including rosin size, cationic size, or wax size, and from 2% to as much as 30% of the usual fillers and pigments, including alkaline fillers such as calcium carbonate.

The evidence is that any type of cellulose fiber is benefited by the process of the present invention, and that the greatest percentile increases in dry strength result when the polymers are applied to weak fibers, that is, to lightly beaten fibers.

The preferred strengthened papers of the present invention possess the following characteristics. The basis of comparison in each instance is corresponding paper which contains no strengthening agent.

(1) The papers of the present invention, if made on the acid side, retain their dry strength although subsequently exposed to alkaline conditions, and conversely, if made under alkaline conditions, they retain their dry strength although exposed to acid conditions. As a re-

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sult, they are not significantly affected by the presence of normally alkaline fillers such as calcium carbonate and may be used for packaging normally acidic or alkaline materials such as acid fertilizers and alkaline cements.

(2) The papers of the present invention possess greatly increased dry strength, increases of up to 30%–50% in dry tensile strength being common.

(3) The papers need not have any metal content or content of combined formaldehyde, and thus are advantageously used for analytical laboratory filtration paper and as photographic paper.

(4) The papers possess substantially the same caliper, porosity, density, odor, color, "feel" and printing qualities as ordinary paper.

(5) The papers, unless otherwise desired, possess low wet strength. As a result, unless intentionally given high wet strength properties, the papers of the present invention are readily repulped by ordinary beating without need for special equipment.

The process for manufacturing strengthened paper according to the present invention comprises three principal steps; forming an aqueous suspension of cellulosic fibers; adding an aqueous solution of the strengthening agent thereto, thereby adsorbing the strengthening agent on the fibers; and sheeting and drying the fibers to form the desired cellulosic web.

The first step of forming an aqueous suspension of cellulosic fibers is performed by any conventional method. It usually involves beating and refining the fibers, the suspension thereafter being adjusted to a convenient consistency between about 0.1% and 3–6%. However, the primary effect of beating is to increase the bonding capacity of the cellulose fibers. Hence, in those instances when paper of ordinary strength is satisfactory, addition of the dry strength polymer permits a sharp curtailment in the duration of beating which would otherwise be necessary for this purpose.

The second step is performed by adding an aqueous solution of the strengthening agent to the cellulosic suspension and rapidly and uniformly distributing the solution therethrough so as to minimize uneven adsorption of the agent by the fibers. The step is most conveniently performed by adding the solution to a turbulent stream of the suspension at the headbox or other point near the web-forming wire. It is practical, however, to incorporate the strengthening agent in the beater or even in a stock storage tank, in the latter event the stock being most advantageously agitated during the addition and the solution being added in rather dilute form. The pH of the suspension may be any value between 3 and 11, but in most instances slightly better results are obtained in the range of 4.5–9.0.

Manipulatively, the third step is performed in conventional manner, but it is a feature of the present invention that agents which are free from combined formaldehyde develop substantially their maximum strengthening effect when the paper during its entire manufacture is maintained at a low temperature and are not significantly affected by exposures to elevated temperature for such time as are common in the manufacture of ordinary paper. As a result, no additional heat is required, and in certain instances heat may be saved, while producing a paper of low or negligible wet strength. On the other hand, when the paper is subjected to normal drying conditions, for example 200°–250° F. for ½ to 3 minutes and the resin contains combined formaldehyde, the dry strength increases only slightly over corresponding resin-treated paper which has not been heated whereas the wet strength values obtained rise markedly. As a result, when paper is produced with the broke recovery problem in view a minimum effective drying temperature will be employed or a resin will be selected which contains no combined formaldehyde and a formaldehyde-containing resin will be used at a higher drying temperature when the paper is expected to exhibit substantial wet strength. There is no sharp line

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of division between these two ranges, the wet strength rising steadily as the drying temperature is increased while the dry strength values rise similarly but at a much slower rate.

It is possible to incorporate the method just described in many of the commercially important processes for the manufacture of sized paper.

For example, before addition of the strengthening agent the fibers may be sized in normal manner by the addition of rosin size and alum, or by the addition of wax size and alum, or by the addition of the substitutively adsorbed sizing agents of Argentine Patent Nos. 86,126 and 86,826. Argentine Patent No. 86,126 discloses the manufacture of alkali-resistant sized paper by beater addition of the cationic condensation product of 1–2 mols of epichlorohydrin with one mol of one or more aliphatic amines containing at least 16 carbon atoms. Argentine Patent No. 86,826 discloses a similar paper manufacturing method wherein the fibers are sized by addition of a polyalkylene-polyamine-fatty acid condensate in the form of an aqueous dispersion of a water-soluble salt thereof. The strengthening agents of the present invention are not adversely affected by the small amount of residual alum normally remaining after such sizing operations.

Alternatively, a colloidal cationic amine-aldehyde wet strength resin may be added such as that shown in U.S. Patent No. 2,345,543, preferably before or after the addition of the dry strength resin.

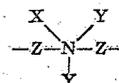
Alternatively still, impregnated paper may be formed by adding subsequent to incorporation of the dry strength polymer a hydrophobic organic impregnating agent in dispersed form as disclosed in U.S. Patent No. 2,563,897, the dry strength resin acting in manner similar to the melamine-aldehyde there employed to flocculate and irreversibly deposit on the fibers the dispersed impregnating agent.

The manufacture of rosin-sized paper containing an acid-sensitive inorganic filler such as calcium carbonate in the past has been regarded as impractical, the alum normally added to precipitate rosin sizing changing the pH of the suspension to the acid side resulting in foam from decomposition of any calcium carbonate present. On the other hand, if addition of the calcium carbonate is deferred until the rosin size is deposited on the fibers, the calcium carbonate raises the pH of the suspension causing the rosin to be desorbed by the fibers.

A recent development of the paper art is the series of cationic alkali resistance sizes disclosed in the Argentine patents referred to. The dry strength resins of the present invention are compatible therewith and paper of improved dry strength may be readily manufactured by first adding the cationic alkali resistance size as described in said patents, then adding one of the dry strength resins of the present invention, and finally adding the calcium carbonate.

Strengthening agents suitable for use in the present invention may be made by three principal methods.

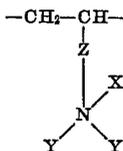
According to one method, a preformed polyazaalkane is employed containing tertiary nitrogen groups such as polymerized N-methyl-ethylenimine having a viscosity of about 60–120 seconds as measured by the fall time of a 3 mm. steel ball through 20 mm. of a 50% aqueous solution of the polymer at 20° C. This polymer may be quaternized by the addition of a small amount of an alkyl or aryl halide. The product is a heterogeneous chain composed of recurring alkylene groups between recurring quaternized N atoms. If desired, the two steps may be combined by coreacting a compound containing two tertiary amino groups such as tetramethyl p-phenylenediamine with ethylene dibromide. The resulting polymers contain linkage of the type



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wherein X represents halogen or hydroxyl, Y represents alkyl or aryl, and Z represents alkylene or arylene groups.

According to a second method, a linear polymer is employed which carries halogenated substituents, quaternization being effected by addition of a tertiary amine. Thus, for example, polymerized allyl chloroacetate may be quaternized with pyridine, polymerized p-(chloromethyl) styrene may be quaternized by reaction with triethylamine, and the quaternary ammonium compound formed by reacting N-(dimethylamino)propionamide may be reacted with polymerized N-hydroxymethylacrylamide. The resulting polymers contain linkages of the type



wherein Z represents essentially inert groups such as arylene, alkylene,  $\text{---CONH(CH}_2\text{)}_3\text{---}$ ,  $\text{---COOCH}_2\text{CH}_2\text{---}$ ,



$\text{---CHCOOCH}_2\text{---}$ , and  $\text{---CONHCH}_2\text{NHCOCCH}_2\text{CH}_2\text{---}$ , and X and Y as shown above. Moreover, Z and N may be present in one grouping, as in the case of a heterocyclic ring, for example, pyridine.

The third method is based upon copolymerization of a monomeric or low molecular weight quaternary ammonium compound with one or more monomers or low molecular weight compounds copolymerizable therewith. Thus, for example, an  $\alpha,\beta$ -unsaturated quaternary ammonium compound such as trimethyl vinylbenzyl ammonium chloride may be copolymerized with an  $\alpha,\beta$ -unsaturated hydrocarbon, amine, amide, ester, or mixtures thereof such as styrene, acrylamide, ethyl acrylates, etc. to give a linear chain carbon polymer carrying a desirable proportion of quaternary ammonium groups. Other polymerizable quaternary ammonium compounds may be prepared from dimethylaminopropyl-acrylamide and benzyl chloride; from ethyl diethylamino-acrylate and benzyl bromide; and from methylene bisacrylamide reacted with diisopropylamine followed by quaternization with butyl bromide.

When adjusted to pH 7 the polymers are stable and may be stored for at least several months before use. They are prepared for addition to the pulp suspension by dilution with water to a convenient solids content normally 5-10% and the pH of the resulting solutions may be maintained between 4 and 9 for several hours without harm.

Very satisfactory results have been obtained in the case of polymers having molecular weights (calculated from viscosity measurements) of 50,000, 100,000, and 150,000, practically the same dry strength being imparted in each case, and there, therefore, does not appear to be any theoretical maximum to the molecular weight which the polymer may attain. It is to be expected, however, that the strengthening effect will fall considerably when the low molecular weight stage is approached too closely, and from experience with similar polymers the evidence is that the reaction should be controlled by known means so that a molecular weight of at least about 10,000-25,000 is obtained to make the polymer practically useful.

At the other extreme, with increase in molecular weight the polymers become more and more viscous, and a practical maximum is set when the polymer is so viscous that 2% aqueous solutions thereof are beyond pumpable viscosity. Generally, polymers of a molecular weight of 200,000 are satisfactorily fluid and give substantially the best results of their respective types.

The number of quaternary ammonium groups present should be at least one, on the average, for every macro-

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molecule present, and for best results because of the heterogeneity of the reactions employed it is preferred to provide considerably more. In general, therefore, at least about one quaternary ammonium group is present for every 1,000 atoms forming the chain, and no more than about 50 such groups calculated on the same basis is required to provide satisfactory dry strength.

It is necessary, however, that the polymers be water-soluble or water-dispersible in the sense that when mixed with water they form a completely homogeneous and usually clear or colloidal cationic dispersion therewith, and it is possible to form polymers containing a large proportion of hydrophobic or insolubilizing groups.

Quaternary ammonium groups have a solubilizing action and hence, an additional proportion of these groups may be present over the amounts recited above in order to confer on them a solubility which otherwise would be lacking. Thus, when a monomeric  $\alpha,\beta$ -unsaturated quaternary ammonium compound is copolymerized with styrene or an acrylate ester, the phenyl or ester groups in the resulting polymer exert their normal strongly hydrophobic influence. In such instances an excess of the quaternary ammonium compound is necessary to form a water-soluble polymer. On the other hand, when a polymer is formed by copolymerizing acrylamide with an  $\alpha,\beta$ -unsaturated quaternary ammonium compound, the amide groups in the resulting polymer act as solubilizing groups permitting the use of a comparatively low amount of the quaternary ammonium compound for formation of a water-soluble or water-dispersible polymer. In general, hydrocarbons and ester groups act in hydrophobic manner when formed into linear polymers and require the presence of a comparatively large proportion of quaternary ammonium groups whereas amine, hydroxy, polyglycol and amide groups are hydrophilic when formed into linear polymers and require minimum amounts of the quaternary ammonium compound for development of water-soluble polymers. A similar relationship holds with regard to the structure of the chains, fewer quaternary ammonium groups being required in the case of polyazaalkyl chains than in the case of straight chain carbon or polyalkane chains because of the solubilizing effect of the nitrogen atoms therein.

The minimum effective amount of the quaternary ammonium compound necessary in each instance is thus a function of the type of linear chain employed and the number and type of substituent groups attached thereto. As a result, the proportion of quaternary ammonium groups which should be present can be most conveniently determined by actual trial, a resin being formed first employing a comparatively small amount of the quaternary ammonium monomer and, if the resulting resin proves insoluble, increasing the proportion of the quaternary ammonium monomer until a water-soluble resin is obtained.

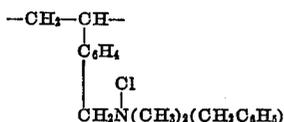
The dry strength resins prepared by copolymerization of monomers which contain only such groups as ester, carboxylic acid, alkoxy, aryloxy, and unsubstituted or hydrocarbon substituted amide and amine groups yield paper which has negligible wet strength. Such polymers are essentially chemically inert under the conditions employed and, therefore, form bonds with the cellulose which are loosened by the presence of water.

It is readily feasible to modify the polymers described so as to make them chemically reactive whereby on heating they will form a water-insoluble composition giving wet strength as well as dry strength. Most simply, this is done by ensuring that the polymer, before addition to the fibrous cellulose suspension, contains combined formaldehyde. Thus, a very minor amount of an  $\alpha,\beta$ -quaternary ammonium compound may be copolymerized with a major amount of an  $\alpha,\beta$ -unsaturated N-methylol amide such as N-hydroxymethyl-acrylamide. The resulting polymer is employed in the same manner as the polymers described above, except that the paper during



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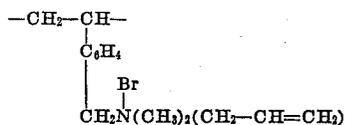
which time a precipitate of polymerized benzyl dimethyl vinylphenyl ammonium chloride had formed. The product was collected on a Buchner funnel, washed with 100 ml. of benzene and dried under vacuum. The dry tan polymer weighed 3.8 g. and contained recurring linkages of the theoretical formula



The above polymer was dissolved in water to form a colloidal cationic dispersion containing 5% solids.

#### Example 7

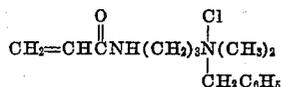
A 2.5 g. sample of the reprecipitated methanol-washed para-(dimethylamino) styrene polymer prepared in Example 6 was dissolved in 25 ml. of benzene. 6.2 g. of allyl bromide (200% excess) was then added. The solution was maintained at room temperature. Quaternization was complete within about 1 hour. The product was a precipitate which was collected on a Buchner funnel, washed with 100 ml. of benzene and dried under vacuum. The dry tan polymer weighed 4.5 g. When dissolved in water at 1% solids the polymer formed a hazy colloidal cationic dispersion, and contained recurring linkages of the theoretical formula



#### Example 8

The preparation of a dry strength resin by copolymerization of a preformed monomeric  $\alpha,\beta$ -unsaturated quaternary ammonium compound with  $\alpha,\beta$ -unsaturated compounds is illustrated by the following.

(3-acrylamidopropyl) benzyl dimethyl ammonium chloride



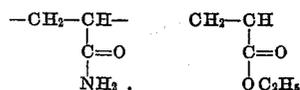
was prepared as follows.

Into 624 g. of N-[3-(dimethylamino)propyl] acrylamide in 1100 ml. of benzene in a round-bottomed flask fitted with stirrer, thermometer, and reflux condenser was slowly stirred 506 g. of benzyl chloride. The temperature was held at 50° C. by an ice-water bath. The reaction mass set to a thick paste, which was cooled to room temperature, was washed with benzene and air-dried. The product was dissolved in 1500 ml. of water and the benzene layer removed in a separatory funnel. The aqueous solution was treated with activated charcoal and filtered, and then diluted to 30% solids with water and adjusted to pH 8.7 with HCl. Titration indicated that the quaternization was 85% complete.

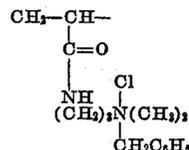
The product was copolymerized as follows. Into a three-necked, round-bottomed flask fitted with reflux condenser, thermometer, stirrer and dropping funnel and provided with an electric mantle heater were charged 28.0 g. of monomeric acrylamide, 8.0 g. of monomeric ethyl acrylate, 13.3 g. of the 30% aqueous solution containing the aforementioned (3-acrylamidopropyl) benzyl dimethyl ammonium chloride and 350.6 g. of water. The reagents were stirred and the pH was adjusted to 6.5 with NaOH. 0.1 g. of powdered ammonium persulfate was then added. The turbid solution was heated to 80° C. and maintained at this temperature for about 4 hours, after which the clear syrup which formed was cooled to room temperature. The pH was again adjusted to 7.5 with sodium

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hydroxide. The product which contained the recurring groups



and

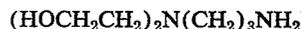


was a viscous water-soluble cationic syrup.

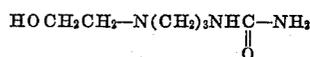
(3-acrylamidopropyl) benzyl dimethyl ammonium chloride and methods for the preparation thereof are disclosed and claimed in co-pending application Serial No. 286,003, filed May 3, 1952, by John A. Price. The application discloses further quaternary ammonium salts which are advantageously used in the process of the present invention, and these samples are incorporated in the present specification by reference.

#### Example 9

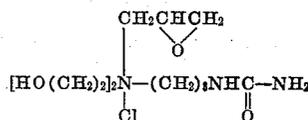
3-[bis(2-hydroxyethyl)] amino propylamine,



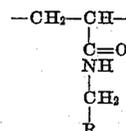
was reacted with potassium cyanate and to form 3-[bis(2-hydroxyethyl)] aminopropylurea



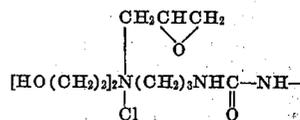
41.0 (0.2 mol) of the product was dissolved in water and 23.1 g. (0.25 mol) of epichlorohydrin added. The mixture was heated at 60° C. for 24 hours. 4 g. of the aqueous solution containing about 50% by weight of ureidopropyl - bis(2 - hydroxyethyl)glycidyl ammonium chloride of the theoretical formula



was added to 10 g. of 37% formaldehyde. The mixture was added to 71 g. of a 10% aqueous polyacrylamide solution. The resulting solution was acidified to pH 6.0, heated to 180° F. for 30 minutes, and then diluted to a solids content of 7.5% by weight. The product was an aqueous dispersion of a linear polymer in cationic form which, when further diluted with water, exhibited a bluish colloidal haze. It contained recurring linkages of the theoretical formula



wherein R is



or a hydrolysis product thereof.

#### Example 10

The procedure of Example 9 was followed, using 3-(dimethylamino)-propylamine in place of the 3-[bis(2-hydroxyethyl)]aminopropylamine. A similar colloidal cationic linear polymer was obtained, which also exhib-



stance and the amounts thereof being shown in the table. Results are as follows:

of the stock being 4.5. The strengthening agents contained combined formaldehyde, and was formed by co-

Test No.	Polymer Reagents (Parts by Weight)					Stock pH	Basis, Wt. % Lb.	Tensile Strength <sup>4</sup>		
	Quat. <sup>1</sup>	Acryl- amide	Methylol Acryl- amide	Acrylo- Nitrile	Ethyl Acrylate			Dry		Wet- Found <sup>2</sup>
								Found <sup>3</sup>	Percent Increase	
Control A							44.9	21.7	0.6	
1	5		90	5		4.5	45.9	30.3	3.7	
2	5		90	5		9.0	46.2	30.2	2.3	
3	5		85	10		4.5	50.2	28.9	3.1	
4	5		85	10		9.0	48.0	30.4	1.6	
5	5		80	15		4.5	45.9	29.4	2.4	
6	5		80	15		9.0	46.9	29.4	1.4	
Control B							44.1	24.2	0.7	
7	5		95			4.5	44.6	32.0	4.9	
8	5		95			9.0	43.6	33.3	2.9	
9	5	95				4.5	42.8	33.8	1.2	
10	5	95				9.0	44.1	33.3	3.6	
Control C							51.1	25.2	0.5	
11	10	90				4.5	50.8	32.5	2.7	
12	10	90				9.0	50.5	38.2	3.8	
13	10	70			20	4.5	49.7	30.3	2.4	
14	10	70			20	9.0	48.2	33.2	2.8	

<sup>1</sup> 3-(Acrylamidopropyl) benzyl dimethyl ammonium chloride.  
<sup>2</sup> 25" x 40"/500.  
<sup>3</sup> Corrected to 50 lb. basis weight.  
<sup>4</sup> Lb./in.

The test sheets were indistinguishable in appearance and feel from the control sheets.

Example 17

The manufacture of high dry strength, well-sized paper is illustrated by the following.

The paper-forming process of the previous example was followed with two exceptions.

(1) The fibers were sized by the addition of 3% liquid gum rosin size (solids based on the dry weight of the fibers) followed by the addition of 4% of alum, and

(2) The sheets were prepared in duplicate, one set of sheets being dried at room temperature (75° F.), the other set being dried at the normal temperature of 240° F.

The strengthening agent employed was formed by copolymerizing 90 parts by weight of acrylamide with 10 parts by weight of 3-(acrylamidopropyl)benzyl dimethyl ammonium chloride by the method of Example 9 to a molecular weight as estimated from viscosity measurement of about 150,000. Three percent of the strengthening agent based on the dry weight of the fibers was added in each case except the controls, which therefore contained only rosin size and alum.

Results are as follows:

Run	Rosin Added, <sup>1</sup> Percent	Copolymer Added, <sup>1</sup> Percent	Basis Wt. <sup>2</sup> Lb.	Drying Temp., ° F.	Tensile Strength			Curler Test <sup>3</sup> (Secs.)
					Dry		Wet- Found <sup>3</sup>	
					Found <sup>3</sup>	Percent Increase		
Control	3	Nil	45.3	75	19.3		0.9	34
1	3	3	47.4	75	31.0	60.6	2.1	36
Control	3	Nil	42.8	240	21.2		1.5	52
2	3	3	42.1	240	33.0	55.6	4.7	50

<sup>1</sup> Solids based on dry weight of the fibers.  
<sup>2</sup> 25" x 40"/500.  
<sup>3</sup> Corrected to 45 lb. basis weight.

This test shows that the strengthening agents of the present invention are compatible with rosin size, and that very satisfactory dry strength paper can be made therewith. The results show that the effect of the application of heat during drying on the strength of the paper is to decrease the dry strength and to increase the wet strength.

Example 18

A paper of both high wet strength and high dry strength was prepared from unbleached northern kraft pulp according to the procedure of Example 16, the pH

polymerizing 5 parts by weight of 3-(acrylamidopropyl) benzyl dimethyl ammonium chloride with 95 parts by weight of N-hydroxymethylacrylamide (prepared from acrylamide and formaldehyde). 3% of the resin was added based on the dry weight of the fibers. The paper was dried for 10 minutes at 260° F., and the results are shown in comparison with one control which contained no polymer and a second control which was dried at room temperature.

Run	Percent Polymer	Basis, Wt. Lb. <sup>1</sup>	Drying		Tensile Strength <sup>2</sup>	
			Temp., ° F.	Time, Min.	Dry	Wet
Control A	Nil	45.1	260	10	20.0	0.6
Control B	3	44.3	75		28.5	0.6
1	3	44.6	260	10	29.1	8.4

<sup>1</sup> Sheets 25" x 40"/500.  
<sup>2</sup> Lb./in. corrected to 45 lb. basis weight.

We claim:

1. Dry paper of improved dry strength composed of 50 water-laid cellulose fibers bonded together by an irre-

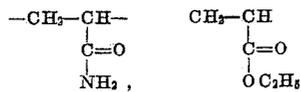
versibly and uniformly adsorbed content of between about 0.01% and 5% of their weight of a normally hydrophilic water-soluble cationic linear polyalkane chain polymer having an average molecular weight of at least about 10,000 and containing quaternary ammonium groups.

2. Paper according to claim 1 wherein the polymer has an average molecular weight between about 50,000 and 200,000.

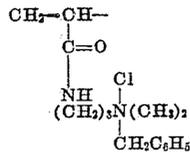
3. Paper according to claim 1 wherein the weight of polymer is between about 1% and 3% of the weight of the fibers.

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4. Paper according to claim 1 wherein the polymer contains the recurring groups



and



5. Dry paper of improved dry strength composed of water-laid cellulose fibers bonded together by an irreversibly and uniformly adsorbed content of between about 0.1% and 5% of their weight of a normally hydrophilic water-soluble cationic linear polyalkane chain polymer having an average molecular weight of at least about 25,000 and containing between about 1 and 15 quaternary ammonium groups for each 1000 linear chain atoms.

6. Filled dry paper of improved dry strength composed of water-laid cellulose fibers bonded together by an irreversibly and uniformly adsorbed content of between about 0.1% and 5% of their weight of a normally hydrophilic water-soluble cationic linear polyalkane chain polymer having an average molecular weight of at least about 25,000 and containing quaternary ammonium groups, said paper having a uniformly distributed content of from 2% to 30% of a carbonate filler.

7. Paper according to claim 6 wherein the filler is calcium carbonate.

8. Sized dry paper of improved dry strength composed of rosin-sized water-laid cellulose fibers bonded together by an irreversibly and uniformly adsorbed content of between about 0.1% and 5% of their weight of a normally hydrophilic water-soluble cationic linear polyalkane chain polymer having an average molecular weight of at least about 25,000 and containing quaternary ammonium groups.

9. A method of manufacturing paper of improved

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dry strength which consists essentially in forming an aqueous suspension of paper-making cellulosic fibers, mixing therewith from 0.01% to 5% of their weight of a hydrophilic water-soluble cationic linear polyalkane chain polymer having a molecular weight of at least 10,000 and containing quaternary ammonium groups whereby said polymer is irreversibly and uniformly adsorbed by said fibers, and sheeting and drying said fibers, whereby said fibers are bonded together by said adsorbed polymer.

10. A method according to claim 9 wherein the polymer has an average molecular weight of between about 50,000 and 200,000.

11. A method according to claim 9 wherein the paper is dried at a temperature below about 160° F., whereby a paper of low wet strength is obtained.

12. A method according to claim 9 wherein a carbonate filler is added to the aqueous suspension subsequent to adsorption of the polymer by the fibers.

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