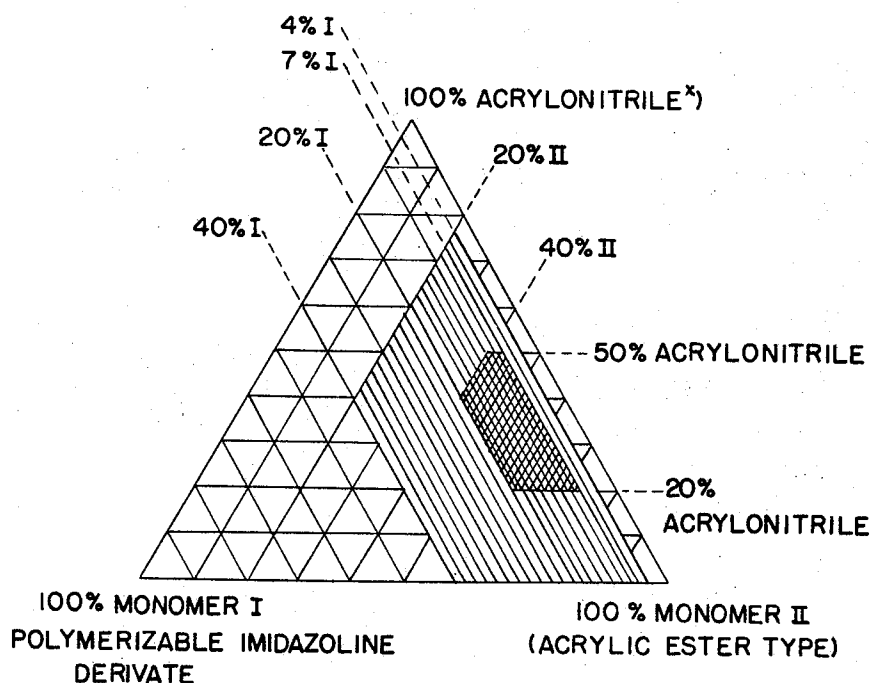


July 4, 1967

O. VON SCHICKH ETAL 3,329,560
QUATERNARY VINYLIMIDAZOLINIUM COPOLYMER DISPERSIONS, METHODS
OF APPLICATION OF SAME TO PAPER
AND SIZED PAPER THEREOF
Filed June 28, 1966

RATIO OF MONOMERS IN POLYMER DISPERSIONS
(PERCENTAGES ARE BY WEIGHT)



CLAIMED RANGE



PREFERRED RANGE

*)OR UP TO 50% OTHER MONOMERS AS SET FORTH IN SPECIFICATION

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3,329,560

QUATERNARY VINYLIMIDAZOLINIUM COPOLYMER DISPERSIONS, METHODS OF APPLICATION OF SAME TO PAPER AND SIZED PAPER THEREOF

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B 68,940

12 Claims. (Cl. 162—168)

This application is a continuation-in-part of our application Ser. No. 240,349, filed Nov. 27, 1962, now abandoned.

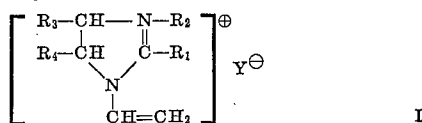
This invention relates to compositions for paper sizing consisting substantially of dispersions of cationic copolymers of quaternary vinylimidazolinium salts, esters of unsaturated carboxylic acids and, if desired, further olefinically unsaturated polymerizable compounds. Furthermore, the invention relates to methods of applying said compositions and to the paper sized in this way.

From Belgian patent specification No. 599,540 and U.S. patent specification No. 3,174,874 it is known to use for the stock sizing and surface sizing of paper, dispersions of cationic copolymers of vinyl-substituted monomers containing an aromatic or heterocyclic-aromatic radical and at least one quaternary nitrogen atom in the molecule and further polymerizable compounds.

It is an object of this invention to provide sizes for the stock sizing and surface sizing of paper which give a particularly good sizing effect and are very simple to use. Another object of the invention is to provide sizes which are compatible with other sizes as well as with the auxiliaries and fillers usual in the paper industry.

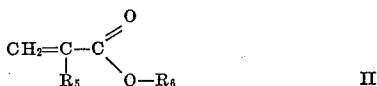
These objects are accomplished with particularly good success by using for the stock sizing and surface sizing of paper dispersions of copolymers of

(a) 4 to 40% by weight of a quaternary vinylimidazolinium salt of the general formula



where R_1 denotes an alkyl, aralkyl, aryl or hydroxy-alkyl group, R_2 denotes an alkyl, aralkyl or hydroxy-alkyl group, R_3 and R_4 denote hydrogen or a lower alkyl group, and Y^- denotes the anion of a strong acid; and

(b) at least 20% by weight of an ester of the general formula:



where R_5 denotes hydrogen or a lower alkyl group having from one to four carbon atoms and R_6 denotes a lower alkyl group having from two to eight carbon atoms; and if desired,

(c) acrylonitrile and/or

(d) one or more other olefinically unsaturated polymerizable compounds.

We prefer dispersions of copolymers obtained from

(a) 7 to 20% by weight of monomers of general Formula I,

(b) 40 to 80% by weight of monomers of general Formula II, and

(c) 20 to 50% by weight of acrylonitrile.

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The monomer ratios in the copolymer dispersions to be used in accordance with the invention are illustrated in the diagram in the accompanying drawing. The limits shown therein are not, however, critical. Copolymers having compositions lying outside these limits may also be used, but give less satisfactory results. Instead of or besides acrylonitrile, the copolymers may contain in polymerized form up to 50% by weight of other unsaturated polymerizable compounds, for example of the comonomers listed further below.

Suitable monomers of general Formula I include those in which R_1 denotes a methyl, ethyl, propyl, benzyl, methylol or phenyl group, R_2 denotes a methyl, ethyl, benzyl or β -hydroxyethyl group, R_3 and R_4 denote methyl or ethyl groups or, preferably, hydrogen, and Y^- denotes a chlorine, bromine, methyl sulfate or ethyl sulfate ion.

Specific examples of such vinylimidazolinium salts are:

- 1-vinyl-2-ethyl-3-methylimidazolinium(Δ^2)-methyl sulfate,
- 1-vinyl-2-phenyl-3-methylimidazolinium(Δ^2)-methyl sulfate,
- 1-vinyl-2-propyl-3-benzylimidazolinium(Δ^2)-chloride,
- 1-vinyl-2-ethyl-3-hydroxyethylimidazolinium(Δ^2)-chloride,
- 1-vinyl-2-isopropyl-3-ethylimidazolinium(Δ^2)-ethyl sulfate, and particularly
- 1-vinyl-2,3-dimethylimidazolinium(Δ^2)-methyl sulfate.

Suitable monomers of general Formula II are particularly the esters of acrylic and methacrylic acids and, among these, especially the n-butyl, isobutyl and tertiary butyl esters and the various amyl, hexyl and octyl esters.

Instead of or besides acrylonitrile, there may be used, for example, styrene, vinyl esters such as vinyl propionate, esters of unsaturated dicarboxylic acids, such as dibutyl maleate, high molecular weight acrylic esters such as decyl acrylate and dodecyl acrylate, methyl methacrylate, vinyl halides such as vinyl chloride and vinylidene chloride, acrylic amides, methacrylic amides, and vinyl lactams such as N-vinylcaprolactam and N-vinylpyrrolidone.

The monomers of general Formula I may be prepared, for example, by condensation of ethylenediamine with carboxylic acids of the formula R_1-COOH and subsequent vinylation and quaternization. The copolymers and copolymer dispersions may advantageously be prepared by the process described in British Patent 976,547. These methods of preparation are not claimed in the present specification.

The dispersions which are obtainable from the said monomers and which, from their manufacture, as a rule contain also soluble components, are very finely divided, very stable, have good storage properties and are resistant to biological degradation. They may be diluted with water to any desired concentration and are largely insensitive to changes in pH and increased temperatures. For these reasons and because they are compatible with many other auxiliaries conventionally used in paper manufacture (provided such auxiliaries are not distinctly anionic), the dispersions to be used according to this invention are suitable for sizing all types of paper, for example kraft paper, writing paper, printing paper, tissue paper and other special papers, and also papers containing plastics fibers. Some of the conventional paper auxiliaries, for example polyethyleneimine and amino-plasts, are even capable of enhancing the sizing effect obtainable with the copolymer dispersions. The composition of the copolymer is selected mainly in dependence on the type of paper desired, but also on the other auxiliaries to be coemployed and on the manufacturing conditions. It can easily be ascertained by simple preliminary experiments which copolymers are most suitable for a specific purpose.

The solids content of the dispersions is usually from about 2 to 20% by weight for stock sizing, and from about 0.5 to 5% by weight for surface sizing. In general, the amount of size used is such that the finished paper contains from 0.5 to 10%, preferably from 0.5 to 3%, by weight of the copolymer after stock sizing, and from 0.2 to 5%, preferably from 0.2 to 1%, by weight after surface sizing. The amount of size required for each type of paper can easily be ascertained by preliminary experiments. The sizes to be used in accordance with the invention are adsorbed practically quantitatively by the cellulose fibers of the pulp or paper.

The sizes to be used according to this invention exhibit a number of outstanding properties. As compared with conventional rosin sizes, the dispersions according to this invention offer the great advantage that sizing may be carried out at any stage in paper manufacture. The dispersions may be added to the aqueous paper pulp, for example after the fibrous material has been reduced in the beater, to the chests ahead of the paper machine or to the breast box. They may also be applied at any point in the paper machine, for example by spraying in the wet end, or with special advantage by means of applicator devices in the dry end of the paper machine. It is particularly simple to apply the very dilute dispersion by means of a sizing press incorporated in the dry end of the paper machine. In this method, it is very advantageous that the degree of sizing can be varied as desired in a simple and reliable way during the operation by varying the solids content of the dispersion or the amount of dispersion applied. Also, finished paper, if undersized, may be resized in a simple aftertreatment, for example on a coating machine. Because of these possibilities and because only very small amounts of dispersion are required for standard sizing, the use of these dispersions is very economical. Furthermore, no special aftertreatment of the paper, for example with heat or at increased pressures, is necessary because paper sized with such dispersions can be dried also at room temperature without the quality of the sizing effect being impaired.

It is advantageous to use very finely divided dispersions because these are particularly economical in use. In stock sizing, the dispersions often improve filler retention. Also, fine fibers are retained better, so that the treatment of wastes is simplified. The sizing effect achieved with such dispersions is largely resistant to alkaline-reacting liquids, for example to 10% caustic soda solution, and is impaired only very slowly by acids.

The resistance of the sizing effect to alkalies is of great importance, for example for packaging alkaline-reacting substances or for the manufacture of base papers which are subsequently to be coated with alkaline-reacting preparations, such as pigment formulations or adhesives.

By appropriate selection of the percentages and types of monomers used, particularly by varying the amount and type of the imidazolinium component, the degree of water repellency obtainable with these dispersions can be varied within fairly wide limits without too greatly impairing the stability of the sizing effect to ink or printing colors. Thus, for example, it is possible to manufacture papers which have excellent ink resistance, but nevertheless have a certain absorbency for water. This is very important for papers which after manufacture have to be subjected to an aftertreatment with aqueous preparations such as aqueous pigment formulations, in order to ensure adequate absorption of such preparation.

Another advantage of the dispersions is that they are also compatible with pigments of all kinds and are therefore suitable for the manufacture of pigment coating colors. In these cases, the dispersions act not only as sizes, but also as vehicles for the pigment.

The invention will be further illustrated by the following examples, but is not limited thereto. The parts

and percentages specified in the examples are by weight. The ink resistance is tested by the following methods:

- I. Test by the absorption method: A strip 2 x 10 cm. is cut from a sheet of paper having a weight of about 80 g./sq. m. and suspended with the lower end dipping 1 cm. into ink. After fifteen minutes, the height to which the ink has been drawn up is measured in millimeters.
- II. Ink flotation test according to P. Klemm, *Handbuch der Papierkunde*, 3rd edition, page 219. The flotation time until penetration of the surface is measured in minutes.
- III. Cobb test according to Tappi Standard T 441 M-45.
- IV. Alkali resistance: The time is measured in minutes which is required for one drop of 10% caustic soda solution to penetrate a sheet of paper having a weight of about 80 g./sq. m.

Example 1

Strips of unsized paper from 100% bleached sulfite pulp are dipped for ten seconds into 0.1% and 1.0% dispersions of copolymers of 70 parts of butyl acrylate, 30 parts of acrylonitrile and the following amounts of 1-vinyl-2,3-dimethylimidazolinium methyl sulfate: (a) 8 parts, (b) 20 parts, (c) 45 parts and, for comparison, (d) 2 parts and (e) 0 part. The strips are then squeezed between blotting paper, dried at 100° C. and tested for ink resistance by method I. In this test, the papers thus treated, which contain about 0.1% and 1.0% of polymer, show the values summarized in Table 1:

TABLE 1

Test	Percentage of 1-vinyl-2,3-dimethylimidazolinium methyl sulfate in the copolymer	Height in mm. to which ink is drawn up when using a dispersion of the strength—	
		0.1%	1.0%
a	7.4	0	0
b	16.5	0	0
c	31	20	1
d	2.0	55	5
e	0	>90	70

In the Cobb test (method III), values are obtained which increase in the sequence (a) to (e), the paper in case (e) behaving like unsized paper.

Dispersions (a) to (d) are prepared as follows:

200 parts of water, 16, 40, 90 or 4 parts of a 50% solution of 1-vinyl-2,3-dimethylimidazolinium methyl sulfate prepared as described below, 1 part of diethyldodecylammonium sulfate and 2 parts of polyvinylpyrrolidone are placed in a polymerization vessel equipped with agitator, supply vessel, reflux condenser and thermometer, and heated to 85° C. Then 2 parts of 30% hydrogen peroxide is added and a mixture of 70 parts of butyl acrylate and 30 parts of acrylonitrile is allowed to flow in the course of two hours, the temperature being maintained at 85° to 90° C. The reaction mixture is kept for another two hours at this temperature and then cooled. The finely divided dispersions thus obtained are adjusted to a solids content of 35% and then have K-values (according to Fikentscher) between 58 and 65 and surface tensions of about 36 dynes/cm.

The 50% 1-vinyl-2,3-dimethylimidazolinium methyl sulfates solution is prepared as follows:

126 parts of water is placed in a reaction vessel which can be cooled and which is provided with an agitator, two supply vessels and an internal thermometer. One supply vessel is charged with 110 parts of 1-vinyl-2-methylimidazoline (Δ^2) and the other with 127 parts of dimethyl sulfate. The two substances are allowed to flow into the reaction vessel in the course of about one hour. During this operation, vigorous agitation and occasional external cooling are used to ensure that the temperature does not rise above 30° C. The reaction is then allowed to continue

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for another two hours and the pH of the solution adjusted to 6 by adding a small amount of ammonia. The solution is yellowish and contains 50% of the quaternary salt.

The comparison dispersion (e), which has a solids content of 35%, a K-value of 72 and a surface tension of 40 dynes/cm., is prepared at 85° C. by emulsion polymerization of 70 parts of butyl acrylate and 30 parts of acrylonitrile in the course of two hours in a previously prepared solution of 190 parts of water, 2 parts of sodium decylphenyl sulfonate and 0.2 part of potassium persulfate.

Example 2

0.3, 0.6, 0.9, 1.2 and 1.5 parts of a dispersion diluted to 2% solids content, prepared as described below, is added to 100 parts of a 3% aqueous suspension of bleached sulfite pulp of 38° S-R fineness, stirred slowly for ten minutes, diluted with 50 parts of water to 0.2% solids content and made into papers having a weight of 80 g./sq. m.

The papers are conditioned for twelve hours at 20° C. and 50% relative humidity. They contain approximately the following amounts of polymer: (a) 0.2%, (b) 0.4%, (c) 0.6%, (d) 0.8% and (e) 1.0%. The values obtained in testing the papers for ink resistance by method I and method II are given in Table 2.

TABLE 2

Test	Percentage of polymer in finished paper	Height in mm. to which ink is drawn up	Ink flotation time in minutes
a.....	0.2	25	1
b.....	0.4	3	12
c.....	0.6	0	50
d.....	0.8	0	>60
e.....	1.0	0	>60

The polymer dispersion is prepared from 128 parts of water, 20 parts of the imidazolinium salt solution described in Example 1, 1 part of dimethyldodecylammonium sulfate, 2 parts of 30% hydrogen peroxide, 60 parts of isobutyl acrylate and 40 parts of acrylonitrile by emulsion polymerization at between 85° and 90° C. in the course of 1½ hours. The dispersion contains 40% of solids, has a K-value of 58 and a surface tension of 37 dynes/cm.

Example 3

Unsize sulfite paper having a weight of 80 g./sq. m. is sized in a sizing press incorporated in the dry end of the paper machine with a dispersion prepared as described in Example 2 and having a strength of (a) 0.2% and (b) 1.0%. The amount of dispersion taken up during sizing is 80% with reference to the weight of the dry paper. When tested by methods I, II and IV for ink and alkali resistance, the papers show the values stated in Table 3.

TABLE 3

Test	Percentage of polymer in dispersion	Height in mm. to which ink is drawn up	Ink flotation time in minutes	Alkali resistance in minutes
a.....	0.2	0	ca. 40	ca. 30
b.....	1.0	0	>60	>60

Example 4

Strips of unsize paper from 100% bleached sulfite pulp are dipped for ten seconds into 0.1% and 1.0% dispersions of copolymers of 60 parts of isobutyl acrylate, 40 parts of acrylonitrile and 10 parts of a 1-vinyl-3-methylimidazolinium methyl sulfate which is substituted in the 2-position with (a) an ethyl group, (b) a propyl group and (c) a phenyl group. The strips are then squeezed between blotting paper, dried at 100° C. and

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tested for ink resistance by method I. The results are given in Table 4.

TABLE 4

Test	Substituent in 2-position of imidazolinium salt	Height in mm. to which ink is drawn up when using dispersions of the following strengths—	
		0.1%	1.0%
a.....	Ethyl.....	0	0
b.....	Propyl.....	4	0
c.....	Phenyl.....	7	0

The vinylimidazolinium salts are prepared as described in Example 1, and the dispersions as described in Example 2.

Example 5

Strips of unsize paper from 100% bleached sulfite pulp are dipped for ten seconds into 0.1% and 1.0% dispersions of copolymers of 20 parts of 1-vinyl-2,3-dimethylimidazolinium methyl sulfate and the following monomers:

- (a) 67 parts of isooctyl acrylate and 47 parts of acrylonitrile
- (b) 80 parts of tertiary butyl acrylate
- (c) 40 parts of butyl acrylate and 40 parts of styrene
- (d) 110 parts of butyl methacrylate and 70 parts of acrylonitrile
- (e) 53 parts of tertiary butyl acrylate and 53 parts of ethyl acrylate
- (f) 60 parts of butyl acrylate and 20 parts of methyl methacrylate.

The strips are squeezed between blotting paper, dried at 100° C. and tested for ink resistance by method I. The values observed are given in Table 5.

TABLE 5

Test	Parts of comonomers in the polymer dispersion besides 20 parts of imidazolinium salt	Height in mm. to which ink is drawn up when using dispersions of the following strengths—	
		0.1%	1.0%
a.....	67 isooctyl acrylate.....	9	0
b.....	47 acrylonitrile.....		
c.....	80 butyl acrylate.....	20	0
d.....	40 butyl acrylate.....		
e.....	40 styrene.....	24	0
f.....	110 butyl methacrylate.....		
g.....	70 acrylonitrile.....	0	0
h.....	53 tertiary butyl acrylate.....		
i.....	53 ethyl acrylate.....	15	0
j.....	60 butyl acrylate.....		
k.....	20 methyl methacrylate.....	22	0

Dispersion (a) is prepared from 187 parts of water, 40 parts of the imidazolinium salt solution described in Example 1, 2.7 parts of N-tridecyl-N,N,N-trimethylammonium chloride, 2.7 parts of 30% hydrogen peroxide, 67 parts of isooctyl acrylate and 47 parts of acrylonitrile by emulsion polymerization in the course of 3½ hours at 90° C.

Dispersion (b) is prepared in an analogous manner from 135 parts of water, 40 parts of the imidazolinium salt solution, 1 part of dimethyldodecylammonium sulfate, 2 parts of polyvinylpyrrolidone, 2 parts of 30% hydrogen peroxide and 80 parts of tertiary butyl acrylate in the course of three hours at 85° C.

Dispersion (c) is obtained from 135 parts of water, 40 parts of the imidazolinium salt solution, 0.75 part of trimethyldodecylammonium methyl sulfate, 2.5 parts of polyvinylpyrrolidone, 2 parts of 30% hydrogen peroxide solution, 40 parts of styrene and 40 parts of butyl acrylate by emulsion polymerization in the course of four hours at 90° to 95° C. The ratio of the feed rates of the butyl acrylate and the styrene is 4:3.

Dispersion (d) is prepared from 290 parts of water,

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40 parts of the imidazolinium salt solution, 4 parts of dimethyldodecylammonium sulfate, 4 parts of 30% hydrogen peroxide solution, 110 parts of butyl methacrylate and 70 parts of acrylonitrile by emulsion polymerization at 85° C. in the course of 2½ hours.

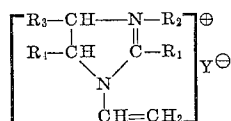
Dispersion (e) is prepared from 187 parts of water, 40 parts of the imidazolinium salt solution, 1.3 parts of dimethyldodecylammonium sulfate, 1.3 parts of polyvinylpyrrolidone, 2.6 parts of 30% hydrogen peroxide solution, 53 parts of ethyl acrylate and 53 parts of tertiary butyl acrylate by emulsion polymerization at 80° C. in the course of three hours.

Dispersion (f) is prepared from 135 parts of water, 40 parts of the imidazolinium salt solution, 2 parts of an emulsifier prepared by reaction of 1 mole equivalent of oleylamine and 4 mole equivalents of ethylene oxide and subsequent quaternization with dimethyl sulfate, 2 parts of 30% hydrogen peroxide solution and a mixture of 20 parts of methyl methacrylate and 60 parts of butyl acrylate by emulsion polymerization at 80° C. in the course of four hours.

We claim:

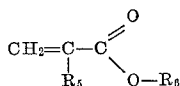
1. A composition for paper sizing comprising an aqueous dispersion of a copolymer of

(a) 4 to 40% by weight of an N-vinylimidazolinium salt of the general formula



where R_1 is a member selected from the class consisting of methyl, ethyl, propyl, isopropyl, benzyl, methylol and phenyl group, R_2 is a member selected from the class consisting of methyl, ethyl, benzyl and hydroxyethyl group, R_3 and R_4 are members selected from the class consisting of hydrogen and methyl and ethyl groups, and Y^- is an anion selected from the groups consisting of chlorine, bromine, methyl sulfate and ethyl sulfate; and

(b) at least 20% by weight of an ester of the general formula



where R_5 is a member selected from the class consisting of hydrogen and an alkyl group containing from 1 to 4 carbon atoms and R_6 is an alkyl group containing from 2 to 8 carbon atoms; and

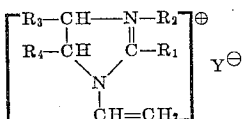
(c) not more than 76% by weight of acrylonitrile; and

(d) not more than 50% by weight of comonomers selected from the class consisting of styrene, low molecular weight vinyl esters of up to 3 carbon atoms, acrylic esters, methacrylic esters, maleic esters, vinyl chloride, vinylidene chloride, acrylic amides, methacrylic amides and N-vinyl lactams with from 5 to 7 ring atoms.

2. A composition as claimed in claim 1 wherein the copolymer contains 7 to 20% by weight of the salt component (a), 40 to 80% by weight of the ester component (b), and 20 to 50% by weight of the acrylonitrile component (c).

3. A method of sizing paper which comprises applying to said paper from an aqueous dispersion of a copolymer of

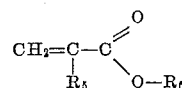
(a) 4 to 40% by weight of an N-vinylimidazolinium salt of the general formula



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where R_1 is a member selected from the class consisting of methyl, ethyl, propyl, isopropyl, benzyl, methylol and phenyl group, R_2 is a member selected from the class consisting of methyl, ethyl, benzyl and hydroxyethyl group, R_3 and R_4 are members selected from the class consisting of hydrogen and methyl and ethyl groups, and Y^- is an anion selected from the group consisting of chlorine, bromine, methyl sulfate and ethyl sulfate; and

(b) at least 20% by weight of an ester of the general formula



where R_5 is a member selected from the class consisting of hydrogen and an alkyl group containing from 1 to 4 carbon atoms and R_6 is an alkyl group containing from 2 to 8 carbon atoms; and

(c) not more than 76% by weight of acrylonitrile; and

(d) not more than 50% by weight of comonomers selected from the class consisting of styrene, low molecular weight vinyl esters of up to 3 carbon atoms, acrylic esters, methacrylic esters, maleic esters, vinyl chloride, vinylidene chloride, acrylic amides, methacrylic amides and N-vinyl lactams with 5 to 7 ring atoms.

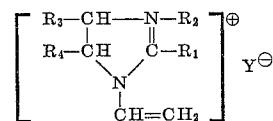
4. A method as claimed in claim 3 wherein said copolymer contains 7 to 20% by weight of the salt component (a), 40 to 80% by weight of the ester component (b), and 20 to 50% by weight of the acrylonitrile component (c).

5. A method as claimed in claim 3 wherein said paper is subjected to stock sizing by application of said aqueous dispersion in which said copolymer has a concentration of about 2 to 20% by weight, said copolymer being applied to said paper in an amount of about 0.5 to 10% by weight, with reference to the weight of the finished paper.

6. A method as claimed in claim 3 wherein said paper is subjected to surface sizing by at least one application of said aqueous dispersion in which said copolymer has a concentration of about 0.5 to 5% by weight, said copolymer being applied to said paper in an amount of about 0.2 to 5% by weight, with reference to the weight of the finished paper.

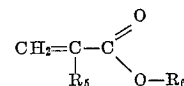
7. A sized paper containing a copolymer of

(a) 4 to 40% by weight of an N-vinylimidazolinium salt of the general formula



where R_1 is a member selected from the class consisting of methyl, ethyl, propyl, isopropyl, benzyl, methylol and phenyl group, R_2 is a member selected from the class consisting of methyl, ethyl, benzyl and hydroxyethyl group, R_3 and R_4 are members selected from the class consisting of hydrogen and methyl and ethyl groups, and Y^- is an anion selected from the group consisting of chlorine, bromine, methyl sulfate and ethyl sulfate

(b) at least 20% by weight of an ester of the general formula



where R_5 is a member selected from the class consisting of hydrogen and alkyl group containing from 1 to 4 carbon atoms and R_6 is an alkyl group containing from 2 to 8 carbon atoms; and

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(c) not more than 76% by weight of acrylonitrile; and

(d) not more than 50% by weight of comonomers selected from the class consisting of styrene, low molecular weight vinyl esters of up to 3 carbon atoms, acrylic esters, methacrylic esters, maleic esters, vinyl chloride, vinylidene chloride, acrylic amides, methacrylic amides and N-vinyl lactams with from 5 to 7 ring atoms.

8. A sized paper as claimed in claim 7 wherein the copolymer contains 7 to 20% by weight of the salt component (a), 40 to 80% by weight of the ester component (b), and 20 to 50% by weight of the acrylonitrile component (c).

9. A stock sized paper as claimed in claim 7 containing 0.5 to 10% by weight of said copolymer, with reference to the weight of the finished paper.

10. A stock sized paper as claimed in claim 7 con-

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taining 0.5 to 3% by weight of said copolymer, with reference to the weight of the finished paper.

11. A surface sized paper as claimed in claim 7 containing 0.2 to 5% by weight of said copolymer, with reference to the weight of said paper.

12. A surface sized paper as claimed in claim 7 containing 0.2 to 1% by weight of said copolymer, with reference to the weight of said paper.

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