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EP-A- 0 085 330	EP-A- 0 122 617
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JP-A- 5 845 730	US-A- 3 046 186
US-A- 3 288 770	US-A- 3 666 512
US-A- 4 040 900	US-A- 4 279 794

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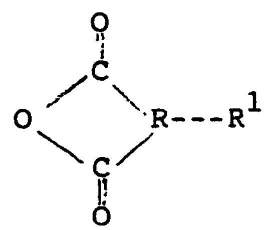
Description

Alkenyl succinic anhydrides (ASA) useful in the sizing of cellulosic materials have gained considerable commercial success. These materials were first fully disclosed in U.S. patent 3,102,064. This patent discloses a certain class of chemical materials generally having the structural formula



wherein R represents a dimethylene or trimethylene radical, and wherein R^1 is a hydrophobic group containing more than 5 carbon atoms which may be selected from the group consisting of alkyl, alkenyl, aralkyl or aralkenyl groups. For effective utilization, the sizing agents must be used in conjunction with a material which is either cationic in nature or is capable of ionizing or disassociating in such a manner to produce one or more cations or other positively charged groups. The cationic agents are disclosed as "alum, aluminum chloride, long chain fatty amines, sodium aluminate, polyacrylamide, chromic sulfate, animal glue, cationic thermosetting resins, and polyamide polymers". Preferred cationic agents are the various cationic starch derivates including primary, secondary, tertiary, or quaternary amine starch derivates and other cationic nitrogen substituted starch derivates, as well as cationic sulfonium and phosphonium starch derivatives. Such derivatives may be prepared from all types of starches including corn, tapioca and potato. A similar paper sizing composition is the subject matter of the EP-A 122 617. This composition contains two different ASA compounds and a dispersing agent which may be selected from the group consisting of cationized starch, gelatine, polyvinyl alcohol, cationic polyacrylamide and polyethyleneimine.

With the growing commercial use of sizes of the type above described, serious problems have remained in the application of the sizes to paper stock or pulp prior to its formation into sheet or other useful forms. Part of the problem has been that the ASA sizing materials are not water soluble, and must, accordingly, be uniformly suspended in the pulp so that the size can make adequate contact with the cellulosic fibers and thus create the desired effect of the final product.

In the EP-A 85 330 sizing agents are disclosed which comprise 1 - 60 parts by weight of a sizing accelerating agent per 10 parts by weight of a hydrophobic sizing such as ketene dimers. Useful accelerators are polymers containing primary, secondary or tertiary amino and/or quaternary ammonium groups directly bonded or present as pendant groups, such as a quaternized terpolymer which contain N,N-dimethylaminoethyl methacrylate, styrene and methyl methacrylate, acrylonitrile or n-butylacrylate units. ASA sizings are not exemplified or tested. Although the molecular weight of these polymers is not specificly investigated it seems that the tested sizing accelerators are high molecular weight water-soluble polymers.

The US patent 36 66 512 discloses an aqueous sizing dispersion consisting of hydrophobic paper-sizing carboxylic acid anhydride particles and a latent catalyst therefor which is a water-soluble salt of a cationic polyamine having a molecular weight of more than 1,000. Thus a distearic acid anhydride sizing is catalyzed with the polyamine salt of cationic starch.

The method of US patent 4 040 900 for sizing paper products utilizes a sizing emulsion consisting of 80-97 parts of substituted cyclic dicarboxylic anhydride such as ASA and 3-20 parts of a polyoxyalkylene alkyl or alkylaryl ether or the corresponding mono or diester. In the paper stock a cationic retention agent can be dispersed.

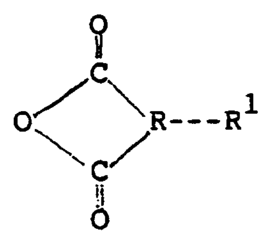
In the JP-A 58-45730 a papermaking sizing agent is disclosed which consists of an aqueous dispersion of substituted succinic anhydrides wherein the aqueous medium also contains an ampholytic acrylamide type polymer. Preferably this ampholytic polymer is an acrylamide type polymer having 3-50 mol% of cationic groups and 5-15 mol% of anionic groups. The cationic groups can be the result of a Mannich reaction. The term "ampholytic" does not include the cationic or cationically modified vinyl addition polymers used in the present invention.

The EPA 141 641 (post-published) discloses aqueous sizing dispersions prepared by dilution of anhydrous concentrates comprising a reactive size such as ketene dimer or alkenyl succinic anhydride and a polyelectrolyte which can be cationic, anionic or non-ionic. Copolymers of acrylamide with quaternized dimethylaminoethyl acrylate or methacrylate can be used as cationic polyelectrolyte. An advantage is that the polyelectrolyte can have a higher molecular weight. Tested compositions contain polyelectrolytes which have a molecular weight in the order above 10^6.

While the cationic agents disclosed in U.S. patent 3,103,061 have met with success, there has been a need within the paper industry to provide a more effective "cationic agent" for ASA sizes. In addition, such cationic agent should preferably aid in the retention of the size on the fiber, and should increase, where desired, the wet and/or dry strength of the final sheet material.

It is an object of this invention to provide an emulsified sizing agent containing an additive which will serve to emulsify or disperse the ASA size in the pulp and allow for retention of the size onto the fiber.

The present invention provides a method for preparing an emulsified sizing agent useful in the preparation of sized paper products, such emulsion containing water, a cyclic dicarboxylic acid anhydride having the following structural formula:

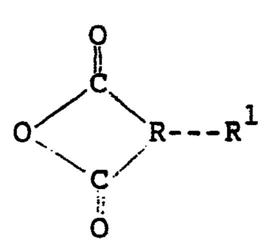


wherein R represents a dimethylene or trimethylene radical, and wherein R^1 is a hydrophobic group containing more than 5 carbon atoms which may be selected from the group consisting of alkyl, alkenyl, aralkyl or aralkenyl groups, and a water soluble cationic vinyl addition polymer, characterized in that the cationic vinyl addition polymer has a molecular weight of between 20.000 and 750.000 and is made of at least 10 weight-% and up to 100 weight-% of the mer content of the polymer from one or more cationic or cationically modified vinyl addition monomers selected from the group consisting of

b) methacrylamidopropyltrimethyl ammonium chloride;
c) dimethylaminoethylmethacrylate;
d) dimethylaminoethylmethacrylate quaternaries;
e) dimethylaminoethylacrylate;
f) dimethylaminoethylacrylate quaternaries;
g) diethylaminoethylacrylate;
h) diethylaminoethylacrylate quaternaries;
i) acrylamide reacted with formaldehyde and a lower secondary amine through the Mannich reaction; and
j) manniched acrylamide quaternaries.

In addition the present invention provides a method for the sizing of paper, wherein such an emulsion of a cyclic dicarboxylic acid anhydride is applied to the paper stock and the cyclic dicarboxylic acid anhydride is emulsified by the water soluble cationic vinyl addition polymer.

Above that the present invention also provides an emulsion of a cyclic dicarboxylic acid anhyride having the following structural formula:



wherein R represents a dimethylene or trimethylene radical, and wherein R^1 is a hydrophobic group containing more than 5 carbon atoms which may be selected from the group consisting of alkyl, alkenyl, aralkyl or aralkenyl groups, the emulsion comprising:

a) 50 to 99.9% by weight water
b) .01 to 40 percent by weight of said cyclic dicarboxylic acid anhydride

c) .001 to 10.0 percent by weight of the water soluble cationic vinyl addition polymer.

The invention provides for utilization of certain specific cationic water soluble vinyl addition polymers having molecular weights of between 50 000 and 150 000 as additives and emulsifying agents for ASA sizes. Such cationic vinyl addition polymers serve as useful emulsifying agents for the ASA size and in addition increase the retention of the size upon the cellulosic sheet.

The ASA sizes to which this invention is applicable include those mentioned in U.S. patents 3,102,061, 4,040,900, 3,968,005, and 3,821,069.

The ASA sizes utilized in this invention are generally described by the structural formula shown above.

In a particular useful embodiment of this invention, a surfactant has also been employed in making the ASA sizes of this invention. This surfactant may be anionic, non-ionic, or cationic in nature. Surfactants employed are generally water soluble and have HLB values ranging from about 8 to about 30 or higher, and preferably from about 8-15. The surfactant is generally used to prepare the ASA size by simply mixing it with the raw ASA material. The ASA size used in this invention accordingly, and in a preferred embodiment of this invention, will generally contain 75-99.5 parts by weight of ASA and preferably 90-99 parts by weight of ASA with 0.5-25 parts, preferably .75-10 parts, and most preferably 1.0-5 parts by weight of surfactant.

The surfactants are preferably added to the ASA prior to emulsification in the aqueous medium. The surfactants can also be added to the aqueous medium prior to the addition of the ASA.

The surfactants useful in this invention are further described in U.S. patent 4,040,900 previously mentioned.

Classes of materials useful as surfactants include; ethoxylated alkyl phenols, such as nonyl phenoxy polyethoxy ethanols and octyl phenoxy polyethoxy ethanols; poly ethyleneglycols such as PEG 400 monooloate, and PEG 600 dilaurate; at well is other materials including certain ethoxylated phosphate esters.

Preferred surfactants for use are free acids of complex organic phosphate esters, commercial availible as GAFAC^{R}RM510 and GAFAC^{R}RE610.

The water soluble polymers

The water soluble polymers used as cationic agents are water soluble vinyl addition homopolymers and copolymers having molecular weights of betweeen 50 000 and 150 000 where at least 10 weight percent and up to 100 weight percent of the mer content of the polymer is a cationic monomer, or cationically modified monomer selected from the indicated group. Preferably at least 15 and up to 95 weight percent of the mer units in the polymer is provided by the cationic or cationically modified monomers. Most preferably from 20-75 percent by weight of the mer units in the polymer or copolymer are cationic or cationically modified. These polymers are not ampholytic.

Polymers which can be employed in the practice of this invention include, but are not limited to the following exemplary copolymers and homopolymers:
acrylamide-dimethylaminoethylactylate,
acrylamide-dimethylaminoethylacrylate quaternaries,
acrylamide-diethylaminoethylacrylate,
acrylamide-diethylaminoethylacrylate quaternaries. acrylamide-dimethylaminoethylmethacrylate,
acrylamide-dimethylaminoethylmethacrylate quaternaries.
acrylamide-diallyldimethyl ammonium chloride,
polydimethylaminoethylmethacrylate and its quaternaries,
polymethacrylamidopropyltrimethyl ammonium chloride and,
acrylamide-methacrylamidopropyltrimethyl ammonium chloride.

Also useful are polymers and copolymers of acrylamide which have been subjected to a "Mannich" reaction with formaldehyde and a lower alkyl secondary amine. These polymers may or may not be quaternized.

As seen, all of the polymers useful in this invention are cationically charged, non-ampholytic and water-soluble.

The polymers employed may be copolymers and even terpolymers of the various vinyl addition monomers. While acrylamide is a preferred nonionic monomer for use in preparing copolymers useful in this invention, other nonionic monomers such as methacrylamide can be employed.

Polymers as used in this invention may be in the form of water-in-oil emulsions (such as those described in U.S. Re. patent 28,474 and 28,576), dry powders, or dilute aqueous solutions. Preferably the polymers form an oil-in-water emulsion of the alkenyl succinic anhydride sizing material.

In order to employ the polymers in the emulsification of ASA sizes, an aqueous solution must first be prepared of the polymer. In the case of the water-in-oil emulsions of vinyl addition polymers, the water soluble surfactants used to invert the water-in-oil emulsions have no detrimental effect on the activity of the polymer used to emulsify the ASA size. When preparing a polymer solution from a water-in-oil emulsion polymer, a useful method or device for forming the solution is exemplified in U.S. patent 4,057,223 which dicloses a mixing block.

Depending upon the molecular weight and cationic charge of the polymer, from 0.01 % to 25 %, and preferably .01-10 % by weight of the final size emulsion to be added to the pulp furnish may be polymer.

The ASA emulsions fed to the pulp slurry accordingly to this invention will generally contain:

50 - 99.9 % by weight water
.01 - 50 % by weight ASA
.001 - 25.0 % by weight (preferably .005 - 3.0 %) of the water soluble polymer

Preferably, these emulsions will contain:

60 - 99.9 % water
.01 - 40 % ASA
.010 - 10 % polymer

Most preferably the ASA emulsion contain .01 - 5.0 and generally .01 - 1.0 parts by weight of the polymer and even more preferable, .05 - .9 parts polymer for each part of ASA in the emulsion.

Most preferably the ASA emulsion contains .01 - 7.5 and generally .01 - 5.0 parts by weight of the polymer.

The polymers may be used to emulsify the ASA, or may be added to previously formed ASA emulsions. In either case, the polymer will increase the performance of the emulsion compared to emulsions not containing the polymer. When the polymer is added to an ASA emulsion that has already been formed, conventional emulsifying agents should be used in addition to the polymer. When added or used during the makeup of the ASA emulsion, no additional emulsifier need be employed.

In order to test the subject invention, the following experiments were conducted. The polymers listed below were obtained commercially or prepared in the form indicated.

EXAMPLE 1

A solution acrylamide copolymer of type MAPTAC, was evaluated as ASA emulsification and retention aid. This novel sizing composition was compared in terms of ASA particle size, physical emulsion stability and sizing performance to conventional ASA emulsions in water or cationic starch. Description of these polymers are given in Table I.

ASA emulsions in water were prepared by combining 95 parts of distilled water and 5 parts of ASA in an Eberbach semi-microemulsion cup. The mixture was dispersed for 3 minutes at high speed. The emulsion formed was diluted with distilled water to 0.50 percent ASA solids basis and used in Example 1. ASA emulsions in cationic starch were prepared by first hydrating 5 parts of a pregelatinized cationic potato starch in 95 parts of water and agitating for 30 minutes. Size emulsions were then prepared by combining 75 parts of the starch solution with 25 parts of ASA in the emulsion cup and dispersing for 20 seconds. This emulsion was diluted to 0.50 percent ASA solids basis and used in Example 2. Lastly, ASA emulsions in vinyl addition polymers were prepared by dispersing ASA in polymer solutions at a ratio of 5:1 dry solids basis. These emulsions were diluted to 0.50 percent ASA solids basis by the method described above. Examples 3-8 illustrate the novel use of these addition polymers.

The ASA emulsions were tested separately in a paper slurry of composition 50 percent recycled corrugated boxboard, 50 percent recycled newsprint. Other slurry parameters were 0.5 percent consistency, 400 Canadian Standard Freeness, pH 7.5, and 25 degrees Celsius to which was added 12.5 parts per million of hydrated aluminum sulfate. Handsheets of basis weight 22.7kg (50 pounds) per 306.9m^2 (3300 square feet) were prepared in accordance with TAPPI T-205 procedures. The sizing compositions listed above were added to the paper slurry shortly before wet-web formation at dosages of 0.10 and 0.15 percent on paper solids. Handsheets were immediately dried on rotary drum to 98 percent solids basis. Results are shown on Table I.

TABLE I

Designation	Polymer Description	Weight Ratio	Molecular Weight[1] calculated from (Intrinsic Viscosity)
D	acrylamide - MAPTAC	75:25	50,000 (0,40)

Example No.	Medium for Size[2] Emulsifications	Ratio of Size to Medium Solids	Average Particle Size of Emulsion (µm)	Physical Emulsion[4] Stability (Form)	Acid Ink Penetration Test (in seconds)[5] Versus Percent by Weight of Size on Pulp Solids 0.100%	0.150%
1	Distilled Water	-	2-10	Nonstable, two sistinct phases	2	15
2	Cationic Potato Starch(STALOK® 500)[3]	5:1	1-2	Nonstable, precipitated settled	157	377
6	Polymer D	5:1	1-2	Stable	71	204

TABLE I

1 Intrinsic Viscosity $(n)_I$ run in 1M $NaNO_3$ at 30°C
Molecular weights (MW) calculated from Mark-Houwink Equation: $(n)_I=(K)(MW)^a$

2 Commercial paper grade alkenyl succinic anhydride

3 Available from A. E. Staley, Decatur, Illinois

4 Physical emulsion form after one week, room temperature aging

5 Hercules' size test apparatus conducted at 80% reflectance with 1% formic acid, 1.25% naphthol green test ink

EXAMPLE 2

Vinyl addition polymers, such as copolymers of acrylamide with DMAEM-MeCl quat or MAPTAC, were further evaluated as ASA emulsification and retention aids. These novel sizing compositions were compared in terms of ASA emulsion particle size, physical emulsion stability with aging, and sizing performance to conventional ASA emulsions in water or cationic starch. A description of these polymers is shown in Table II.

ASA emulsions in water were prepared by combining 95 parts of distilled water and 5 parts of ASA in a laboratory 8 ounce Osterizer cup. The mixture was dispersed at high speed for 3 minutes. The emulsion formed was diluted with distilled water to 0.50 percent ASA solids basis and used in Example 9. ASA emulsions in cationic starch solutions were prepared by first hydrating 5 parts of a pregelatinized cationic potato starch in 95 parts of water and agitating for 30 minutes. Size emulsions were then prepared by combining 95 parts of the starch solution with 5 parts of ASA in the Osterizer cup and dispersing the size for 25 seconds. This emulsion was diluted to 0.50 percent ASA solids basis and used in Example 10. ASA emulsions in vinyl addition polymers were prepared by dispersing ASA in the polymer solutions at a ratio of 1:1 ASA to polymer solids in the Osterizer cup for 5 to 30 seconds.

These emulsions are then diluted to 0.50 percent ASA solids as described above. Examples 11-16 illustrate the novel use of these vinyl addition polymers.

Each ASA emulsion was tested separately in a paper slurry of composition 50 percent bleached softwood kraft and 50 percent bleached hardwood kraft pulps. The other slurry parameters were 0.5 percent consistency, 330 Canadian Standard Freeness, pH 7.3, and 27 degrees Celsius. Handsheets of basis weight 22.7kg (50 pounds) per 306,9m^2 (3300 square feet) were prepared in accordance with TAPPI T-205 procedures. The sizing compositions listed below were added to the paper slurry shortly before wet web formation at the dosage of 0.20 percent ASA solids on paper solids. Handsheets were immediately pressed to approximately 50 percent residual moisture and dried on a rotary drum dryer to 98 percent paper solids basis. Results are shown in the attached Table II.

TABLE II

Designation	Polymer Description	Weight Ratio Acrylamide to Quat	Molecular Weight[1] calculated from (Intrinsic Viscosity)
C	acrylamide - MAPTAC	50:50	140,000
E	acrylamide - DMAEM methyl chloride Quat.	50:50	90,000

Example No.	Medium for ASA[2] Emulsification	Ratio of ASA to Medium Solids	Average Particle Size of ASA (µm)	Physical[4] Emulsion Stability (Form)	Neutral Ink Penetration Test[5] (Seconds) at 0.40% ASA on Pulp Solids
8	Distilled Water	-	1-5	Nonstable, two distinct phases	<1
9	Cationic Potato Starch(STALOK 500)[3]	1:1	1-3	Nonstable, precipitate settled	273
12	Polymer C	1:1	1-2	Stable	246
14	Polymer E	1:1	0.5-2	Stable	17

1 Intrinsic Viscosities $(n)_I$ run in 1M $NaNO_3$ at 30°C
Molecular weights (MW) calculated from Mark-Houwink Equation: $(n)_I=(K)\ (MW)^a$
2 Commercial paper grade alkenyl succinic ahydride
3 Available from A. E. Staley, Decatur, Illinois
4 Physical emulsion form after one week, room temperature aging
5 Hercules' size test apparatus conducted at 80% reflectance with 1 % sodium formate (pH 7.0) and 1.25 % napthol green test ink

EXAMPLE 3

The following comparative examples further illustrate the use of acrylamide copolymers of type DMAEM-MeSQ, DMAEA-MeSQ, DFAEA-MeSQ, and DADMAC of molecular weights greater than 1 000.000 as emulsifiers and retention aids for alkenyl succinic anhydride sizing compositions, and conventional emulsions prepared from cationic starch.

For comparison, ASA emulsions in water were prepared by combining 95 parts of distilled water and 5 part of ASA in an Eberbach semi-microemulsion cup and dispersing the size for 60 seconds. The resulting emulsion was diluted to 0.50 percent ASA solids basis with water and used in Example 17. The ASA emulsions in cationic starch were prepared by first hydrating three parts of a pregelatinized cationic potato starch in 97 parts agitated cold water for 30 minutes. Emulsions were then prepared at two ASA to starch solid ratios of 10:1 and 3:1 by dispersing 30 parts of ASA in 70 parts of 3 percent cationic starch or 9 parts of ASA in 91 parts of 3 percent cationic starch respectively with the aid of the semi-microemulsion cup. The resulting emulsions were diluted to 0.5 percent ASA solids basis with water and used in Examples 17 and 18 accordingly.

Polymer solutions were prepared by hydrating 0.6 parts (as polymer solids) of those copolymers of acrylamide listed below in 99.4 parts of water respectively, allowing sufficient time and mixing for complete hydration. Emulsions were than prepared at two ASA to polymer solids ratios of 10:1 and 3:1 by dispersing 6 parts of ASA in 94 parts of 0.6 percent polymer solids solution or 1.8 parts of ASA in 98.2 parts of 0.6 percent polymer solids solution respectively with the aid of the semi-microemulsion cup.

A further dilution to 0.5 percent ASA solids was then taken. The following examples illustrate the advantages offered by this invention: the ability of these cationic water soluble acrylamide copolymers to initiate an ASA emulsion and to render the ASA emulsion particles cellulose substantive.

Each of the below cited ASA emulsions were separately added to a 0.5 percent consistency pulp slurry of composition 40 percent bleached hardwood sulfate pulp. 40 percent bleached softwood sulfate pulp, and 20 percent calcium carbonate of 300 Canadian Standard Freeness [pH 8.2). Handsheets of basis weight 22.7kg (50 pounds) per 306.9m^2 (3300 square feet) were prepared in accordance with TAPPI T-205 procedures. Emulsions of ASA were added to the pulp slurry shortly before wet-web formation at dosages of 0.250 and 2.00 percent on dry pulp solids. Handsheets were immediately dried on a rotary drum dryer to 98 percent solids basis (2 percent residual moisture). Results are shown in Table III.

This example clearly illustrates the novel use of cationic vinyl addition copolymers as ASA emulsification aids and retention aids. Improved water resistance is realized over conventional ASA in water or cationic starch emulsions. Secondly, the improved water resistance offered by this invention cannot be attributed simply to improved papermachine retention as demonstrated by separate additions of these same cationic polymers to the paper furnish.

The use of polymers in the high molecular weight range, however, can lead to the formation of tacky deposits and unstable emulsions. The use of polymers having molecular weights in the range of from 50,000 - 150,000 led to the elimination of the deposit formation noted above, and increased the stability of the ASA emulsions so prepared.

TABLE III

Designation	Acrylamide Copolymer Quats	Molecular Weight[1] calculated from Intrinsic Viscosity	Form
I	DMAEA, methylchloride quat.	5,700,000	dry powder
J	12 wt.%-DEAEA, monomethyl sulfate salt	9,200,000	dry powder
K	12.5 wt.%-DMAEM, dimethyl sulfate quat.	-	dry powder
L	35 wt.%-DMAEM, monomethyl sulfate quat.	8,900,000	emulsion
M	28.6 wt.%-DADMAC	4,300,000	emulsion

Example No.	Medium for Size[2] Emulsification	Ratio of Size To Medium Solids	Avg. Particle Size of Emulsion (μm)	Neutral Ink Penetration Test[5] (in seconds) vs. Percent By Weight Size on Dry Pulp Solids 0.250%	2.000%
15	Distilled Water	-	2-20	1	423
16	Distilled Water Plus Surfactant[3]	-	1-4	1	255
17	Cationic Potato Starch (STALOK 400)[4]	3:1	1-2	310	-
18	STALOK 400[4]	10:1	1-3	282	-
19	Polymer I	3:1	1-3	656	-
20	Polymer J	3:1	1-3	426	-
21	Polymer K	3:1	1-3	464	-
22	Polymer L	10:1	0.5-4	468	-
23	Polymer M	10:1	0.5-2	313	-

1 Intrinsic Viscosity $(\eta)_I$ run in 1M $NaNO_3$ at 30°C. Molecular weights (MW) calculated from Mark Houwink Equation: $(\eta)_I = (K)(MW)^a$.
2 Commercial paper grade ASA
3 Surfactant type: nonylphenol ethoxylate dosed at 5.0 % by weight of sizing agent
4 Available from A. E. Staley, Decatur, Illinois
5 Hercules' size test apparatus conducted at 80 % reflectance

DMAEA - dimethylaminoethylacrylate
DEAEA - diethylaminoethylacrylate
DMAEM - dimethylaminoethylmethacrylate
DADMAC - diallyldimethylammoniumchloride

EXAMPLE 4

The effect of various other polymers on the emulsification of ASA sizing materials and the results obtained using such polymers were investigated. In this group of experiments, 3 different classes of polymers were employed (see below). All of these materials were prepared as water-in-oil emulsions of the polymer. Aqueous solutions of the polymers were prepared to yield an approximate 2% product basis or approximately .6% by weight aqueous polymer solution. The polymer solution was prepared by mixing together 288 grams of deionized water, 6.0 mls. of a 2% by weight aqueous solution of an ethoxylated (9) nonyl phenol surfactant followed by adding approximately 6 cc of the water-in-oil emulsion to the stirred mixture. The aqueous solutions were then adjusted to yield 2% by weight polymer product.

The ASA chosen for this and all subsequent studies is a substituted (alkenyl) cyclic dicarboxylic acid anhydride wherein the alkenyl groups are derived from a mixture of 14-22 carbon atoms.

The ASA size measure used in these tests was prepared by mixing 196 gms. of the polymer solution with 4.0 gms. of a commercial paper grade alkenyl succinic anhydride size available from Chevron Chemical Company, containing 1.0% by weight of Gafac® RM-510 surfactant available from GAF Corporation. The resultant mixture was then emulsified by mixing for 30 seconds in an Eberbach semi-microemulsion cup followed by a final dilution of 0.5% ASA solids. The ASA emulsions were added to a commercial, calcium carbonate filled bleached Kraft furnish dosed at 0.25 % on dry pulp solids.

The neutral ink penetration test describes the paper's resistance to aqueous fluid penetration and is a measurement of time (in seconds) for ink to penetrate paper to a predetermined degree (80 percent reflectance endpoint). The greater the time, the greater the paper's resistance to ink penetration. Those skilled in the art will readily recognize this test as the generally practiced Hercules'Size Penetration Test. Results are found in Table IV.

Polymer	Mole Ratio
P Acrylamide-MAPTAC	97.5:2.5
Q Acrylamide-MAPTAC	95 :5
R Acrylamide-MAPTAC	85 :15
S Acrylamide-DMAEA-Q	97.5:2.5
T Acrylamide-DMAEA-Q	95 :5
U Acrylamide-DMAEA-Q	85 :15
V Acrylamide-DMAEM-Q	97.5:2.5
W Acrylamide-DMAEM-Q	95 :5
X Acrylamide-DMAEM-Q	85 :15
Y Acrylamide-DMAEM-Q	92.3:7.7

TABLE IV

Example No.	Medium For Size[1] Emulsifications	Ratio of Size to Medium Solids	Average Particle Size of Emulsion (μm)	Acid Ink[2] Penetration Test (in seconds)
24	Distilled Water	-	3 - 15	4
25	Cationic Corn Starch (CATO F)[3]	1 : 2.5	2 - 3	605
26	Polymer P	1 : 0.3	2 - 5	-
27	Polymer Q	1 : 0.3	1 - 3	427
28	Polymer R	1 : 0.3	1 - 3	464
29	Polymer S	1 : 0.3	1 - 3	711
30	Polymer T	1 : 0.3	1 - 3	642
31	Polymer U	1 : 0.3	0.5 - 2	1069
32	Polymer V	1 : 0.3	0.5 - 2	284
33	Polymer W	1 : 0.3	1 - 3	629
34	Polymer X	1 : 0.3	1 - 3	815
35	Polymer Y	1 : 0.3	1 - 3	528

1 Commercial paper grade alkenyl succinic anhydride

2 Hercules' size test apparatus conducted at 80% reflectence using pH 2 acid ink from Monsanto, St. Louis, Missouri

3 Available from National Starch Company, Bridgewater, New Jersey

EXAMPLE 5

The following examples further illustrate the novel use of acrylamide copolymers of type DMAEM-MeSQ as emulsifiers and retention aids for alkenyl succinic anhydride sizing compositions. The ASA emulsions thus formed were compared in terms of particle size and sizing performance with respect to ASA water emulsions and conventional emulsions prepared from cationic starch.

For comparison, ASA emulsions in water were prepared by combining 95 parts of distilled water and 5 parts of ASA in an Eberbach semi-microemulsion cup and dispersing the size for 60 seconds. The resulting emulsion was diluted to 0.50 percent ASA solids basis with water and used for the two sets. The ASA emulsions in cationic starch were prepared by first hydrating three parts of a pregelatinized cationic potato starch in 97 parts agitated cold water for 30 minutes. Emulsions were then prepared at two ASA to starch solid ratios of 10:1 and 1:1 by dispersing 30 parts of ASA in 70 parts of 3 percent cationic starch or 3 parts of ASA in 97 parts of 3 percent cationic starch respectively with the aid of the semi-microemulsion cup. The resulting emulsions were diluted to 0.5 percent ASA solids basis with water and used accordingly.

Polymer solutions were prepared by hydrating 0.6 parts (as polymers) of those copolymers of acrylamide listed below in 99.4 parts of water respectively, allowing sufficient time and mixing for complete hydration. Emulsions of ASA in polymer were then prepared by dispersing 6 parts of ASA in 94 parts of 0.6 percent polymer for 60 seconds with the aid of the semi-microemulsion cup. A further dilution to 0.5 percent ASA solids was then taken. Also this example illustrates the advantages offered by this invention: the ability of these cationic water soluble acrylamide copolymers to initiate and maintain a stable ASA emulsion and to render the ASA emulsion particles cellulose substantive. Polymers tested include the following:

Polymer	Mole Percent (M%) Acrylamide Copolymer Quat
AA	3.5 M% DMAEM[1]-MeSQ
BB	7.7 M% DMAEM-MeSQ
CC	10.9 M% DMAEM-MeSQ

[1] Dimethylaminoethylmethacrylate methylsulfate quat.

Each of the below cited ASA emulsions were separately added to a 0.5 percent consistency pulp slurry of compostion 40 percent bleached hardwood sulfate pulp, 40 percent bleached softwood sulfate pulp, and 20 percent calcium carbonate of 300 Canadian Standard Freeness (pH 8.2). Handsheets of basis weight 22.7kg (50 pounds) per 306.9m^2 (3300 square feet) were prepared in accordance with TAPPI T-205 procedures. Emulsions of ASA were added to the pulp slurry shortly before wet-web formation at dosages ranging from 0.125 to 2.00 percent. Handsheets were immediately dried on a rotary drum dryer to 98 percent solids basis (2 percent residual moisture). In another variation of this procedure, 0.025 percent of a polymer was added to the pulp slurry separately after addition of sizing emulsions. Results are shown in Table V.

This example clearly illustrates the novel use of cationic vinyl addition copolymers as ASA emulsification aids and emulsion retention aids. Improved water resistance is realized over conventional ASA in water or cationic starch emulsions. Secondly, the improved water resistance offered by this invention cannot be attributed simply to improved paper-machine retention as demonstrated by separate additions of these same cationic polymers to the paper furnish.

TABLE V

Example No.	Medium[1] for Size Emulsifications	Ratio of Size of Medium Solids	Average Particle Size of Emulsion (µm)	Separate polymer[2] Addition Percent Solids Basis	Neutral Ink Penetration Test (seconds)[3] Percent by Weight Size on Pulp Solids 0.125	0.250	1.000
36	Distilled Water	-	2-10	None	-	1	11
37	Distilled Water	-	2-10	0.025	-	3	535
38	Cationic Potato Starch (STALOK® 400)[4]	10:1	1-3	None	23	282	-
39	Polymer AA	10:1	1-4	None	20	451	-
40	Polymer BB	10:1	1-4	None	32	471	-
41	Polymer BB	10:1	1-4	0.025	24	510	-
42	Polymer CC	10:1	0.5-4	None	16	468	-

1 Commercial paper grade alkenyl succinic anhydride

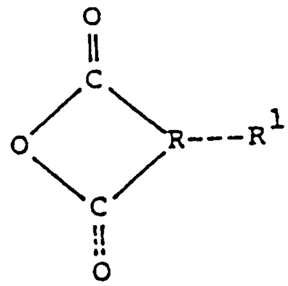
2 A 7.7 mole percent DMAEM-methyl sulfate copolymer with acrylamide

3 Hercules' size test apparatus conducted at 80% reflectance using neutralized 1% formic acid test ink to pH 7.0

4 Available from A. E. Staley Company, DeCatur, Illinois

Claims

1. A method for preparing an emulsified sizing agent useful in the preparation of sized paper products, such emulsion containing water, a cyclic dicarbocylic acid anhydride having the formula:



wherein R represents a dimethylene or trimethylene radical, and wherein R^1 is a hydrophobic group containing more than 5 carbon atoms which may be selected from the group consisting of alkyl, alkenyl, aralkyl or aralkenyl groups, and
a water soluble cationic vinyl addition polymer, **characterized** in that the cationic vinyl addition polymer has a molecular weight of between 50.000 and 150.000 and is made of at least 10 weight-% and up to 100 weight-% of the mer content of the polymer from one or more cationic or cationically modified vinyl addition monomers selected from the group consisting of

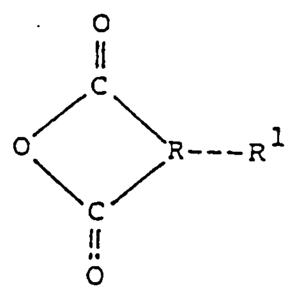
a) methacrylamidopropyltrimethyl ammonium chloride;
b) dimethylaminoethymethacrylate;
c) dimethylaminoethylmethacryate quaternaries;
d) dimethylaminoethylacryate;
e) dimethylaminoethylacrylate quaternaries;
f) diethylaminoethylacrylate quaternaries;
g) diethylaminoethylacrylate quaternaries;
h) acrylamide reacted with formaldehyde and a lower secondary amino through the Mannich reaction; and
i) manniched acrylamide quaternaries.

2. The method according to claim 1, wherein the polymer is present in the alkenyl succinic anhydride size emulsion at a level of from 0,01 - 10,0 percent by weight polymer solids.

3. The method according to claim 2, wherein the polymer is present in the alkenyl succinic anhydride size emulsion at a level of from 0,01 - 5,0 percent by weight polymer solids.

4. The method according to one of claims 1 to 3, wherein the polymer is added to the alkenyl succinic anhydride size emulsion so as to provide from 0,05 - 0,9 part by weight polymer for each part of alkenyl succinic anhydride present in such emulsion.

5. A method for the sizing of paper, wherein an emulsion of a cyclic dicarboxylic acid anhydride having the formula:



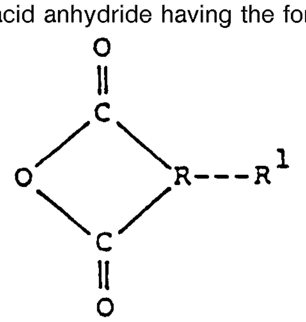
wherein R represents a dimethylene or trimethylene radical and wherein R^1 is a hydrophobic group containing more than 5 carbon atoms which may be selected from the group consisting of alkyl, alkenyl, aralkyl or aralkenyl groups,
is applied to the paper stock, said cyclic dicarboxylic acid anhydride being emulsified by a water soluble cationic vinyl addition polymer, which has a molecular weight of between 50.000 and 150.000 and is made of at least 10 weight-% and up to 100 weight-% of the mer content of the polymer from

one or more cationic or cationcally modified vinyl addition monomers selected from the group consisting of:

a) methacrylaminodpropyltrimethyl ammonium chloride;
b) dimethylaminoethylmethacrylate;
c) dimethylaminoethylmethacrylate quaternaries;
d) dimethylaminoethylacrylate;
e) dimethylaminoethylacrylate quaternaries;
f) diethylaminoethylacrylate;
g) diethylaminoethylacrylate quaternaries;
h) acrylamide reacted with formaldehyde and a lower secondary amine through the Mannich reaction; and
i) manniched acrylamide quaternaries.

6. The method of claim 5, wherein the emulsion containing the water soluble polymer is added to the paper stock.

7. Am emulsion of a cyclic dicarboxylic acid anhydride having the formula:



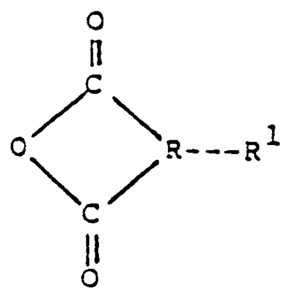
wherein R represents a dimethylene or trimethylene radical and wherein R^1 is a hydrophobic group containing more than 5 carbon atoms which may be selected from the group consisting of alkyl, alkenyl, aralkyl or aralkenyl groups in water, the emulsion comprising:

a) 50 to 99,9 % by weight water
b) 0,01 to 40 % by weight of said cyclic dicarboxylic acid anhydride
c) 0,001 to 10,0 % by weight of a water soluble cationic vinyl addition polymer having a molecular weight of between 50.000 and 150.000 and being made of at least 10 weight-% and up to 100 weight-% of the mer content of the polymer from one or more cationic or cationically modified vinyl addition monomers selected from the group consisting of:

a) methacrylamidopropyltrimethyl ammonium chloride;
b) dimethylaminoethylmethacrylate;
c) dimethylaminoethylmethacrylate quaternaries;
d) dimethylaminoethylacrylate;
e) dimethylaminoethylacrylate quaternaries;
f) diethylaminoethylacrylate;
g) diethylaminoethylacrylate quaternaries;
h) acrylamide reacted with formaldehyde and a lower secondary amine through the Mannich reaction; and
i) manniched acrylamide quaternaries.

Patentansprüche

1. Verfahren zur Herstellung eines emulgierten Leimungsmittels, das zur Erzeugung von geleimten Papierprodukten geeignet ist, wobei die Emulsion Wasser, ein cyclisches Dicarbonsäureanhydrid der Formel



und ein wasserlösliches kationisches Vinyladditionspolymer enthält und in der Formel R einen Dimethylen- oder Trimethylenrest darstellt, und R^1 eine hydrophobe Gruppe ist, die mehr als 5 Kohlenstoffatome enthält, die ausgewählt werden kann aus der Gruppe: Alkyl, Alkenyl, Aralkyl oder Aralkenyl, **dadurch gekennzeichnet,** daß das kationische Vinyladditionspolymer ein Molekulargewicht zwischen 50 000 und 150 000 aufweist und aus mindestens 10 Gew.-% und bis zu 100 Gew.-% des Mergehalts des Polymers hergestellt ist aus einem oder mehreren kationischen oder kationisch modifizierten Vinyladditionsmonomeren, ausgewählt aus der Gruppe:

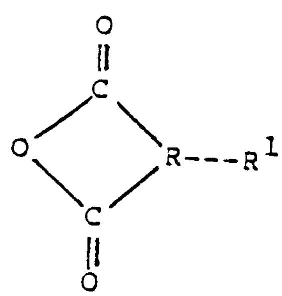
a) Methacrylamidopropyltrimethylammoniumchlorid;
b) Dimethylaminoethylmethacrylat;
c) Dimethylaminoethylmethacrylat-Quaternärprodukte;
d) Dimethylaminoethylacrylat;
e) Dimethylaminoethylacrylat-Quaternärprodukte;
f) Dietyhlaminoethylacrylat;
g) Dietyhlaminoethylacrylat-Quaternärprodukte;
h) mit Formaldehyd und einem niederen sekundären Amin durch Mannichreaktion umgesetztes Acrylamid; und
i) Mannich-Acrylamid-Quaternärprodukte.

2. Verfahren nach Anspruch 1, worin das Polymer in der Alkenylsuccinanhydrid-Leimungsmittelemulsion in einer Konzentration von 0,01 bis 10,0 Gew.-% Polymerfeststoffe enthalten ist.

3. Verfahren nach Anspruch 2, worin das Polymer in der Alkenylsuccinanhydrid-Leimungsmittelemulsion in einer Konzentration von 0,01 bis 5,0 Gew.-% Polymerfeststoffe enthalten ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, worin das Polymer der Alkenylsuccinanhydrid-Leimungsmittelemulsion in der Weise zugesetzt wird, daß 0,05 bis 0,9 Gew.-Teile Polymer je Teil Alkenylsuccinanhydrid in dieser Emulsion vorliegen.

5. Verfahren zum Leimen von Papier, bei dem eine Emulsion eines cyclischen Dicarbonsäureanhydrids der Formel

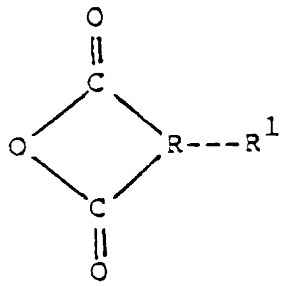


in der R einen Dimethylen- oder Trimethylenrest darstellt und R^1 eine hydrophobe Gruppe ist, die mehr als 5 Kohlenstoffatome enthält, die ausgewählt werden kann aus der Gruppe: Alkyl, Alkenyl, Aralkyl oder Aralkenyl, dem Papieransatz zugegeben wird, wobei dieses cyclische Dicarbonsäureanhydrid durch ein wasserlösliches kationisches Vinyladditionspolymer emulgiert wird, das ein Molekulargewicht zwischen 50 000 und 150 000 aufweist und zu mindestens 10 Gew.-% und bis zu 100 Gew.-% des Mergehalts des Polymers aus einem oder mehreren kationischen oder kationisch modifizierten Vinyladditionsmonomeren aus der Gruppe hergestellt ist:

a) Methacrylamidopropyltrimethylammoniumchlorid;
b) Dimethylaminoethylmethacrylat;
c) Dimethylaminoethylmethacrylat-Quaternärprodukte;
d) Dimethylaminoethylacrylat;
e) Dimethylaminoethylacrylat-Quaternärprodukte;
f) Diethylaminoethylacrylat;
g) Diethylaminoethylacryrlat-Quaternärprodukte;
h) mit Formaldehyd und einem niederen sekundären Amin durch Mannichreaktion umgesetztes Acrylamid; und
i) Mannich-Acrylamid-Quaternärprodukte.

6. Verfahren nach Anspruch 5, wobei die das wasserlösliche Polymer enthaltende Emulsion dem Papieransatz zugegeben wird.

7. Emulsion eines cyclischen Dicarbonsäureanhydrids der Formel



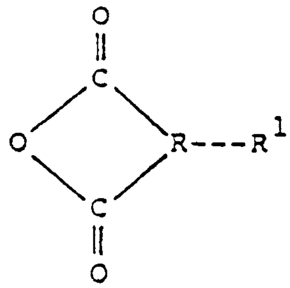
in Wasser,
worin R einen Dimethylen- oder Trimethylenrest darstellt und R^1 eine hydrophobe Gruppe ist, die mehr als 5 Kohlenstoffatome enthält, die ausgewählt werden kann aus der Gruppe: Alkyl, Alkenyl, Aralkyl oder Aralkenyl, wobei die Emulsion enthält

a) 50 bis 99,9 Gew.-% Wasser
b) 0,01 bis 40 Gew.-% dieses cyclischen Dicarbonsäureanhydrids,
c) 0,001 bis 10,0 Gew.-% eines wasserlöslichen kationischen Vinyladditionspolymers mit einem Molekulargewicht zwischen 50 000 und 150 000, das aus mindestens 10 Gew.-% und bis zu 100 Gew.-% des Mergehalts des Polymers aus einem oder mehreren kationischen oder kationisch modifizierten Vinyladditionsmonomeren hergestellt ist, ausgewählt aus der Gruppe:

a) Methacrylamidopropyltrimethylammoniumchlorid;
b) Dimethylaminoethylmethacrylat;
c) Dimethylaminoethylmethacrylat-Quaternärprodukte;
d) Dimethylaminoethylacrylat;
e) Dimethylaminoethylacrylat-Quaternärprodukte;
f) Diethylaminoethylacrylat;
g) Diethylaminoethylacrylat-Quaternärprodukte;
h) mit Formaldehyd und einem niederen sekundären Amin durch Mannichreaktion umgesetztes Acrylamid; und
i) Mannich-Acrylamid-Quaternärprodukte.

Revendications

1. Procédé pour la préparation d'un agent émulsionné d'encollage, utile dans la préparation de produits de papier encollés, une telle émulsion contenant de l'eau, un anhydride d'acide cyclique dicarboxylique répondant à la formule:



dans laquelle R représente un radial diméthylène ou triméthylène et dans laquelle R^1 représente un groupe hydrophobe contenant plus de 5 atomes de carbone et pouvant être choisi parmi le groupe comprenant un groupe alkyle, un groupe alcényle, un groupe aralkyle ou un groupe aralcényle et un polymère d'addition vinylique cationique hydrosoluble, **caractérisé en ce que** le polymère cationique d'addition vinylique a un poids moléculaire allant de 50 000 à 150 000 et est constitué d'au moins 10 % en poids et jusqu'à 100 % en poids, de la teneur monomère du polymère obtenu à partir d'un ou de plusieurs monomères d'addition vinylique cationiques ou à modification cationique, choisis parmi le groupe comprenant

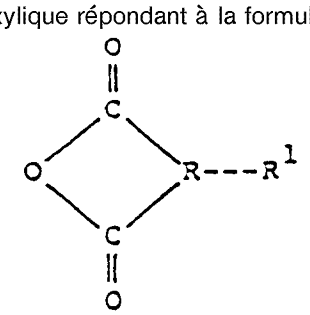
a) le chlorure de méthacrylamidopropyltriméthylammonium;
b) le diméthylaminoéthylméthacrylate;
c) les dérivés quaternaires du diméthylaminoéthylméthacrylate;
d) le diméthylaminoéthylacrylate;
e) les dérivés quaternaires du diméthylaminoéthylméthacrylate;
f) le diéthylamincéthylacrylate;
g) les dérivés quaternaires du diéthylaminoéthylméthacrylate;
h) l'acrylamide que l'on a fait réagir avec du formaldéhyde et une amine secondaire inférieure, par le biais de la réaction de Mannich; et
i) des dérivés quaternaires d'acrylamide que l'on a soumis à la réaction de Mannich.

2. Procédé selon la revendication 1, dans lequel le polymère est présent dans l'émulsion d'encollage à l'anhydride alcénylsuccinique, en une quantité allant de 0,01 à 10,0 pour cent en poids de produits solides polymères.

3. Procédé selon la revendication 2, dans lequel le polymère est présent dans l'émulsion d'encollage à l'anhydride alcénylsuccinique, en une quantité allant de 0,01 à 5,0 pour cent en poids de produits solides polymères.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel on ajoute le polymère à l'émulsion d'encollage à l'anhydride alcénylsuccinique, de façon à obtenir de 0,05 à 0,9 partie en poids de polymère pour chaque partie d'anhydride alcénylsuccinique présent dans une telle émulsion.

5. Procédé pour l'encollage de papier, dans lequel on applique à la pâte de papier une émulsion d'anhydride d'acide cyclique dicarboxylique répondant à la formule

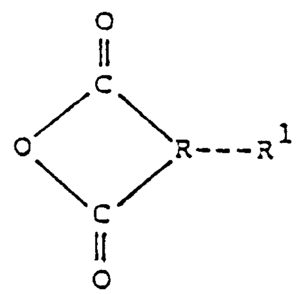


dans laquelle R représente un radial diméthylène ou triméthylène et dans laquelle R^1 représente un groupe hydrophobe contenant plus de 5 atomes de carbone et pouvant être choisi parmi le groupe comprenant un groupe alkyle, un groupe alcényle, un groupe aralkyle ou un groupe aralcényle, l'anhydride d'acide cyclique dicarboxylique étant émulsionné par un polymère d'addition vinylique cationique hydrosoluble, dont le poids moléculaire va de 50 000 à 150 000 et qui est constitué d'au moins 10 % en poids et jusqu'à 100 % en poids de la teneur monomère du polymère obtenu à partir d'un ou de plusieurs monomères d'addition vinylique cationiques ou à modification cationique, choisis parmi le groupe comprenant

a) le chlorure de méthacrylamidopropyltriméthylammonium;
b) le diméthylaminoéthylméthacrylate;
c) les dérivés quaternaires du diméthylaminoéthylméthacrylate;
d) le diméthylaminoéthylacrylate;
e) les dérivés quaternaires du diméthylaminoéthylméthacrylate;
f) le diéthylaminoéthylacrylate;
g) les dérivés quaternaires du diéthylaminoéthylméthacrylate;
h) l'acrylamide que l'on a fait réagir avec du formaldéhyde et une amine secondaire inférieure, par le biais de la réaction de Mannich; et
i) des dérivés quaternaires d'acrylamide que l'on a soumis à la réaction de Mannich.

6. Procédé selon la revendication 5, dans lequel, à la pâte de papier, on ajoute l'émulsion contenant le polymère hydrosoluble.

7. Emulsion d'un anhydride d'acide cyclique dicarboxylique répondant à la formule



dans R représente un radial diméthylène ou triméthylène et dans laquelle R^1 représente un groupe hydrophobe contenant plus de 5 atomes de carbone et pouvant être choisi parmi le groupe comprenant un groupe alkyle, un groupe alcényle, un groupe aralkyle ou un groupe aralcényle, dans de l'eau, l'émulsion comprenant:

a) de 50 à 99,9 % en poids d'eau;
b) de 0,01 à 40 % en poids de l'anhydride de l'acide cyclique dicarboxylique;
c) de 0,001 à 10,0 % en poids d'un polymère d'addition

vinylique cationique hydrosoluble, ayant un poids moléculaire allant de 50 000 à 150 000 et étant constitué d'au moins 10 % en poids et jusqu'à 100 % en poids, de la teneur monomère du polymère obtenu à partir d'un ou de plusieurs monomères d'addition vinylique cationiques ou à modification cationique, choisis parmi le groupe comprenant

a) le chlorure de méthacrylamidopropyltriméthylammonium;
b) le diméthylaminoéthylméthacrylate;
c) les dérivés quaternaires du diméthylaminoéthylméthacrylate;
d) le diméthylaminoéthylacrylate;
e) les dérivés quaternaires du diméthylaminoéthylméthacrylate;
f) le diéthylaminoéthylacrylate;
g) les dérivés quaternaires du diéthylaminoéthylméthacrylate;
h) l'acrylamide que l'on a fait réagir avec du formaldéhyde et une amine secondaire inférieure, par le biais de la réaction de Mannich; et
i) des dérivés quaternaires d'acrylamide que l'on a soumis à la réaction de Mannich.