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(54) A method of controlling microbiological deposits on paper making equipment and paper obtained thereby.

(57) The invention relates to a method of controlling productivity disturbing microbiological deposits, e.g. slime, on paper making equipment, which method is characterized by applying to any locus or surface of said equipment a deposition-controlling amount, preferably at least about 0.1 parts per million of dilution water, of a cationic polymer or a cationic surfactant or a mixture thereof.

Said application is preferably performed by spraying an aqueous solution of said polymer or surfactant directly onto the equipment to be cleaned.

The invention also relates to the improved paper prepared by such a method.

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Description

A METHOD OF CONTROLLING MICROBIOLOGICAL DEPOSITS ON PAPER MAKING EQUIPMENT AND PAPER OBTAINED THEREBY.

Technical field of the invention

The present invention relates to an improved method of providing a clean sheet forming equipment and the like for paper production and, more particularly, to chemical treatment of paper making equipment to control productivity disturbing, microbiologically originated deposits thereupon. The invention also relates to the paper produced by said improved method.

Background of the invention

The manufacture of paper typically involves the processing of a carefully prepared aqueous fiber suspension to produce a highly uniform dry paper sheet. Three steps included in the typical process are sheet forming, where the suspension is directed over a porous mesh or "wire" upon which fibers are deposited while liquid filters through the wire; sheet pressing, where the formed sheet is passed through presses covered with porous "felt" to extract retained water from the sheet, to improve the sheet's uniformity, and to impart surface quality to the sheet; and paper drying, where residual water is evaporated from the sheet. The sheet may then be further processed into the finished paper product.

It is well known that evaporation of water is energy intensive and thus relatively expensive. Consequently, efficient paper making is dependent upon extracting water during the forming and pressing operations, and avoiding sheet defects which render the dried sheet unfit for use. Felts and wires are thus particularly important because they affect not only water removal but, because of their intimate contact with the sheet, the quality of the sheet itself. Deposits allowed to collect on the wire can affect its water removal efficiency and can be transferred to the sheet material to create defects.

The quality of the aqueous fiber suspension used to produce the sheet is dependent upon many factors, including the wood and water used as raw materials, the composition of any recycled material added to the process, and the additives used during preparation of the suspension. Thus a variety of dissolved or suspended materials can be introduced into the manufacturing process, including both inorganic materials such as salts and clays, and materials which are organic in nature such as resins or "pitch" from the wood, as well as inks, latex, and adhesives from recycled paper products. A build up of deposits contaning inorganic and/or organic materials on felts and other sheet forming equipment during the manufacturing process is recognized as a troublesome obstacle to efficient paper making.

Another particularly troublesome deposit is the slimy gelatinous material produced by certain bacteria that naturally occur in the paper making system. (This material is hereafter referred to as "slime"). Since the conditions in a paper machine system normally are very favourable for the growth and reproduction of bacteria the problems with slime deposit build-ups on paper machine parts often become severe and will, if not inhibited, lead to significant productivity disturbances in the paper making process.

A typical problem caused by slime deposits occurs when big lumps of built-up slime fall down from the position where they were formed onto the paper sheet, thus causing a sheet defect and/or break.

Methods of quickly and effectively removing slime deposits from the paper mill equipment are of great importance to the industry. The paper machines could be shut down for cleaning, but ceasing operation for cleaning is undesirable because of the consequential loss of productivity. On-line treatment is thus greatly preferred where it can be effectively practised.

The most commonly and successfully used way of removing slime from paper machine equipment has been to treat the aqueous fiber suspension with various types of biocides. Examples of such biocides are methylene-bis-thiocyanate, 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

Chemicals of this type are, however, often very unpleasant to handle and are from an environmental and health and safety point of view often regarded as objectionable. For these reasons there is a strong driving force within the industry to, wherever it is possible, avoid the use of biocides in the paper making process.

Another approach to slime control has been to combine the biocide treatment of the fiber suspension with addition of anionic dispersants. The success of this approach has, however, been very limited, especially in paper systems working with a high degree of white water closure.

Yet another approach to slime control has been to treat the fiber suspension with enzymes. The commercial success of this method has, however, also been very limited.

With this in mind it is easy to realize that a method which would enable effective control of slime deposits on paper machines, without the disadvantages connected with biocides, would be a significant step ahead in the progress of a more environmentally acceptable paper making process.

It has now unexpectedly been found that productivity problems caused by the deposition of organic matter derived from microbiological activities can be effectively controlled without any use of toxic biocides or while using reduced amounts of such biocides, viz. by the use of certain polymers or surfactants and without incorporating the substances into the paper pulp. The polymers or surfactants referred to are previously known per se, but as far as we know they have never been used or suggested for use in the way claimed by the present invention. In this respect and with respect to the prior art mentioned above reference is made to the following prior art: CA 365 778, EP 82400266.1, US 3 582 461 and US 4 190 491 which all relate to pitch control in connection with paper making; US 1 486 396 and US 4 140 798 which both relate to chemical substances which are known per se to inhibit the growth of microorganisms; and GB 2 186 895 which discloses a group of chemicals which are useful in accordance with the present invention but which are not suggested for such a use therein.

General summary of the invention

Thus, in accordance with the present invention it has unexpectedly been found that certain cationic polymers or cationic surfactants or mixtures thereof can be effectively used, without any noxius biocides or in combination with such biocides in greatly reduced amounts, to control the deposition in connection with paper making of productivity disturbing microbiological deposits, said cationic polymers or surfactants being utilized in a novel way.

Therefore, one object of the invention is to provide an improved paper making method where the deposition of organic matter of the above-mentioned type is controlled, i.e. prevented or inhibited completely or at least to a very great extent if not already having been formed, or reduced or dispersed completely or to a great extent if already having been formed. The invention is especially interesting in connection with the control of slime caused by slime forming microorganisms.

Another object of the invention is to provide a new method, by which the use of toxic biocides is eliminated or greatly reduced, i.e. to provide a paper mill deposit control method which is environmentally acceptable.

Still another object of the invention is to provide a new method, by which the incorporation of chemicals into the paper pulp is avoided or reduced.

A further object of the invention is the provision of a method, by which considerably reduced concentrations of chemicals are utilized to control the deposit problems referred to above.

A still further object of the invention is the provision of a method, by which the productivity and product quality in paper making is increased.

A still further object of the invention is the provision of a high quality paper whenever manufactured by the method claimed.

These and other objects and advantages of the present invention will become apparent from the following more detailed description of the invention.

Detailed description of the invention

In accordance with the invention the above-mentioned objects and other objects are accomplished by the provision of a method of controlling productivity disturbing microbiological deposits on paper making equipment, said method being characterized by applying to any locus or surface of said paper making equipment which locus or surface is sensitive to build-ups of such microbiological deposits, a deposition-controlling amount of a deposition-controlling substance selected from the group consisting of cationic polymers and cationic surfactants, which includes mixtures thereof.

As was mentioned above the term "control" should be given a broad sense in the meaning of the invention. That is, according to the invention it has unexpectedly been found that the application of the cationic polymer or surfactant or mixture thereof can be utilized to prevent or inhibit the formation of deposits as well as to dissolve or disperse deposits which have already been formed.

With reference to the meaning of the expression "any locus or surface of the paper making equipment which is sensitive to build-ups of such deposits" or similar, it should be noted that the general meaning thereof is that the cationic polymer or surfactant is not incorporated into the pulp or paper but is applied onto any strategical part or position of the paper making equipment. Thus, by experience a person skilled in the art knows what locus or surface shows the greatest tendency of forming deposits, i.e. where the cationic polymer or surfactant should primarily be applied to obtain the best results. Of course this also means that the polymer or surfactant can be applied onto more than one such locus or surface if necessary or advisable.

The invention is generally applicable to any water soluble cationic polymer or surfactant of the type referred to, which primarily means that an aqueous solution of said polymer or surfactant is utilized. This in turn means that an especially preferable method of applying the cationic polymer or surfactant onto said locus or surface is by means of a spraying operation, as this is generally a simple operation and as such an operation has been shown to be very effective in connection with the invention. That is, it has unexpectedly been shown that very low concentrations of the polymer can be utilized in this way for outstanding results.

The method claimed is generally applicable to the control of any deposits caused by microorganisms, but it has been found to be especially interesting to control deposits caused by bacteria, e.g. slime caused by slime-forming bacteria.

As the major characteristic feature of the invention is the application of the cationic polymer or surfactant directly onto the locus or surface to be treated, said polymer or surfactant being utilized in unexpectedly low concentrations, the precise nature of the polymer or surfactant to be used is not the main characteristic of the invention, provided it is of the cationic type. Thus, a considerable variety of different polymers and surfactants may be used within the scope of the invention, i.e. also based on previously known microbiocidal activities. However, a number of especially preferable polymers and surfactants will be disclosed below. Typically a water soluble polymer or surfactant is used.

Thus, according to one preferable enbodiment of the invention a cationic polymer is utilized which has a molecular weight within the range of 1,000 - 5,000 000, e.g. between about 10,000 and about 300,000. A preferable embodiment within said ranges is from about 20,000 to 300,000, especially from about 20,000 to 50,000. Another preferable range is from about 10,000 to 50,000.

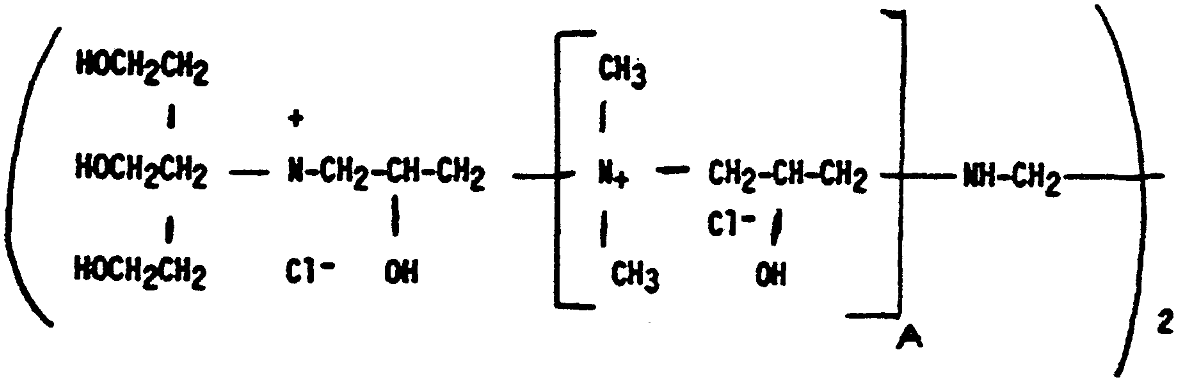
As to the cationic surfactant a preferable range of the molecular weight thereof is between about 200 and about 600.

According to another preferable embodiment of the invention an aqueous solution of the polymer or surfactant is used which is substantially free from anionic macromolecules.

The charge density of the compounds embodied by the invention should be in a range of between about 0.5 milliequivalents/gram and 20 milliequivalents/gram. A preferable embodiment within said range is about 1-10 milliequivalents/gram, especially about 2-8 milliequivalents/gram.

One preferred group of cationic polymers according to the invention comprises dicyandiamide-formaldehyde condensation polymers. Polymers of this type are disclosed in many patients. US 2,774,74, US 2,829,126, GB 1,193,29, DE 917,392, FR 1,484,381, DE 2,017,114, JP 75,111,864, JP 73,16,067, DE OS 2,515,175, CH Application 9,527/72, DE OS 2,451,698, DE 1,128,276, DE OS 2,403,443, FR 1,414,407 and DE 2,321,627 represent some examples thereof.

Another preferable group of cationic polymers to be used in accordance with the invention is those polymers which are formed by reaction between epihalohydrins and various amines. The most preferred epihalohydrin in this respect is epichlorohydrin, and as examples of suitable amines reference can be made to dimethylamine, diethylamine, methylethylamine, ethylene diamine, triethanol amine and a polyalkylene polyamine. Examples thereof include those polymers which are obtained by reaction between a polyalkylene polyamine and epichlorohydrin, as well as those polymers which are obtained by reaction between epichlorohydrin, dimethylamine and either ethylene diamine or a polyalkylene polyamine. A typical amine which can be utilized is N,N,N′,N′-tetra-methylethylene diamine as well as ethylene diamine used together with dimethylamine and triethanolamine. Polymers of this type include those polymers which have the following general formula:



$$\left(\begin{matrix} HOCH_2CH_2 \\ | \\ HOCH_2CH_2 \\ | \\ HOCH_2CH_2 \end{matrix} - \overset{+}{\underset{Cl^-}{N}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2 - \left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N_+}} - CH_2-\underset{OH}{\underset{Cl^-\,/}{CH}}-CH_2 \right]_A - NH-CH_2 - \right)_2$$

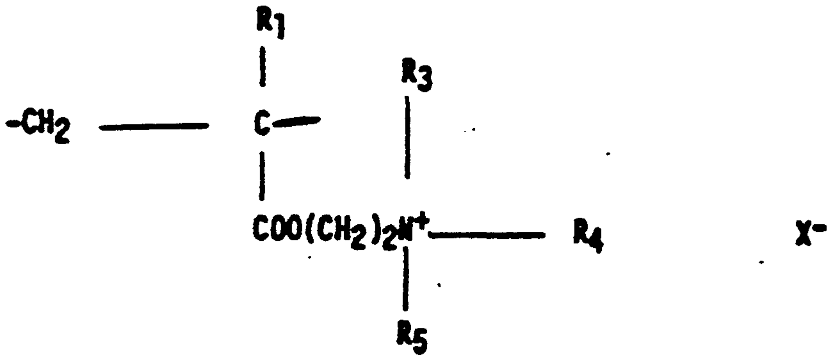
where A is a number within the range of 0-500.

Preferred cationic polymers of this invention also include those made by reacting dimethylamine, diethylamine or methylethylamine, preferably either dimethylamine or diethylamine, with an epihalohydrin, preferably epichlorohydrin. Polymers of this type are disclosed in U.S. Patent No 3 738 945 and Canadian Patent No 1 096 070, the disclosures of which are both hereby incorporated by reference. Such polymers are commercially available as Agefloc A-50, Agefloc A-50HV and Agefloc B-50 from CPS Chemical Company, Inc., of New Jersey, USA. These three products are reported to contain as their active ingredients about 50 percent by weight of polymers having molecular weights of about 75,000 to 80,000, about 200,000 to 250,000 and about 20,000 to 30,000, respectively. Another commercially available product of this type is Magnifloc 573C, which is marketed by American Cyanamide Company of New Jersey, USA, and is believed to contain as its active ingredient about 50 percent by weight of a polymer having a molecular weight of about 20,000 to 30,000.

Another preferable group of cationic polymers for use in accordance with the invention comprises polymers derived from ethylenically unsaturated monomers containing a quaternary ammonium group. Such polymers may comprise homo- and copolymers of vinyl compounds, such as vinyl pyridine and vinyl imidazole, which may be quaternized with, say, a C_1-C_{18}-alkyl halide, a benzyl halide, especially a chloride, or dimethyl or diethyl sulphate, or vinyl benzyl chloride, which may be quaternized with for instance a tertiary amine of formula $NR_1R_2R_3$, wherein R_1, R_2 and R_3 are each and independently lower alkyl, preferable with 1-4 carbon atoms, with the proviso that one of said groups R_1, R_2 and R_3 may be C_1-C_{18}-alkyl; allyl compounds such as diallyldimethyl ammonium chloride; or acrylic derivatives such as dialkyl aminomethyl(meth)acrylamide, which may be quaternized with for instance a C_1-C_{18}-alkyl halide, a benzyl halide or dimethyl or diethyl sulphate, a methacrylamido propyl-tri(C_1-C_4-alkyl, especially methyl) ammonium salt, or a (meth)acryloyloxyethyltri(C_1-C_4-alkyl, especially methyl) ammonium salt, said salt being a halide, especially a chloride, methosulphate, ethosulphate, or 1/n of an n-valent anion.

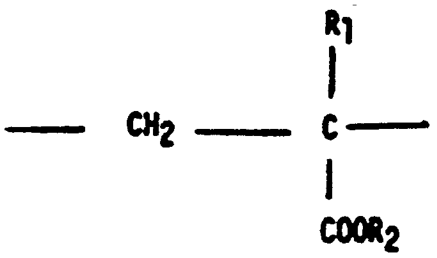
In this context it should also be added that throughout the description and claims the term "lower alkyl" means an alkyl group containing 1-6 carbon atoms, unless otherwise stated.

In the case of copolymers as referred to above the monomers can be copolymerized for instance with a (meth)acrylic derivative such as an acrylamide, an acrylate- or methacrylate-C_1-C_{18}-alkyl ester or acrylonitrile, or an alkyl vinyl ether, vinyl pyrrolidone, or vinyl acetate. Typical such polymers contain 10 to 100 mole percent of recurring units of the formula:



$$-CH_2-C(R_1)(COO(CH_2)_2N^+R_3R_4R_5)- \quad X^-$$

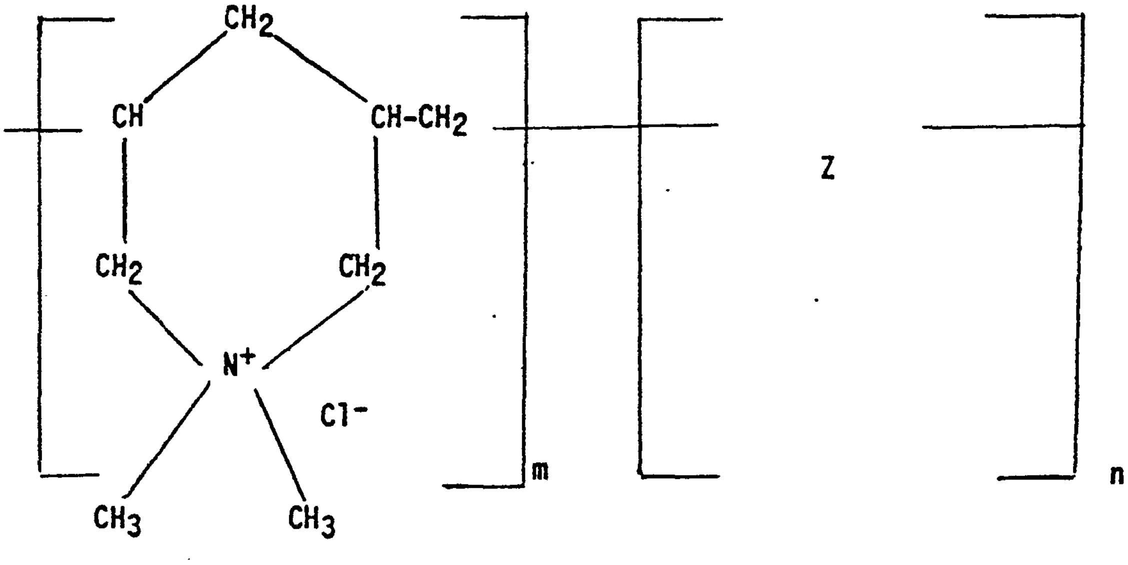
and 0-90 mole percent of recurring units of the formula:



$$-CH_2-C(R_1)(COOR_2)-$$

wherein R_1 represents hydrogen or lower alkyl, preferably alkyl with 1-4 carbon atoms, R_2 represents a long chain alkyl group, typically of from 8 to 18 carbon atoms, R_3, R_4 and R_5 each and independently represents hydrogen or lower alkyl, while X represents an anion, typically a halide ion, a methosulphate ion, an ethosulphate ion, or 1/n of an n-valent anion.

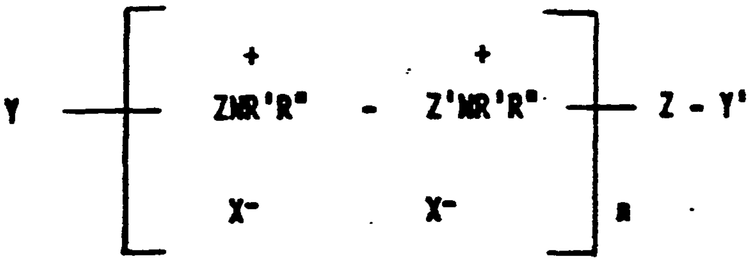
Other quaternary ammonium polymers derived from an unsaturated monomer include homo and copolymers of diallyldimethyl ammoniumchloride which contain recurring or repeating units of the formula:



where Z represents monomeric units, like for instance a (meth)acrylic derivatives such as an acrylamide, an acrylate- or methacrylate -$C_{1\text{-}c18}$-alkylester or acrylonitrile, or an alkyl vinyl ether, vinylpyrrolidone or vinyl acetate, m is within the range of 5-100% and n is within the range of 0-95%.

In this respect, it should be noted that this polymer should be regarded as "substantially linear" since although it contains cyclic groupings, these groupings are connected along a linear chain and there is no cross-linking.

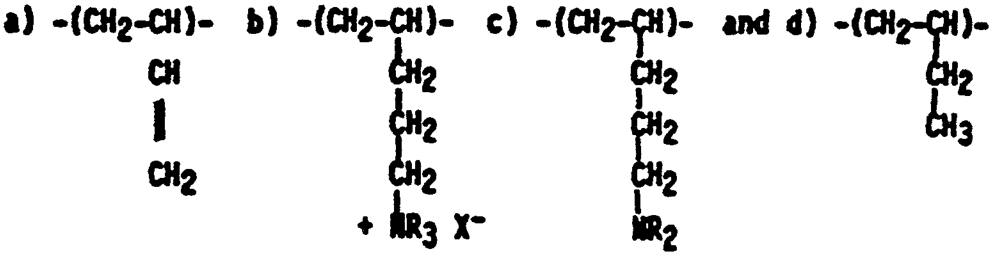
Other polymers which can be used and which are derived from unsaturated monomers include those having the formula:



$$Y-\left[\overset{+}{Z}NR'R''\ -\ Z'\overset{+}{N}R'R''\right]_n-Z-Y' \quad (X^-,\ X^-)$$

where Z and Z′, which may be the same or different, are $-CH_2CH=CHCH_2-$ or $CH_2-CHOHCH_2-$, Y and Y′, which may be the same or different, are either X or $-NR'R''$, X is a halogen of atomic weight greater than 30, n is an integer of from 2 to 20, and R′ and R″ (i) may be the same or different alkyl groups of from 1 to 18 carbon atoms, optionally substituted by 1 to 2 hydroxyl groups; or (ii) when taken together with N represent a saturated or unsaturated ring of from 5 to 7 atoms; or (iii) when taken together with N and an oxygen atom represent the N-morpholino group; especially poly(dimethylbutenyl)ammonium chloride-bis-(triethanol ammonium chloride).

Another class of polymer which can be used and which is derived from ethylenically unsaturated monomers include polybutadienes which have been reacted with a lower alkyl amine and some of the resulting dialkyl amino groups are quaternized. In general, therefore, the polymer will possess recurring units of the formula:

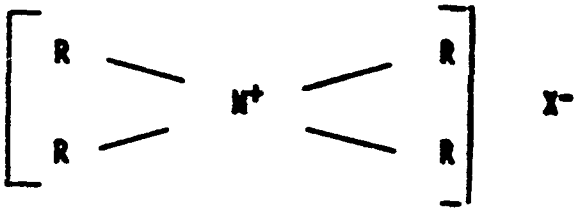


$$\text{a) } -(CH_2-CH(CH{=}CH_2))- \quad \text{b) } -(CH_2-CH(CH_2CH_2CH_2\overset{+}{N}R_3\,X^-))- \quad \text{c) } -(CH_2-CH(CH_2CH_2CH_2NR_2))- \quad \text{and d) } -(CH_2-CH(CH_2CH_3))-$$

in the molar proportions a:b:c:d, respectively, where R represents a lower alkyl radical, typically a methyl or ethyl radical. It should be understood that the lower alkyl radicals need not all be the same. Typical quaternizing agents include methyl chloride, dimethyl sulphate, and diethyl sulphate. Varying ratios of a:b:c:d may be used with the amine amounts (b+c) being generally from 10 to 90 % with (a+d) being from 90 to 10%. These polymers can be obtained by reacting polybutadiene with carbon monoxide and hydrogen in the presence of an appropriate lower alkyl amine.

Other cationic polymers which are capable of interacting with anionic macromolecules and/or slimy material in paper making pulp may also be used within the scope of this invention. These may include cationic tannin derivatives, such as those obtained by a Mannich-type reaction of tannin (a condensed polyphenolic body) with formaldehyde and an amine, formed as a salt, e.g. acetate, formate, hydrochloride, or quaternized, as well as polyamine poly mers whioh have been cross-linked, such as polyamideamine/polyethylene polyamine copolymers cross-linked with, say, epichlorohydrin. Yet another suitable type of polymer is that formed by reacting a polyamido amine with epihalohydrine. Such crosslinked polyamidoamines are described in US patents 3,250,664, 3,893,885, 3,642,572 and 4,250,299, which are hereby incorporated by reference.

According to a preferable embodient of the invention the cationic surfactant is of the general formula



wherein each R is independently selected from the group consisting of hydrogen, alkyl groups having between about 1 and 22 carbon atoms, aryl groups, and aralkyl groups, at least one of said R groups being an alkyl group having at least about 8 carbon atoms and preferably an n-alkyl group having between about 12 and 16 carbon atoms; and wherein X^- is an anion, preferably a halide ion, e.g. chloride, or 1/n of an n-valent anion. Mixtures of these compounds can also be used as the surfactant of this invention.

Preferably two of the R groups of the surfactant are selected from the group consisting of methyl and ethyl, most preferably methyl. Preferably also one R group is selected from the aralkyl groups $Ph-CH_2-$ and $Ph-CH_2-CH_2-$, where Ph is phenyl. The most preferable aralkyl group is benzyl.

Thus, particularly useful surfactants include alkyl dimethyl benzyl ammonium chlorides having alkyl groups of between about 12 and 16 carbon atoms. One commercially available product of this type includes a mixture of alkyl dimethyl benzyl ammonium chlorides wherein about 50% of the surfactant has a $C_{14}H_{29}$ n-alkyl group, about 40% of the surfactant has a $C_{12}H_{25}$ n-alkyl group, and about 10% of the surfactant has a $C_{16}H_{33}$ n-alkyl group. This product is known per se for its microbiocidal effectiveness.

As was mentioned above it has been found that when the cationic polymers and/or cationic surfactants of this invention are applied directly, preferably by spraying, onto paper machine parts at low concentrations slime and other microbiological deposits on said parts or equipment are significantly reduced or eliminated. More specifically, it has been found that generally such a low concentration of the polymer or surfactant as from about 0.1 parts per million of dilution water will give a deposit-reducing effect. Preferably said amount is from about 5 parts per million of dilution water where continuous treatment is used, while preferably from about 50 parts per million of dilution water is utilized during the application period where the application is intermittent. As to the upper limit this can easily be determined by a person skilled in the art in each specific case, but in general said amount or concentration is kept at as low level as possible to avoid an unnecessary contamination of the paper therewith. A preferable upper limit is 500 parts per million of dilution water.

While the mechanism of the phenomenon obtained by this invention is not completely understood, it is believed that the cationic components of this invention disperse the slime at an embryonic stage thus preventing build-up of big lumps. The recharged cationic dispersed slime can then easily be removed from the system together with the paper sheet. In any case the tendency of slime to pass by paper making equipment rather than adhering to the same is greatly increased by the treatment in accordance with this invention.

As was mentioned above the polymer or surfactant of this invention is applied, such as by spraying, in aqueous solution directly onto the equipment being treated.

As has also been mentioned the aqueous solution containing the cationic polymer and/or surfactant should be substantially free from anionic macromolecules. These anionic materials include natural materials such as wood lignins, by products of chemical pulping such as sodium lignosulfonates, and synthetic materials such as polyacrylates.

The polymers and surfactants of this invention are typically supplied as liquid compositions comprising aqueous solutions of the polymer and/or surfactant. Polymer concentrations of the compositions may range from such relatively dilute solutions having polymer concentrations suitable for continuous application up to the solubility or gelling limits of the polymer, but generally the compositions are relatively concentrated for practical shipping and handling purposes. Moreover, the liquid compositions may comprise additional materials which enhance the dissolution of the polymers so as to allow more concentrated compositions to be obtained. As an example of such materials reference can be made to alkoxyethanols such as butoxyethanol. Suitable aqueous compositions will generally contain between 5 and 50 percent by weight of the cationic products of this invention. It should also be understood that, if desired, the compounds embodied by this invention can be added in solid form, e.g. as granulates.

The most appropriate treatment dosage depends on such system factors as the soiling level of the adhesive material, and whether cleaning is continuous or periodic. Even liquid compositions comprising relatively high concentrations of a polymer of the invention (for example 50%) may be employed at full strength (100% as the liquid composition) for example by spraying the undiluted liquid composition directly onto the machine parts. However, particularly where continuous treatment is practiced, the compositions may be advantageously diluted at the treatment location with clean fresh water or other aqueous liquid. Where necessary for water economy, process water may be adequate for dilution.

Generally the method claimed can be performed continuously in order to continuously control the deposits referred to. In some cases, however, continuous treatment is not practical and then the treatment with the cationic polymers and surfactants of this invention may be periodic. For example, aqueous solutions of the polymer or surfactant may be sprayed on the deposited surface until said surface is satisfactorily cleaned, and the spraying may then be discontinued until further treatment becomes necessary.

The invention will now be further described by means of the following non-limiting example.

Example

A commercial paper machine of twin wire type produces newsprint paper. In order to inhibit microbiological growth and the corresponding occurrence of slimy deposits biocides are added to the white water circulation system of this machine.

The addition points of the biocides have been fixed to the wire chest and to the shower water tank. Further, a cationic polymer of dicyandiamide-formaldehyde type is used as deposit control aid and as such added to the fiber suspension in a position corresponding to the suction side of the Deculator pump. The complete dosage situation as well as machine capacity status is shown in table 1, No. A.

In the first trial the addition point of the polymer was moved from the pulp suspension to the water used for the high pressure shower system, thus enabling the diluted cationic polymer to directly, through the high pressure spray bars, come in contact with machine parts sensitive to slimy deposition. The actual surfaces connected to the high pressure shower system is the top and bottom wire, the forming roll, the pick up felt and the press felts. The effect of the new treatment on the machine status is shown in Table 1, No B.

In the second trial two measures were taken. Firstly the biocide addition to the shower water tank was interrupted. Secondly the polymer shower treatment was extended to comprise also the low pressure shower system. In addition to the first trial it was by this extension also possible to reach other deposition sensitive machine parts, i.e. suction boxes in wire and press section and with the polymer shower treatment.

The effect of the extended polymer shower treatment and the reduced biocide addition is shown in Table 1, No C.

TABLE 1

Time No	Product	Dosage point	Dosage rate (kg/day)	"Slime" build-up (visual eval.)	Paper production ton/day
-					
A	1. Biocide A	Wire chest	24	Ref	540 (Ref)
	2. Biocide B	Shower water tank	3.4		
	3. Polymer	Thin stock (Suction side of Deculator pump)	150		
B	1. Biocide A	Wire chest	24	Slower "slime" build-up than ref	5 % increase in comparison to ref
	2. Biocide B	Shower water tank	3.4		
	3. Polymer	Water to high pressure showers	105		
C	1. Biocide A	Wire chest	24	Slower "slime" build-up than ref	5 % increase in comparison to ref
	2. Biocide B	Shower water tank	-		
	3. Polymer	Water to high pressure showers	105		
	4. Polymer	Water to low pressure showers	50		

Biocide A = Solution of 5-chloro-2-methyl-4 isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one; commercially available as DARACIDE 856 (W R Grace AB, Helsingborg, Sweden)

Biocide B = Dibromonitrilo-propianamide; commercially available as DARACIDE 855 (W R Grace AB, Helsingborg, Sweden)

Polymer = Condensation product of Dicyandiamide-Formaldehyde; commercially available as DARASPERSE 7951 (W R Grace AB, Helsingborg, Sweden)

Claims

1. A method of controlling productivity disturbing microbiological deposits, e.g. slime, on paper making equipment, ***characterized*** by applying to any locus or surface of said paper making equipment which locus or surface has a tendency of causing build-ups of such microbiological deposits, a deposition-controlling amount, preferably at least about 0.1 parts per million of dilution water, of a deposition-controlling substance selected from the group consisting of cationic polymers and cationic surfactants, preferably water soluble polymers and surfactants.

2. A method according to claim 1, ***characterized*** by applying said cationic polymer or cationic surfactant by spraying an aqueous solution thereof onto said locus or surface.

3. A method according to claim 2, ***characterized*** in that said aqueous solution is substantially free from anionic macromolecules.

4. A method according to any one of the preceding claims, ***characterized*** in that the cationic polymer has a molecular weight within the range of 1.000 - 5,000 000, especially between about 10,000 and about 300,000, and/or that the cationic surfactant has a molecular weight of between about 200 and about 600.

5. A method according to claim 4, ***characterized*** in that the cationic polymer is selected from the group consisting of

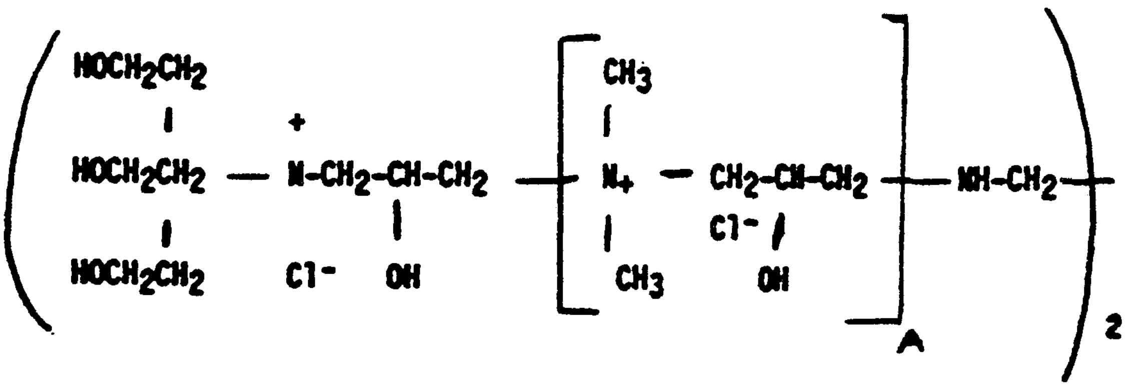
(a) dicyandiamide-formaldehyde condensation polymers, optionally including as polymerization reactant(s) at least one compound selected from the group consisting of formic acid and ammonium salts, preferably ammonium chloride;

(b) polymers formed by reaction between epihalohydrins and at least one amine, and

(c) polymers derived from ethylenically unsaturated monomers containing a quaternary ammonium group.

6. A method according to claim 5, ***characterized*** in that in polymer (b) the epihalohydrin is epichlorohydrin and/or the amine is selected from the group consisting of dimethylamine, diethylamine, methylethylamine, ethylene diamine, triethanolamine and a polyalkylene polyamine.

7. A method according to claim 6, ***characterized*** in that the polymer is represented by the general formula:



$$\left(\begin{matrix} HOCH_2CH_2 \\ | \\ HOCH_2CH_2 \\ | \\ HOCH_2CH_2 \end{matrix} - \overset{+}{N}\text{-}CH_2\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_2 \; Cl^- \left[\begin{matrix} CH_3 \\ | \\ N_+ \\ | \\ CH_3 \end{matrix} - CH_2\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_2 \; Cl^- \right]_A NH\text{-}CH_2 \right)_2$$

where A is a number within the range of 0-500.

8. A method according to claim 5, ***characterized*** in that polymer (c) comprises a homo- or copolymer of

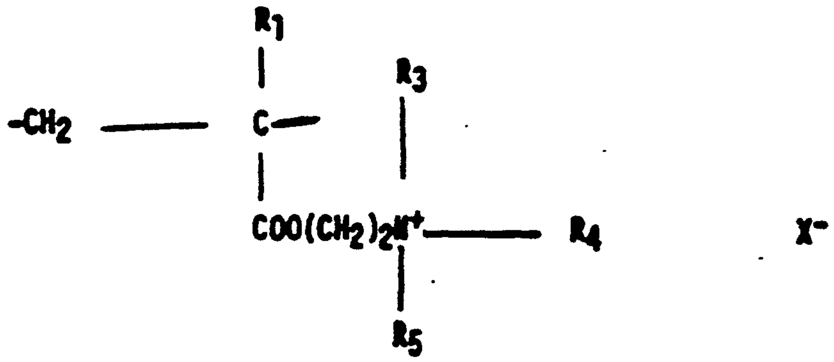
(i) a vinyl compound, e.g. vinyl pyridine or vinyl imidazole, quaternized with a C_1-C_{18} alkyl halide or a benzyl halide, preferably the chloride, or with dimethyl or diethyl sulphate, or a vinyl compound, e.g. vinyl benzyl chloride, quaternized with a tertiary amine of the formula $NR_1R_2R_3$, where R_1, R_2 and R_3 are each and independently lower alkyl, preferably with 1-4 carbon atoms, with the proviso that one of R_1, R_2 and R_3 can be C_1-C_{18}-alkyl;

(ii) an alkyl compound, e.g. diallyldimethyl ammonium chloride; or

(iii) an acrylic derivative, e.g. dialkylamino-methyl(meth)acrylamide, which may be quaternized with a C_1-C_{18}-alkyl halide, a benzyl halide or dimethyl or diethyl sulphate, a methacrylamidopropyl-tri(C_1-C_4-alkyl, especially methyl)ammonium salt or a (meth)acryloyloxyethyl-tri(C_1-C_4-alkyl, especially methyl) ammonium salt, preferably a halide, e.g. chloride, methosulphate, ethosulphate, or 1/n of a n-valent anion.

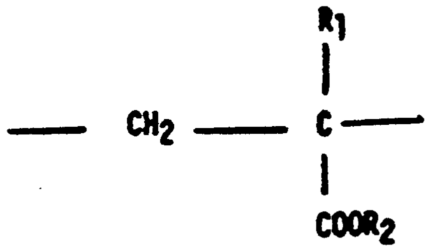
9. A method according to claim 8, ***characterized*** in that said copolymer is derived from a comonomer selected from the group consisting of a meth(acrylic) derivative, e.g. an acrylamide, an acrylate- or methacrylate-(C_1-C_{18})-alkyl ester or acrylonitrile, and an alkyl vinyl ether, vinyl pyrrolidone and vinyl acetate.

10. A method according to claim 9, ***characterized*** in that said copolymer contains 10-100 mole percent of recurring units of the formula



$$-CH_2-C(R_1)(COO(CH_2)_2N^+R_3R_4R_5)-\quad X^-$$

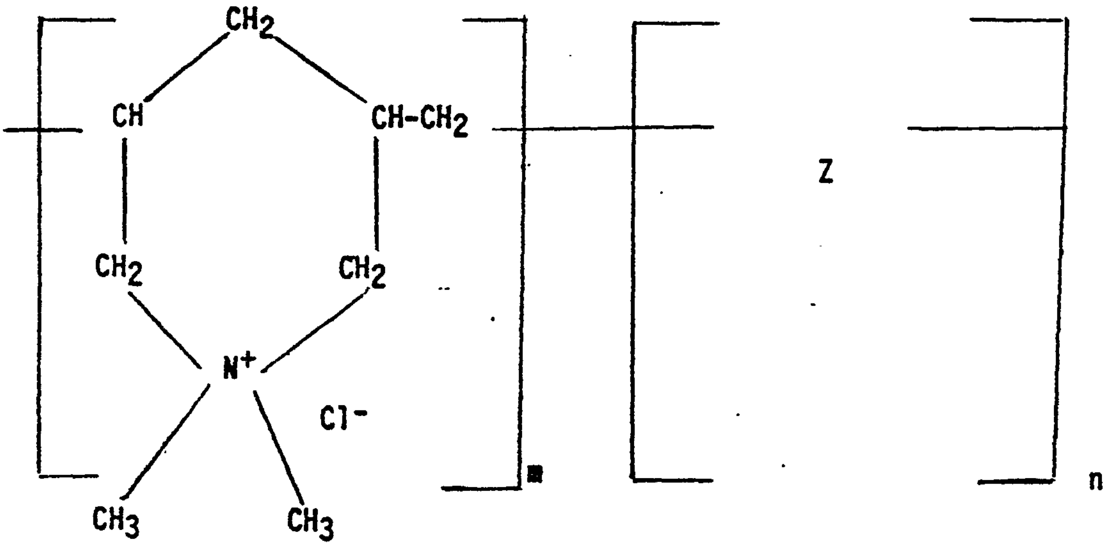
and 0-90 mole percent of recurring units of the formula:



$$-CH_2-C(R_1)(COOR_2)-$$

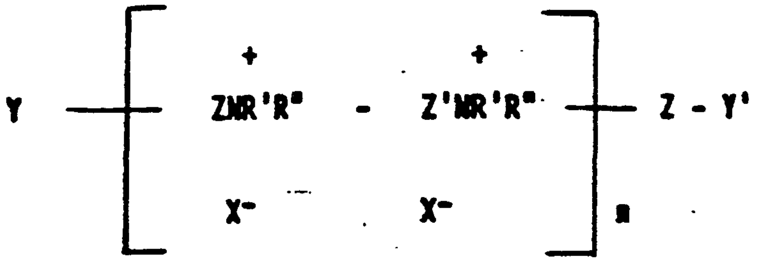
wherein R_1 represents hydrogen or lower alkyl, preferably with 14 carbon atoms, R_2 represents a long chain alkyl group, preferably with 8-18 carbon atoms, R_3, R_4 and R_5 each and independently represent hydrogen or lower alkyl, and X represents an anion, preferably a halide ion, a methosulphate ion, an ethosulphate ion or 1/n of a n-valent ion.

11. A method according to claim 5, ***characterized*** in that polymer (c) comprises a homo- or copolymer of diallyldimethyl ammonium chloride having recurring units of the formula:



where Z represents monomeric units, preferably from a (meth)acrylic derivative, such as an acrylamide, an acrylate- or methacrylate-(C_1-C_{18})-alkylester or acrylonitrile, or an alkylvinyl ether, vinylpyrrolidone or vinyl acetate;m is within the range of 5-100%; and
n is within the range of 0-95%.

12. A method according to claim 5, ***characterized*** in that polymer (c) is derived from monomers of the general formula:



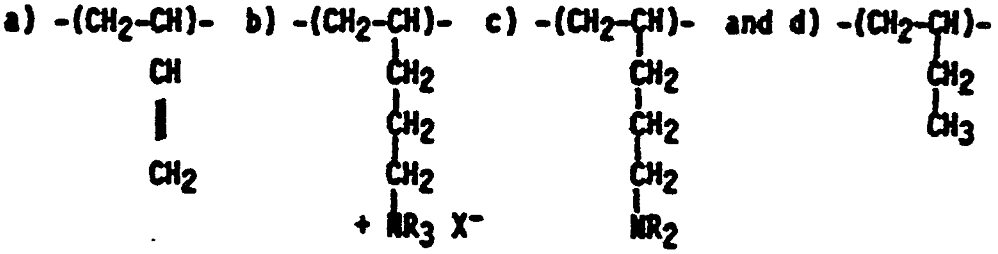
$$Y - \left[\underset{X^-}{\overset{+}{ZNR'R''}} - \underset{X^-}{\overset{+}{Z'NR'R''}} \right]_n - Z - Y'$$

where Z and Z′, which may be the same or different, are $-CH_2CH=CHCH_2-$ or $-CH_2-CHOHCH_2-$, Y and Y′, which may be the same or different, are X or $-NR'R''$, X is a halogen having an atomic weight greater than 30, n is an integer of from 2 to 20, and R′ and R″

(i) may be the same or different alkyl groups of from 1 to 18 carbon atoms, optionally substituted by 1 to 2 hydroxyl groups; or (ii) when taken together with N represent a saturated or unsaturated ring of from 5 to 7 atoms; or

(iii) when taken together with N and an oxygen atom represent the N-morpholino group; especially poly(dimethylbutenyl)ammonium chloride-bis-(triethanol ammonium chloride).

13. A method according to claim 5, ***characterized*** in that polymer (c) is derived from polybutadienes which have been reacted with a lower alkyl amine and where some of the resulting dialkyl amino groups have been quaternized, especially a polymer comprising recurring units of the formulae:



a) $-(CH_2-\underset{\underset{CH_2}{\|}}{CH})-$ b) $-(CH_2-\underset{\underset{\underset{\underset{+NR_3\,X^-}{|}}{CH_2}}{\underset{|}{CH_2}}}{\underset{|}{CH_2}}}{CH})-$ c) $-(CH_2-\underset{\underset{\underset{\underset{NR_2}{|}}{CH_2}}{\underset{|}{CH_2}}}{\underset{|}{CH_2}}}{CH})-$ and d) $-(CH_2-\underset{\underset{CH_3}{|}}{\underset{|}{CH_2}}}{CH})-$

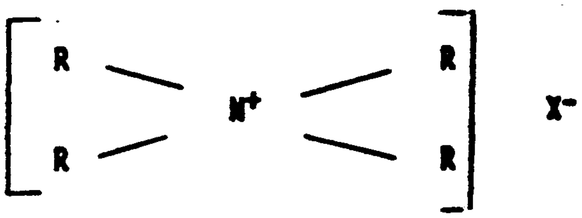
in the molar proportions a:b:d:d, where R represents lower alkyl, preferably methyl or ethyl.

14. A method according to claim 13, ***characterized*** in that the quaternizing agent comprises methyl chloride, dimethyl sulphate or diethyl sulphate and/or (b+c) is from 10 to 90% and (a+d) is from 90 to 10%.

15. A method according to any one of the preceding claims, ***characterized*** in that the molecular weight of the cationic polymer is from about 20,000 to 300,000, preferably from about 20,000 to 50,000.

16. A method according to any one of claims 1-14, ***characterized*** in that the molecular weight of the cationic polymer is from about 10,000 to 50,000.

17. A method according to any one of claims 1-4, ***characterized*** in that the cationic surfactant is of the general formula:



wherein each R is independently selected from the group consisting of hydrogen, alkyl groups having between about 1 and 22 carbon atoms, aryl groups, and aralkyl groups, at least one of said R groups being an alkyl group having at least about 8 carbon atoms and preferably an n-alkyl group having between about 12 and 16 carbon atoms; and wherein X^- is an anion, preferably a halide ion, e.g. chloride, or 1/n of an n-valent anion.

18. A method according to claim 17, ***characterized*** in that two of the R groups are selected from the group consisting of methyl and ethyl, preferably methyl.

19. A method according to claim 17 or 18, ***characterized*** in that one R group is $Ph-Ch_2-$ or $Ph-CH_2-CH_2-$ where Ph is phenyl, preferably benzyl.

20. A method according to any one of claims 17-19, ***characterized*** in that said surfactant comprises alkyldimethylbenzyl ammonium chloride(s) having alkyl group(s) of between about 12 and 16 carbon atoms.

21. A method according to any one of the preceding claims, ***characterized*** by applying said polymer or surfactant in an amount of at least about 5 parts per million of dilution water in a continuous treatment

operation.

22. A method according to any one of claims 1-20, ***characterized*** by applying said polymer or surfactant in an amount of at least about 50 parts per million of dilution water in an intermittent treatment operation.

23. A method according to any one of the preceding claims, ***characterized*** by applying said cationic polymer or surfactant in an amount of up to 500 parts per million of dilution water.

24. A method according to any one of the preceding claims, ***characterized*** in that the charge density of the cationic polymer or surfactant is within the range of about 0.5-20 milliequivalents/gram, preferably about 1-10 and more preferably about 2-8 milliequivalents/gram.

25. Paper whenever produced by a method as claimed in any one of claims 1-24.