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(54) **Method for inhibiting microbial growth in paper process systems**

(57) A method for inhibiting microbial growth in a paper processing system which method includes adding alkali bromide to the processing system and is characterised in that a chlorinated isocyanurate is also added to the processing system. The chlorinated isocyanurate preferably comprises dichloroisocyanuric acid or a salt thereof or trichloroisocyanuric acid or a salt thereof.

Trichloroisocyanuric acid or sodium dichloroisocyanurate are preferred.

The weight ratio of the chlorinated isocyanurate to the alkali bromide in the composition formed in the paper processing system is preferably greater than 3:1.

The chlorinated isocyanurate and alkali bromide maybe added to the paper processing system as a single composition.

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Description**BACKGROUND OF THE INVENTION****Field of the Invention**

The present invention relates to a method for inhibiting microbial growth in paper processing systems prone to such growth.

Description of the Background Art

A number of important industries, including the paper industry, have experienced serious adverse effects from the activity of biological growth on the raw materials which they employ, in their process waters, on various components of their manufacturing processes and in the finished products which they produce. In these industries, therefore, it is generally desirable to utilize one or more biocides in an attempt to control microorganism populations.

The control of bacteria and fungi in pulp and paper mill water systems which contain aqueous dispersions of papermaking fibers in various consistencies is especially important. The uncontrolled buildup of slime produced by the accumulation of bacteria and fungi causes off-grade production, decreased production due to down-time and greater cleanup frequency, increased raw material usage, and increased maintenance costs. The problem of slime deposits is especially critical in light of the widespread use of closed white water systems in the paper industry. The methods and compositions disclosed in the present invention are particularly applicable to slime control in papermaking processes.

Biocides used in the paper industry typically fall into two categories, oxidizing and non-oxidizing. Oxidizing biocides include, *inter alia*, mixtures of sodium bromide and sodium hypochlorite, hydrogen peroxide and ozone; non-oxidizing biocides include, *inter alia*, dibromodicyanobutane and dodecylguanidine hydrochloride. Both oxidizing and non-oxidizing biocides are used to control microbial growth and/or slime formation in paper making systems. Oxidizing biocides, however, generally have a much faster kill-time than non-oxidizing biocides. Also, oxidizing biocides have been found to be effective against spore forming bacteria which are in the spore state, while non-oxidizing biocides have little or no antimicrobial efficacy against these bacteria when they are in the spore forming state.

Of the oxidizing biocides found effective in paper process systems, oxidizers containing a halogen, such as bromine or chlorine, are particularly common. Halogen oxidizers primarily attack nitrogenous materials and the more reactive organic molecules. Their ability to preferentially attack proteins allows them to be effective at low enough concentrations to minimize interaction with other treatment chemicals such as polymers and phosphonates. The high reactivity of these products means that they do not persist for long periods of time after being discharged; it also means that overdosing a halogen oxidizer can lead to corrosion, chemical interactions, or attack on wood.

The most common of the halogen oxidizers are those containing chlorine or bromine. Chlorine is generally an effective biocide in systems having a pH below about 7.0. Also, chlorine may be preferred in systems exposed to strong sunlight, such as cooling ponds or fountains, since hypochlorous acid can be stabilized against decomposition by UV light but hypobromous acid cannot. Furthermore, chlorine is more attractively priced than bromine, and chlorine is a stronger oxidizer than bromine. Bromine products, however, often offer significant advantages over chlorine products. Bromine products have been used effectively since the 1940's to disinfect pools, spas, cooling water, drinking water and waste water. Bromine is very versatile and has proven to be an excellent microbicide for a large number of bacteria, fungi, algae, amoebic cysts and viruses. Furthermore, bromine has biocidal properties which are superior to chlorine in alkaline environments--that is, where the pH is above about 7.5. As used herein, the terms "biocide", "microbicide", "antimicrobial" and "inhibiting microbial growth" refer to agents useful for the killing of, as well as the inhibition of or control of, biological growth including but not limited to bacteria, algae and fungi such as yeast, mold and mildew.

PCT Application No. WO 93/04987 discloses a water stable tablet for disinfecting recirculating water systems comprising chlorinated isocyanurate, sodium bromide and a stabilizer which regulates the rate at which the chlorinated isocyanurate and the sodium bromide are dissolved or dispersed in flowing water. U.S. Patent No. 4,557,926 (Nelson, et al) discloses a tablet for disinfecting toilets comprising an alkali metal salt of dichloroisocyanuric acid and either sodium bromide or potassium bromide.

U.S. Patent No. 5,015,643 (Jones, et al) discloses a solid disinfecting composition comprising a mixture of 80% to 99% by weight of trichloro-s-triazinetriene and 1% to 20% by weight potassium bromide.

U.S. Patent No. 4,451,376 (Sharp) discloses a method for treating alkaline industrial process waters with a combination of a water-soluble anionic polymeric dispersant and hypobromous acid.

U.S. Patent No. 5,254,526 (Hamilton) claims a method of inhibiting the growth of algae by introducing to the body of water being treated a chlorine-containing oxidizer and a water soluble bromide which has been premixed with an alkali metal, alkaline earth metal or ammonium polyphosphate.

Many of the bromine products currently available do not provide the combination of convenience, cost and safety levels which are desired and needed in such a product. Accordingly, there remains a very real and substantial need for bromine-based antimicrobial compositions capable of effectively controlling microbial growth in paper process systems. Also, there is still a further need to provide biocidal compositions with enhanced antimicrobial effect which are effective in lower doses than previously used. Use of lower amounts of biocides has a favourable impact on the environment, and allows the user to realize significant cost savings.

SUMMARY OF THE INVENTION

According to the present invention there is provided a method for inhibiting microbial growth in a paper processing system which method includes adding an alkali bromide to the processing system and is characterised in that a chlorinated isocyanurate is also added to the processing system.

The chlorinated isocyanurate may comprise dichloroisocyanuric acid or a salt thereof or trichloroisocyanuric acid or a salt thereof. Preferred examples include trichloroisocyanuric acid or a salt thereof. Preferred examples include trichloroisocyanuric acid and alkali metal salts of dichloroisocyanuric acid, eg. anhydrous sodium dichloroisocyanurate.

The weight ratio of the chlorinated isocyanurate to the alkali bromide in the composition formed in the paper processing system is preferably greater than 3:1.

It is preferred that the chlorinated isocyanurate and alkali bromide are added to the paper processing system as a single composition.

When such compositions, which are generally in a dry form, contact the water of the paper process system, effective control of microbial growth may be obtained in a cost effective manner.

Additional advantages of the present invention include ease of use and versatility. For example, the preferred embodiment of the methods disclosed herein provides for the feeding of only one product, which contains two active ingredients, rather than two separate products. The methods of the present invention have the further advantage of providing safer handling characteristics when compared with other biocides, both oxidizing and non-oxidizing. The methods of the present invention allow for use of a chlorinated isocyanurate and alkali bromide at low concentrations while still achieving great biocidal efficacy in paper process systems. Furthermore, by using the methods of the present invention, the user can eliminate safety hazards and feed equipment maintenance problems generally associated with the use of chlorine gas. Finally, the methods of the present invention utilize a product which is about 2.5 to 5 times more soluble than the hydantoin bromine microbicides currently being used; a higher solubility results in a faster release of halogen, a quicker microorganism kill and an overall increase in microbial growth inhibition.

DESCRIPTION OF THE INVENTION

The present invention is directed to a method for inhibiting microbial growth in a paper process system prone to such growth, which method comprises adding to said system an effective amount of a composition comprising: a) a chlorinated isocyanurate; and b) an alkali bromide, preferably sodium bromide, wherein the weight ratio of component a) to component b) is at least 3:1. These two components are preferably delivered to the system as a single composition, but components a) and b) as described above can alternatively be added separately. If the two components are added to the system being treated as a single composition, that composition can be in dry, granular form, but is preferably in stick, tablet or puck form. The sticks, tablets or pucks are formed using the conventional techniques which are familiar to those skilled in the art.

In accordance with the methods of the present invention, the weight ratio of component a) the chlorinated isocyanurate to component b), for example sodium bromide, on an active basis, should exceed about 3:1 and preferably ranges from about 5:1 to about 99.5:0.5 and more preferably ranges from about 10:1 to about 99.5:0.5. In the most preferred case component a) comprises about 85 to 95% by weight on an active basis of said composition and component b) about 5 to 15% by weight on an active basis of said composition. Additionally, these compositions may comprise a measurable percentage, but generally not in excess of about 5% by weight on an active basis, of inert impurities or fillers such as sodium chloride and water. A product in dry tablet form meeting the above specifications is commercially available from the OxyChem Corporation, Grand Island, New York under the name Towerbrom R 90M or from Calgon Corporation, Pittsburgh, PA under the name Towerbrom R 993. These products comprise about 92-93% trichloroisocyanuric acid, about 7% sodium bromide and about 1% or less inert ingredients, with all of the percentages given by weight on an active basis.

A dry, granular product meeting the above specifications is commercially available from the OxyChem Corporation, Grand Island, New York under the name Towerbrom R 60M or from Calgon Corporation, Pittsburgh, PA under the name Towerbrom R 690. These products comprise about 89% sodium dichloroisocyanurate (anhydrous), about 7% sodium bromide and about 4% inert ingredients, with all of the percentages given by weight on an active basis.

While Towerbrom R 993 and Towerbrom R 60M and similar products have been used as antimicrobial agents in

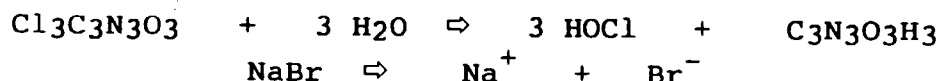
cooling towers, heat exchangers, industrial water scrubbing systems and the like, use of these products as antimicrobial agents in paper process systems was previously unknown.

As used herein, the term "granular" means virtually any particle size ranging from powders to coarse granules, as generally understood by those skilled in the art. It will be further understood by those skilled in the art that the size of the particle is generally unimportant relative to the process of the present invention. Likewise, the size of the sticks, tablets or pucks is not believed to be an important part of the methods as disclosed herein.

The present invention is also directed to compositions comprising aqueous paper process systems such as papermaking streams, furnishes or stocks containing an effective amount, preferably at least 0.1 ppm on an active weight basis, based on the weight of water in said paper process system, of a composition comprising: a) trichloroisocyanuric acid; and b) an alkali bromide wherein the weight ratio of component a) to component b), on an active basis, exceeds about 3:1 and preferably ranges from about 5:1 to about 99.5:0.5 and more preferably ranges from about 10:1 to about 99.5:0.5. Components a) and b) can be added to the aqueous paper process system being treated by any suitable addition means. Point of addition is generally not believed to be critical. The preferred point of addition is generally that point which maximizes contact between the organism(s) comprising the growth to be inhibited. Common points of addition are, for example, to furnishes, stock systems, head boxes, white water streams, fresh water feed streams, filtered and unfiltered shower water streams and additive streams.

An effective amount of the composition of component a) and component b) should be added. As used herein, the term "effective amount" refers to that amount of a composition comprising component a) and an alkali bromide component b) necessary to achieve the desired level of inhibition of microbial growth in the system being treated, for example the amount of a trichloroisocyanuric acid and sodium bromide composition necessary to control microbial growth in a paper process system. Preferably, at least about 0.1 ppm, based on the weight of water in the system being treated, of the composition described above is added. More preferably, from about 0.1 to about 20 ppm, based on the weight of water in the system being treated, is added. Most preferably, the dosage ranges from about 1.0 to about 5.0 ppm.

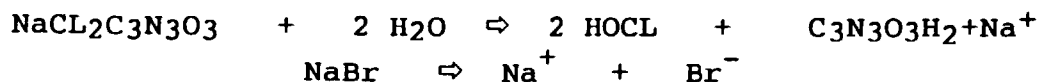
Inhibition of microbial growth according to the methods of the present invention is believed to be achieved by the formation of an effective amount of hypobromous acid in the aqueous paper process system being treated. Hypobromous acid is believed to be formed when the composition of components a) and b) specified above contacts water, such as when introduced to an aqueous paper making stream. For example, trichloroisocyanuric acid ($\text{Cl}_3\text{C}_3\text{N}_3\text{O}_3$) and sodium bromide (NaBr) compositions are believed to hydrolyze to give hypochlorous acid (HOCl), cyanuric acid ($\text{C}_3\text{N}_3\text{O}_3\text{H}_3$), sodium ions (Na^+) and bromide ions (Br^-) according to the following chemical reactions:



Then, hypochlorous acid and bromide ions react to form hypobromous acid (HOBr):



Similarly, sodium dichloroisocyanurate (anhydrous) ($\text{NaCl}_2\text{C}_3\text{N}_3\text{O}_3$) and sodium bromide (NaBr) compositions are believed to hydrolyze to give hypochlorous acid (HOCl), cyanurate anion ($\text{C}_3\text{N}_3\text{O}_3\text{H}_2^-$), sodium ions (Na^+) and bromide ions (Br^-) according to the following chemical reactions:



Then, hypochlorous acid and bromide ions react to form hypobromous acid (BOBr):



The chlorinated isocyanurate and bromide compositions disclosed herein are believed to have a faster dissolution rate, or shorter half life, than other commercially available bromine products. As used herein, the term "half life" of a chemical or chemical species is the amount of time required for the concentration of that chemical or chemical species

in the system to which it is added to be reduced to half of its initial value. The reaction between hypochlorous acid and bromide ions is also believed to occur rapidly, and in a paper process system generally occurs virtually instantaneously. This reaction should continue so long as there is a sufficient number of bromide ions in the system. The user, therefore, preferably should maintain at least a one to one molar ratio of bromide ions and hypochlorous acid to sustain production of the hypobromous acid. Put another way, the bromide ion to available chlorine weight ratio should be maintained at at least 1.127, which number is derived from the mole weight of bromide ion, 80, and the mole weight of chlorine, 71. To initially achieve this ratio, several additions of the isocyanurate and sodium bromide (NaBr) composition may be necessary. The available chlorine in the composition being used according to the method of the present invention is preferably between about 30-95 weight percent of the composition and more preferably between about 80-95 weight percent of the composition. The available chlorine in the Towerbrom R 993 and Towerbrom R 90M products described above is at least about 83% by weight.

The available chlorine in the Towerbrom R 960 and Towerbrom R 60M products described above is about 57% by weight.

As used herein, the term "available chlorine" means the amount of active chlorine, by weight, in a composition; as used herein the term "available chlorine" also includes active chlorine that is replaced by bromine, since bromine atoms replace chlorine atoms on a one for one basis.

When a bromine to chlorine ratio of 1.127 or greater is achieved in the system being treated, the composition as used in the methods of the present invention is believed to function primarily as a bromine microbicide. If the ratio of bromine to available chlorine falls to below 1.127, the composition is believed to behave as a mixed chlorine and bromine microbicide. The user can determine if the composition as used in the methods disclosed herein is functioning primarily as a bromine microbicide or as a chlorine/bromine microbicide by determining the ratio of bromide ion to available halogen (here, available chlorine). The user can then determine whether the ratio should be raised or lowered based upon the particular system being treated. For example, if the pH of the system is acidic, then the microbicidal properties obtained from a mixture of the chlorine and bromine biocides may be desired; if the pH of the system is alkaline, then a bromine system would most likely be desired.

In addition to being effective in both alkaline and acid paper process systems, that is, in systems with a pH ranging from about 3 to 6.9 and about 7.1 to 11, the methods and compositions of the present invention are equally effective in either open or closed paper process systems. An open system is one in which water is continuously discharged and re-filled. A closed system is one in which the same water is recirculated. Paper process systems may be open, closed or a combination of both.

An additional advantage of the methods and compositions of the present invention is that when employed in a closed system the bromide ion can be continuously recycled, thereby minimizing the amount of bromine product which must be added. For example, hypobromous acid is believed to oxidize debris or other organic contaminants typically found in the water of paper process systems to form hydrogen ions (H⁺), bromide ions (Br⁻) and waste products according to the following equation:

$\text{HOBr} + \text{debris} \Rightarrow \text{H}^+ + \text{Br}^- + \text{waste products}$ The bromide ion is then believed to be reoxidized by hypochlorous acid to regenerate hypobromous acid according to the following equation:



This recycling process generally is believed to reduce the amount of bromine product which must be added to the system in order to maintain effective control over microorganism growth.

An additional advantage of the methods and compositions of the present invention is that they generally can be employed without shifting the functional equilibrium of the system being treated. That is, the composition as described above can be added to the system without affecting the net charge of the system. This is because the trichloroisocyanuric acid and alkali bromide components used in the methods of the present invention have neutral charges.

The hypobromous acid produced by the hydrolysis of the trichloroisocyanuric acid and alkali bromide components as used in the methods of the present invention are believed to perform two major functions within the paper process system. First, the hypobromous acid serves as an antimicrobial agent, killing bacteria, fungi and algae in the system. Second, because hypobromous acid is an oxidizing agent, it will oxidize organic material or debris which otherwise would provide a nutrient source for microorganisms.

The compositions of the present invention are believed to be effective irrespective of the method of application. Thus, for example, the cyanurate and alkali bromide compositions disclosed herein can be added to the paper process system being treated via a low level, continuous feed practice, a semi-continuous feed practice or through slug feeding. All of these feeding practices will be familiar to one having ordinary skill in the art.

While oxidizing biocides are typically not slug fed to systems because of their short half life, slug feeding is par-

particularly effective relative to the methods of the present invention and therefore is a preferred manner of employing the methods of the present invention, particularly when dealing with a closed system. This type of feed allows the user to monitor the microorganism concentration in the system and feed product only when microorganism concentrations increase. The user, therefore, realizes a cost savings because the product is fed only when needed. Slug feeding is also a preferred method of feeding the composition described herein when this composition is in granular form.

A continuous feed or semi-continuous feed is generally believed to be preferable when dealing with an open system. Because the biocide is generally discharged with the water in such a system, maintaining an effective amount of the biocide in the system being treated generally requires continuous or semi-continuous feed. Continuous or semi-continuous feeding is also a preferred method of feeding the composition described herein when this composition is in stick, tablet or puck form.

Continuous feed of a granular product is preferably effected by feeding a granular chlorinate isocyanurate and sodium bromide composition via an apparatus such as that disclosed in USP 5427694. Commercially available feeders useful in employing the methods of the present invention when feeding a composition in tablet form include the TB-300 Tablet Feeder and the TB-300S Submersible Tablet Feeder, both of which are available from Calgon Corporation, Pittsburgh, PA.

As discussed above, the methods of the present invention comprise contacting microbial growth in a paper making system with an effective amount of chlorinated isocyanurate and an alkali bromide. It is well within the ordinary skill of one practising in the art to determine the effective amount of biocide for a given system based on various system parameters including but not limited to the size of the system, whether the system is open or closed, operating temperatures, the types of organisms present, the pH of the system and the amount of control desired.

The superior antimicrobial activity of the compositions of the present invention has been confirmed using standard laboratory techniques. Furthermore, it has been demonstrated that satisfactory antimicrobial control can be achieved by using a significantly lower amount of bromine than is required when using other commercially available bromine biocides. Finally, the methods and compositions of the present invention have been found to have a broad spectrum of biocidal efficacy. For example, the present methods have been found effective in controlling microbial growth in both acid and alkaline fine paper stock and have been found effective against: bacterial strains including but not limited to *Pseudomonas aeruginosa*, *Klebsiella pneumonia*, *Escherichia coli*, and other fresh water organisms such as filamentous bacteria; fungi including but not limited to various species of *Penicillium*, *Aspergillus* and *Aureobasidium*; yeast including but not limited to various species of *Candida* and *Saccharomyces*, and algae including but not limited to blue green algae and diatoms. Such organisms are commonly found in paper process systems. Early control of these and other types of microorganisms prevents the formation of the slimes caused by these microorganisms that would otherwise become deposited on the paper process equipment as described above.

EXAMPLES

The following examples are provided to illustrate the invention in greater detail, and should not be construed as limiting the scope of the present invention in any way.

EXAMPLE I

A 1% acid fine paper stock and a 1% alkaline fine paper stock were prepared according to the following methods:

A 2% consistency acid fine paper stock was prepared by slowly adding about 250 grams (g) each of hardwood and softwood to a pulper along with about 21 liters of water. The pulper used was a Valley Laboratory Beater, model number 10920, available from Valley Laboratory Equipment. After addition of the water and wood, the mixture was pulped for about 1 hour. After pulping, about 27.3 g of clay (ansilex), about 5.0 g of titanium dioxide and about 2.5 g of rosin were added to the mixture, and pulping continued for an additional 45 minutes. During this process, the pH of the mixture was adjusted to about 4.8 using 10% sulfuric acid (H_2SO_4). The resulting 2% consistency acid paper stock was diluted with deionized water in a 1 to 1 ratio to form a 1% consistency stock. In addition, the paper stock was sterilized in an autoclave within 24 hours of use.

A 2% consistency alkaline fine paper stock was prepared by slowly adding 250 g each of hardwood and softwood and about 21 liters of water to the pulper described above. After addition of all of the water and wood, the mixture was pulped for about 1 hour. After pulping, about 37.5 g of calcium carbonate was added to the mixture, and pulping continued for an additional 45 minutes. During this process the pH of the mixture was adjusted to about 8.0 using 10% sodium hydroxide (NaOH). The resulting 2% consistency alkaline paper stock was diluted with deionized water in a 1 to 1 ratio to form a 1% consistency stock. In addition, the paper stock was sterilized in an autoclave within 24 hours of use.

100g of the acid paper stock were placed in five tissue culture flasks and 100 g of the alkaline paper stock were placed in an additional five tissue culture flasks; all of the flasks were maintained in a temperature controlled water

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bath equipped with a shaking mechanism. The water bath was a Versa Bath, available from Fischer Scientific Co., Pittsburgh, PA. The 1% alkaline paper stock was maintained at 37°C, pH 8.1, and 80 revolutions per minute (rpm). The 1% acid paper stock was maintained at 37°C, pH 4.9, and 80 rpm. These conditions were intended to simulate the environment of a paper making machine. Five flasks each of the acid and alkaline paper stocks were maintained;

Two of the five flasks were maintained as controls to which no biocide was added. Three different bacteria--*Pseudomonas aeruginosa*, *Klebsiella pneumonia*, and *Escherichia coli*--were introduced to each of the ten flasks containing either the acid or the alkaline paper stock. Each of the three bacteria were separately grown on standard method agar (SMA) and incubated at 37°C for a period of about 24 hours. The bacteria were then swabbed from their respective SMA plate and added to the tissue culture flasks containing either the acid or alkaline paper stock; each of the three bacteria were introduced to each of the flasks. The flasks were stirred to ensure an even mixture of the bacteria throughout the paper stock. A total bacteria concentration of at least 1×10^6 colony forming units per millilitre (cfu/ml) was achieved.

A trichloroisocyanuric acid and sodium bromide composition commercially available from OxyChem Corporation, Grand Island, New York, under the trademark Towerbrom R 90M was used in Example I as the inhibitor. As mentioned earlier, Towerbrom R 90M contains trichloroisocyanuric acid and sodium bromide in a weight ratio of about 13:1. The inhibitor was added directly to three of the flasks containing the 1% acid paper stock and three of the flasks containing the 1% alkaline paper stock in the concentrations indicated in Tables 1 and 2. Concentrations ranged from about 0.1 parts per million (ppm) to about 1.0 ppm. Approximately 2 to 3 minutes elapsed between the addition of each inhibitor concentration to its respective flask.

Two controls were run on each of the acid and alkaline paper stocks, since approximately 10 to 15 minutes elapsed between the addition of the inhibitor to the first flask and the last. The microorganism concentration of Control A was plated before the addition of any inhibitor and the microorganism concentration of Control B was read after the addition of all of the inhibitor. The microorganism concentration of both Controls A and B were additionally read throughout the experiment, at 1, 3 and 24 hours; these six microorganism concentrations were averaged to give an average control value. The average control value was then used to determine percent kill as described below. Eight different control readings were taken to ensure that the concentration of bacteria in the samples did not appreciably change over the time of the Example, which would indicate a problem with the test methods.

At three times throughout the experiment, after 1, 3 and 24 hours, a 1 ml sample of paper stock was removed from each flask. These samples were then plated on a petri dish containing SMA and incubated for 48 hours at 37°C and 85% relative humidity. The actual amount of bacteria, or plate count, after 48 hours was then recorded in colony forming units per millilitre (cfu/ml); the plate count was determined by using a BioTran III automatic plate counter obtained from the New Brunswick Scientific Co., Inc, Edison, N.J.

The percent kill was determined according to the following formula:

$$\frac{\text{average control} - \text{actual amount of bacteria}}{\text{average control}} \times 100 = \% \text{ kill}$$

Both bacteria growth in cfu/ml and percent kill after 1, 3 and 24 hours of exposure to the biocide are recorded in Tables 1 and 2. If percent kill was determined to be a negative number, it was recorded in the tables as "0". Results are presented below.

TABLE 1

ALKALINE FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
90M	0.1	--	1.1×10^7 (37)	1.1×10^7 (34)	2.5×10^7 (0)
90M	0.5	--	1.6×10^7 (9)	1.6×10^5 (99)	---
90M	1.0	--	$<10^2$ (99+)	$<10^2$ (99+)	6.9×10^6 (61)
Control A	--	1.8×10^7	1.2×10^7	1.1×10^7	2.1×10^7
Control B	--	2.2×10^7	8.7×10^6	1.0×10^7	2.3×10^7
Average Control = 1.8×10^7 cfu/ml					

TABLE 2

ACID FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
90M	0.1	--	3.4×10^7 (0)	3.1×10^7 (0)	2.6×10^7 (10)
90M	0.5	--	2.8×10^7 (3)	2.9×10^7 (0)	2.6×10^7 (10)
90M	1.0	--	1.9×10^7 (34)	1.8×10^7 (38)	1.0×10^7 (66)
Control A	--	3.2×10^7	3.0×10^7	2.6×10^7	2.5×10^7
Control B	--	2.9×10^7	3.6×10^7	3.3×10^7	2.8×10^7
Average Control = 2.9×10^7 cfu/ml					

As can be seen in the results presented in Tables 1 and 2, the methods of the present invention were effective in controlling microbial growth in both acid and alkaline paper stock. The percent kill generally increased as the concentration of biocide increased.

EXAMPLE II

The method of the present invention, again using the inhibitor of Example I, was compared against the use of NaBr alone. Antimicrobial efficacy in 1% acid and 1% alkaline fine paper stock, prepared as described in Example I, was evaluated. Twelve tissue culture flasks were prepared, six containing 100 g of acid paper stock and six containing 100 g of alkaline paper stock. The twelve flasks were maintained in a temperature controlled water bath equipped with a shaking mechanism in the manner described above in Example I. In addition, two acid paper stock flasks and two alkaline paper stock flasks were maintained as controls to which no biocide was added. Three different bacteria were introduced to each of the twelve flasks as described above in Example I. The two different biocides used in Example II included Towerbrom R 90M, which had about 7% active bromine, and sodium bromide (NaBr), which had about 40% active bromine. Each biocide was added to two acid paper stock flasks and two alkaline paper stock flasks. The active concentration (ppm) of each biocide added to each flask is recorded in Tables 3 and 4. Following addition of the bacteria and biocide, the procedures as described in Example I were carried out. The results are presented in Tables 3 and 4.

TABLE 3

ALKALINE FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
NaBr	1.0	--	2.6×10^7 (0)	1.3×10^7 (0)	2.6×10^7 (0)
NaBr	3.0	--	1.9×10^7 (0)	1.5×10^7 (0)	2.5×10^7 (0)
90M	1.0	--	1.5×10^3 (99)	$<10^2$ (99+)	$<10^2$ (99+)
90M	3.0	--	1.3×10^3 (99)	$<10^2$ (99+)	$<10^2$ (99+)
Control A	--	2.7×10^7	2.0×10^7	1.9×10^7	2.7×10^7
Control B	--	2.2×10^7	1.7×10^7	1.4×10^7	2.6×10^7
Average Control = 2.05×10^7 cfu/ml					

TABLE 4

ACID FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
NaBr	1.0	--	2.3×10^7 (0)	1.9×10^7 (0)	1.6×10^7 (11)
NaBr	3.0	--	2.0×10^7 (0)	1.8×10^7 (0)	1.5×10^7 (17)
90M	1.0	--	$<10^2$ (99+)	4.0×10^2 (99)	2.2×10^4 (99)
90M	3.0	--	4.0×10^2 (99)	$<10^2$ (99+)	5.0×10^2 (99)
Control A	--	2.2×10^7	2.0×10^7	2.0×10^7	1.0×10^7
Control B	--	2.2×10^7	2.3×10^7	1.6×10^7	1.9×10^7
Average Control = 1.8×10^7 cfu/ml					

As can be seen in Tables 3 and 4, in both the acid and alkaline paper stock the performance of the NaBr alone was clearly inferior to that of the Towerbrom R product, and often failed to achieve any inhibition of microbial growth whatsoever.

The results of Example II demonstrate the superiority of a product containing NaBr with trichloroisocyanuric acid over NaBr alone. These results also show that using a higher concentration of bromine does not necessarily mean a higher percent kill. Here, employing a product with only about 7% active NaBr was effective in reducing microbial growth in both acid and alkaline paper stock while the NaBr, which had a significantly higher bromine concentration, was not effective. Reducing the amount of bromine needed to control microbial growth translates into cost savings for the user.

EXAMPLE III

The present invention, again using the inhibitor of Example I, was compared against the use of a typical oxidizing biocide, namely a mixture containing sodium bromide (NaBr) and sodium hypochlorite (bleach). A 1% acid paper stock and 1% alkaline paper stock were prepared and maintained in a water bath as described in Example I; 24 tissue culture flasks were prepared, with 12 containing the 1% acid paper stock and 12 containing the 1% alkaline paper stock. Three different bacteria were added to all of the flasks in the same manner as described above for Example I. Two flasks each of the acid paper stock and the alkaline paper stock were maintained as controls, again as described in Example I. To five flasks containing the acid paper stock and five flasks containing the alkaline paper stock were added concentrations of the inhibitor of Example I ranging from about 1.0 ppm to about 50.0 ppm as indicated in Tables 5 and 6. To five flasks containing the acid paper stock and five flasks containing the alkaline paper stock were added concentrations of the 0.1% NaBr/bleach mixture ranging from about 1.0 ppm to about 50.0 ppm as indicated in Tables 5 and 6. The 0.1% stock solution of NaBr/bleach was prepared by mixing about 2.65 grams of 40% active NaBr in about 18.9 grams of 5.25% active bleach. The NaBr and bleach were allowed to react for about two minutes, and diluted into about 1000 ml of deionized water. The resulting solution was then added to the paper stock in concentrations ranging from about 1.0 ppm to about 50.0 ppm. To prepare the flasks containing NaBr/bleach concentrations of 1 ppm, about 0.1 ml of the 1% NaBr/bleach stock solution was added to about 100 g of the paper stock; for an NaBr/bleach concentration of 5 ppm, about 0.5 ml of stock solution was added to about 100 g of paper stock; for an NaBr/bleach concentration of 10 ppm, about 1.0 ml of stock solution was added to about 100 g of paper stock; for an NaBr/bleach concentration of 25 ppm about 2.5 ml of stock solution was added to about 100 g of paper stock; and for an NaBr/bleach concentration of 50 ppm about 5.0 ml of stock solution was added to about 100 g of paper stock. All other test methods and conditions were as recited in Example I. The test results for both the alkaline and acid paper stock are illustrated in Tables 5 and 6, respectively.

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TABLE 5

ALKALINE FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
90M	1.0	--	2.4×10^5 (99)	$<10^2$ (99+)	$<10^2$ (99+)
90M	5.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
90M	10.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
90M	25.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
90M	50.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
NaBr + bleach	1.0	--	$<10^2$ (99+)	$<10^2$ (99+)	4.1×10^5 (99)
NaBr + bleach	5.0	--	$<10^2$ (99+)	$<10^2$ (99+)	9.0×10^2 (99)
NaBr + bleach	10.0	--	1.8×10^6 (95)	$<10^2$ (99+)	$<10^2$ (99+)
NaBr + bleach	25.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
NaBr + bleach	50.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
Control A	--	2.5×10^7	2.1×10^7	5.7×10^7	3.4×10^7
Control B	--	3.5×10^6	9.8×10^6	5.2×10^6	5.6×10^7
Average Control = 1.8×10^7 cfu/ml					

TABLE 6

ACID FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
90M	1.0	--	1.0×10^2 (99)	$<10^2$ (99+)	4.0×10^2 (99)
90M	5.0	--	1.0×10^2 (99)	$<10^2$ (99+)	$<10^2$ (99+)
90M	10.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
90M	25.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
90M	50.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
NaBr +	1.0	--	$<10^2$	4×10^2	4.1×10^4

TABLE 6 (continued)

ACID FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
bleach			(99+)	(99)	(99)
NaBr + bleach	5.0	--	<10 ² (99+)	2 x 10 ² (99)	<10 ² (99+)
NaBr + bleach	10.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)
NaBr + bleach	25.0	--	1 x 10 ² (99)	<10 ² (99+)	<10 ² (99+)
NaBr + bleach	50.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)
Control A	--	2.7 x 10 ⁷	1.9 x 10 ⁷	2.1 x 10 ⁷	1.8 x 10 ⁷
Control B	--	2.5 x 10 ⁷	2.6 x 10 ⁷	2.2 x 10 ⁷	1.6 x 10 ⁷
Average Control = 2.0 x 10 ⁷ cfu/ml					

As can be seen from the results presented in Tables 5 and 6, the percent kill when using the Towerbrom R 90M product was comparable to the percent kill when using the NaBr/bleach solution. These results demonstrate that the method of the present invention, which utilizes a composition having between about 5-15% active bromine, yielded results which were comparable to, if not superior to, the results achieved when using the NaBr/bleach solution which contained about 40% active bromine. Such a significant reduction of bromide usage, while retaining approximately the same level of percent kill, demonstrates the clear advantage of the present invention over methods currently employed in the art.

EXAMPLE IV

100 g of the acid paper stock prepared as in Example 1 was placed in seven tissue culture flasks and 100 g of the alkaline paper stock were placed in an additional seven tissue culture flasks; all of the flasks were maintained in a temperature controlled water bath equipped with a shaking mechanism. The water bath was a Versa Bath, available from Fischer Scientific Co., Pittsburgh, PA. The 1% alkaline paper stock was maintained at 37°C, pH 8.1, and 80 revolutions per minute (rpm). The 1% acid paper stock was maintained at 37°C, pH 4.9, and 80 rpm. These conditions were intended to simulate the environment of a paper making machine. Seven flasks each of the acid and alkaline paper stocks were maintained; two of the seven flasks were maintained as controls to which no biocide was added.

Three different bacteria--*Pseudomonas aeruginosa*, *Klebsiella pneumonia*, and *Escherichia coli*--were introduced to each of the fourteen flasks containing either the acid or the alkaline paper stock. Each of the three bacteria were separately grown on standard method agar (SMA) and incubated at 37°C for a period of about 24 hours. The bacteria were then swabbed from their respective SMA plate and added to the tissue culture flasks containing either the acid or alkaline paper stock; each of the three bacteria were introduced to each of the flasks. The flasks were stirred to ensure an even mixture of the bacteria throughout the paper stock. A total bacteria concentration of at least 1 x 10⁶ colony forming units per milliliter (cfu/ml) was achieved.

A sodium dichloroisocyanurate (anhydrous) and sodium bromide composition commercially available from Ox-yChem Corporation, Grand Island, New York, under the trademark Towerbrom R 60M used this Example I as inhibitor. As mentioned earlier, Towerbrom R 60M contains sodium dichloroisocyanurate (anhydrous) and sodium bromide in a weight ratio of between about 12:1 and 13:1. The inhibitor was added directly to five of the flasks containing the 1% acid paper stock and five of the flasks containing the 1% alkaline paper stock in the concentrations indicated in Tables 1 and 2. Concentrations ranged from about 0.1 parts per million (ppm) to about 1.0 ppm. Approximately 2 to 3 minutes elapsed between the addition of each inhibitor concentration to its respective flask.

Two controls were run on each of the acid and alkaline paper stocks as in Example 1.

At three times throughout the experiment, after 1, 3 and 24 hours, a 1 ml sample of paper stock was removed from each flask. These samples were then plated on a petri dish containing SMA and incubated for 48 hours at 37°C and 85% relative humidity. The actual amount of bacteria, or plate count, after 48 hours was then recorded in colony forming

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units per milliliter (cfu/ml); the plate count was determined by using a BioTran III automatic plate counter obtained from the New Brunswick Scientific Co., Inc, Edison, N.J. The percent kill was determined according to the following formula:

$$\frac{\text{average control} - \text{actual amount of bacteria}}{\text{average control}} \times 100 = \% \text{ kill}$$

Both bacteria growth in cfu/ml and percent kill after 1, 3 and 24 hours of exposure to the biocide are recorded in Tables 1 and 2. If percent kill was determined to be a negative number, it was recorded in the tables as "0". Results are presented below.

TABLE 7

ALKALINE FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
1	0.1	--	9.5 x 10 ⁶ (46)	8.1 x 10 ⁶ (54)	2.0 x 10 ⁷ (0)
2	0.3	--	1.2 x 10 ⁷ (32)	4.8 x 10 ⁶ (73)	2.0 x 10 ⁷ (0)
3	0.5	--	4.2 x 10 ⁶ (76)	4.2 x 10 ⁵ (98)	1.3 x 10 ⁷ (26)
4	0.7	--	7.7 x 10 ⁵ (96)	<10 ² (99+)	1.4 x 10 ⁴ (99)
5	1.0	--	1.4 x 10 ³ (99)	<10 ² (99+)	<10 ² (99+)
Control A	--	1.8 x 10 ⁷	1.2 x 10 ⁷	1.1 x 10 ⁷	2.1 x 10 ⁷
Control B	--	2.2 x 10 ⁷	8.7 x 10 ⁶	1.0 x 10 ⁷	2.3 x 10 ⁷
Average Control = 1.8 x 10 ⁷ cfu/ml					

TABLE 8

ACID FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
1	0.1	--	3.2 x 10 ⁷ (0)	2.6 x 10 ⁷ (10)	2.7 x 10 ⁷ (7)
2	0.3	--	3.0 x 10 ⁷ (0)	2.2 x 10 ⁷ (24)	2.6 x 10 ⁷ (10)
3	0.5	--	3.2 x 10 ⁷ (0)	2.7 x 10 ⁷ (7)	2.5 x 10 ⁷ (14)
4	0.7	--	2.5 x 10 ⁷ (14)	1.6 x 10 ⁷ (45)	2.2 x 10 ⁷ (24)
5	1.0	--	2.3 x 10 ⁷ (21)	1.8 x 10 ⁷ (38)	1.2 x 10 ⁷ (58)
Control A	--	3.2 x 10 ⁷	3.0 x 10 ⁷	2.6 x 10 ⁷	2.5 x 10 ⁷
Control B	--	2.9 x 10 ⁷	3.6 x 10 ⁷	3.3 x 10 ⁷	2.8 x 10 ⁷
Average Control = 2.9 x 10 ⁷ cfu/ml					

As can be seen in the results presented in Tables 7 and 8, the methods of the present invention were effective in

controlling microbial growth in both acid and alkaline paper stock. The percent kill generally increased as the concentration of biocide increased.

EXAMPLE V

The method of the present invention, again using the inhibitor of Example I, was compared against the use of NaBr alone. Antimicrobial efficacy in 1% acid and 1% alkaline fine paper stock, prepared as described in Example I, was evaluated. Twelve tissue culture flasks were prepared, six containing 100 g of acid paper stock and six containing 100 g of alkaline paper stock. The twelve flasks were maintained in a temperature controlled water bath equipped with a shaking mechanism in the manner described above in Example I. In addition, two acid paper stock flasks and two alkaline paper stock flasks were maintained as controls to which no biocide was added. Three different bacteria were introduced to each of the twelve flasks as described above in Example I. The two different biocides used in Example II included Towerbrom R 60M, which had about 7% active bromine, and sodium bromide (NaBr), which had about 40% active bromine. Each biocide was added to two acid paper stock flasks and two alkaline paper stock flasks. The active concentration (ppm) of each biocide added to each flask is recorded in Tables 9 and 10. Following addition of the bacteria and biocide, the procedures as described in Example I were carried out. The results are presented in Tables 9 and 10.

TABLE 9

ALKALINE FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
NaBr	1.0	--	2.6×10^7 (0)	1.3×10^7 (0)	2.6×10^7 (0)
NaBr	3.0	--	1.9×10^7 (0)	1.5×10^7 (0)	2.5×10^7 (0)
60M	1.0	--	1.8×10^4 (99)	$<10^2$ (99+)	$<10^2$ (99+)
60M	3.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
Control A	--	2.7×10^7	2.0×10^7	1.9×10^7	2.7×10^7
Control B	--	2.2×10^7	1.7×10^7	1.4×10^7	2.6×10^7
Average Control = 2.05×10^7 cfu/ml					

TABLE 10

ACID FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
NaBr	1.0	--	2.3×10^7 (0)	1.9×10^7 (0)	1.6×10^7 (11)
NaBr	3.0	--	2.0×10^7 (0)	1.8×10^7 (0)	1.5×10^7 (17)
60M	1.0	--	9.1×10^6 (49)	5.7×10^6 (68)	4.4×10^6 (76)
60M	3.0	--	1.4×10^3 (99)	2.4×10^3 (99)	2.0×10^3 (99)
Control A	--	2.2×10^7	2.0×10^7	2.0×10^7	1.0×10^7
Control B	--	2.2×10^7	2.3×10^7	1.6×10^7	1.9×10^7

TABLE 10 (continued)

ACID FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
Average Control = 1.8 x 10 ⁷ cfu/ml					

As can be seen in Tables 9 and 10, in both the acid and alkaline paper stock the performance of the NaBr alone was clearly inferior to that of the Towerbrom R product, and often failed to achieve any inhibition of microbial growth whatsoever.

The results of Example V demonstrate the superiority of a product containing NaBr with sodium dichloroisocyanurate over NaBr alone. These results also show that using a higher concentration of bromine does not necessarily mean a higher percent kill. Here, employing a product with only about 7% active NaBr was effective in reducing microbial growth in both acid and alkaline paper stock while the NaBr, which had a significantly higher bromine concentration, was not effective. Reducing the amount of bromine needed to control microbial growth translates into cost savings for the user.

EXAMPLE VI

The present invention, again using the inhibitor of Example I, was compared against the use of a typical oxidizing biocide--namely a mixture containing sodium bromide (NaBr) and sodium hypochlorite (bleach). A 1% acid paper stock and 1% alkaline paper stock were prepared and maintained in a water bath as described in Example I; 24 tissue culture flasks were prepared, with 12 containing the 1% acid paper stock and 12 containing the 1% alkaline paper stock. Three different bacteria were added to all of the flasks in the same manner as described above for Example I. Two flasks each of the acid paper stock and the alkaline paper stock were maintained as controls, again as described in Example I. To five flasks containing the acid paper stock and five flasks containing the alkaline paper stock were added concentrations of the inhibitor of Example I ranging from about 1.0 ppm to about 50.0 ppm as indicated in Tables 5 and 6. To five flasks containing the acid paper stock and five flasks containing the alkaline paper stock were added concentrations of the 0.1% NaBr/bleach mixture ranging from about 1.0 ppm to about 50.0 ppm as indicated in Tables 5 and 6. The 0.1% stock solution of NaBr/bleach was prepared by mixing about 2.65 grams of 40% active NaBr in about 18.9 grams of 5.25% active bleach. The NaBr and bleach were allowed to react for about two minutes, and diluted into about 1000 ml of deionized water. The resulting solution was then added to the paper stock in concentrations ranging from about 1.0 ppm to about 50.0 ppm. To prepare the flasks containing NaBr/bleach concentrations of 1 ppm, about 0.1 ml of the 1% NaBr/bleach stock solution was added to about 100 g of the paper stock; for an NaBr/bleach concentration of 5 ppm, about 0.5 ml of stock solution was added to about 100 g of paper stock; for an NaBr/bleach concentration of 10 ppm, about 1.0 ml of stock solution was added to about 100 g of paper stock; for an NaBr/bleach concentration of 25 ppm about 2.5 ml of stock solution was added to about 100 g of paper stock; and for an NaBr/bleach concentration of 50 ppm about 5.0 ml of stock solution was added to about 100 g of paper stock. All other test methods and conditions were as recited in Example IV. The test results for both the alkaline and acid paper stock are illustrated in Tables 11 and 12, respectively.

TABLE 11

ALKALINE FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
60M	1.0	--	2.5×10^3 (99)	$<10^2$ (99+)	$<10^2$ (99+)
60M	5.0	--	3.4×10^3 (99)	$<10^2$ (99+)	$<10^2$ (99+)
60M	10.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)
60M	25.0	--	$<10^2$ (99+)	$<10^2$ (99+)	$<10^2$ (99+)

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TABLE 11 (continued)

ALKALINE FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
60M	50.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)
NaBr + bleach	1.0	--	<10 ² (99+)	<10 ² (99+)	4.1 x 10 ⁵ (99)
NaBr + bleach	5.0	--	<10 ² (99+)	<10 ² (99+)	9.0 x 10 ² (99)
NaBr + bleach	10.0	--	1.8 x 10 ⁶ (95)	<10 ² (99+)	<10 ² (99+)
NaBr + bleach	25.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)
NaBr + bleach	50.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)
Control A	--	2.5 x 10 ⁷	2.1 x 10 ⁷	5.7 x 10 ⁷	3.4 x 10 ⁷
Control B	--	3.5 x 10 ⁶	9.8 x 10 ⁶	5.2 x 10 ⁶	5.6 x 10 ⁷
Average Control = 1.8 x 10 ⁷ cfu/ml					

TABLE 12

ACID FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
60M	1.0	--	1.7 x 10 ⁶ (92)	1.6 x 10 ⁶ (92)	1.3 x 10 ⁶ (94)
60M	5.0	--	1.0 x 10 ² (99)	<10 ² (99+)	9.0 x 10 ² (99)
60M	10.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)
60M	25.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)
60M	50.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)
NaBr + bleach	1.0	--	<10 ² (99+)	4 x 10 ² (99)	4.1 x 10 ⁴ (99)
NaBr + bleach	5.0	--	<10 ² (99+)	2 x 10 ² (99)	<10 ² (99+)
NaBr + bleach	10.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)
NaBr + bleach	25.0	--	1 x 10 ² (99)	<10 ² (99+)	<10 ² (99+)
NaBr + bleach	50.0	--	<10 ² (99+)	<10 ² (99+)	<10 ² (99+)

TABLE 12 (continued)

ACID FINE PAPER STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
Control A	--	2.7×10^7	1.9×10^7	2.1×10^7	1.8×10^7
Control B	--	2.5×10^7	2.6×10^7	2.2×10^7	1.6×10^7
Average Control = 2.0×10^7 cfu/ml					

As can be seen from the results presented in Tables 11 and 12, the percent kill when using the Towerbrom R 60M product was comparable to the percent kill when using the NaBr/bleach solution. These results demonstrate that the method of the present invention, which utilizes a composition having between about 5 to 15% active bromine, yielded results which were comparable to, if not superior to, the results achieved when using the NaBr/bleach solution, which contained about 40% active bromine. Such a significant reduction of bromide usage, while retaining approximately the same level of percent kill, demonstrates the clear advantage of the present invention over methods currently employed in the art.

EXAMPLE VII

The methods of the present invention were evaluated using two different types of paper stock obtained from a working paper mill. The two types of paper stock included pulp taken from the Jordan chest (Jordan), which was a thick stock, and pulp taken from the white water silo (WW), which was a thin stock. These two types of stock, both of which are alkaline, will be familiar to one having ordinary skill in the art.

Six flasks containing 100 g of the Jordan stock and six flasks containing 100 g of the WW stock were maintained in a temperature controlled water bath equipped with a shaking mechanism in the same manner as the alkaline paper stock flasks of Example I. Two flasks each of the Jordan and WW stock were maintained as controls, again as described in Example IV. To four of the flasks containing the Jordan stock and four of the flasks containing the WW stock were added the inhibitor of Example IV ranging from about 1.0 ppm to about 10.0 ppm, as indicated in Tables 13 & 14. In this example, the average control was determined individually for each reading, that is the readings at 1 hour, 3 hours and 24 hours, rather than having one average control for all of the readings as was done in Examples IV through VI. All other test methods and conditions were as recited in Example IV. The test results for both the WW and Jordan paper stock are illustrated in Tables 13 and 14, respectively.

TABLE 13

WW STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
60 M	1.0	--	1.3×10^7 (21)	1.1×10^7 (41)	3×10^7 (0)
60 M	3.0	--	6.9×10^4 (100)	8.4×10^4 (100)	4.7×10^7 (0)
60 M	5.0	--	1.0×10^2 (100)	1.0×10^2 (100)	8.8×10^6 (68)
60 M	10.0	--	1.0×10^2 (100)	1.0×10^2 (100)	1.0×10^2 (100)
Control A	--	1.5×10^7	1.3×10^7	1.5×10^7	2.9×10^7
Control B	--	1.4×10^7	2.0×10^7	2.2×10^7	2.6×10^7
Average Control	--	1.5×10^7	1.7×10^7	1.9×10^7	2.8×10^7

TABLE 14

JORDAN STOCK					
Sample	ppm	Bacteria cfu/ml (%Kill)			
		0 hour	1 hour	3 hours	24 hours
60 M	1.0	--	6.9×10^7 (16)	8.2×10^7 (0)	7.6×10^7 (0)
60 M	3.0	--	3.0×10^7 (63)	3.7×10^7 (49)	6.9×10^7 (0)
60 M	5.0	--	3.1×10^5 (100)	1.1×10^5 (100)	4.0×10^6 (39)
60 M	10.0	--	1.0×10^2 (100)	4.0×10^2 (100)	1.3×10^7 (80)
Control A	--	7.1×10^7	8.5×10^7	7.3×10^7	6.9×10^7
Control B	--	7.7×10^7	7.9×10^7	7.1×10^7	6.3×10^7
Average Control	--	7.4×10^7	8.2×10^7	7.2×10^7	6.6×10^7

As can be seen from the results presented in Tables 13 and 14, the methods of the present invention were effective in controlling microbial growth in both the thin and thick alkaline paper stock. In general, the percent kill increased with the amount of inhibitor which was added.

Claims

1. A method for inhibiting microbial growth in a paper processing system which method includes adding alkali bromide to the processing system and is characterised in that a chlorinated isocyanurate is also added to the processing system.
2. A method as claimed in claim 1 and wherein the chlorinated isocyanurate comprises dichloroisocyanuric acid or a salt thereof or trichloroisocyanuric acid or a salt thereof.
3. A method as claimed in claim 2 and wherein the chlorinated isocyanurate comprises trichloroisocyanuric acid.
4. A method as claimed in claim 2 and wherein the chlorinated isocyanurate comprises anhydrous sodium dichloroisocyanurate.
5. A method as claimed in claim 1, claim 2 or claim 3 or claim 4 and wherein the weight ratio of the chlorinated isocyanurate to the alkali bromide in the composition formed in the paper processing system is greater than 3:1.
6. A method as claimed in any one of the preceding claims and wherein the weight ratio of the chlorinated isocyanurate to the alkali bromide is in the range of from about 5:1 to about 99.5:0.5.
7. A method as claimed in any one of the preceding claims and wherein the said alkali bromide is sodium bromide.
8. A method as claimed in any one of the preceding claims and wherein said microbial growth is inhibited by continuously feeding an effective amount of said dichloroisocyanurate in an anhydrous form and said alkali bromide to the system being treated.
9. A method as claimed in any one of the preceding claims and wherein the chlorinated isocyanurate and alkali bromide are added to the paper processing system as a single composition.
10. A method as claimed in claim 9 and wherein the chlorinated isocyanurate is between about 85% and 95% by weight of the composition delivered to the system and the alkali bromide is between about 5% and 15% by weight

of the composition delivered to the system.

11. A method as claimed in claim 9 or claim 10 and wherein said composition delivered to the system contains about 30 to 95% of available chlorine.

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12. A method as claimed in claim 9, 10 or 11 and wherein said microbial growth is inhibited by slug feeding an effective amount of the isocyanurate and said alkali bromide to the system being treated.

13. A method as claimed in claim 9, claim 10, claim 11 or claim 12 and wherein at least about 0.1 ppm of said composition is added to said system being treated.

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14. A composition comprising a paper process stream containing an effective amount of a composition comprising a) a chlorinated isocyanurate and b) an alkali bromide, wherein the weight ratio of component a) to component b) is greater than 3:1.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 3281

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	WO-A-96 11882 (LONZA AG ;SWEENEY PHILIP GERDON (US)) 25 April 1996 * page 6, line 7 - line 23; claims 1,2,4,8 *	1,5,6,9, 10,12,14	D21H21/04
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A	--- US-A-3 328 294 (SELF ET AL) 27 June 1967 see whole document -----		
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			D21H
Place of search	Date of completion of the search	Examiner	
MUNICH	29 July 1996	Naeslund, P	
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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