Abstract:
The present invention relates to the use of quaternary ammonium borate compositions as biocides and/or paper additives in pulp and/or paper processing.
THE USE OF QUATERNARY AMMONIUM BORATES AS ANTI-FUNGAL, ANTI-MILDEW, ANTI-MOLD BIOCIDES FOR PULP AND PAPER PROCESSING

SUMMARY OF THE INVENTION

[0001] The present invention relates to a method of controlling mold, fungus, and/or mildew in pulp and/or paper processing. More particularly, the present invention relates to the use of quaternary ammonium borate compositions as biocides and/or paper additives in pulp and paper processing.

BACKGROUND OF THE INVENTION

[0002] Paper manufacturing generally involves a series of processes that can be roughly grouped into five major manufacturing categories, 1) pulp production, 2) pulp processing and the recovery of chemicals used during pulp processing, 3) pulp bleaching, if a white paper is the desired end product, 4) refining or preparation of the stock used to produce paper, and 5) the manufacturing of a paper product. During the paper manufacturing process, biocidal agents are used to control the growth of many microorganisms because the growth or presence of these microorganisms is detrimental to the paper manufacturing process. For example, the presence of these microorganisms can cause increased sheet breaks, wet-end depositions, and increased usage of various additives used in the papermaking process.

[0003] In the past, oxidizing agents have been used to control microorganisms in the papermaking process. While the use of these oxidizer such as sodium hypochlorite can be effective, by their very nature, oxidizing compounds are not persistent, and are "spent" or "consumed" in a rapid fashion, leaving the system unprotected with regard to biocidal action. In the paper industry this is especially the case because of the presence of organic materials such as fiber, starch, etc. materials in the process. Typically, these organic materials react with and consume the oxidizer, making it much less effective at controlling microbial populations. Thus, it has been common practice to overdose the paper system with oxidizing biocides, which suffers from its own drawbacks. For example, the overdosing of oxidizers can cause an increased usage of wet-end chemicals such as sizing agents along with higher corrosion rates and reduced felt life.

SUMMARY OF THE INVENTION

[0004] The present invention relates to the use of quaternary ammonium borate compositions as a biocide in the manufacturing of paper products. Quaternary ammonium borate compositions suitable for this purpose include quaternary ammonium compounds having the formula:
wherein Y is selected from $\text{H}_2\text{BO}_3^-$; $\text{HBO}_3^{2-}$; $\text{BO}_3^{3-}$; $\text{B}_4\text{O}_7^{2-}$; $\text{HB}_4\text{O}_7^-$; $\text{B}_3\text{O}_5^-$; $\text{B}_5\text{O}_8^{2-}$; and $\text{BO}_2^-$; $R_1$, $R_2$, $R_3$ and $R_4$ are independently selected from $i)$ substituted or unsubstituted alkyl groups or $ii)$ substituted or unsubstituted alkenyl groups, wherein if $i)$ or $ii)$ is substituted, they have one or more substituent groups selected from aryl, heterocycyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or o xo groups; and m is 1, 2, or 3, depending on the selection of Y.

[0005] Although the present invention is suitable for use in both acidic or basic papermaking processes, it is especially well-suited for use in basic (alkaline) papermaking processes.

**DETAILED DESCRIPTION OF THE INVENTION**

[0006] The "quaternary ammonium borate compositions" (sometimes referred to herein simply as quats) used in the present invention have the general formula:

$$\begin{array}{c}
\begin{array}{c}
R_1 \\
R_3 \\
R_4
\end{array} \\
\begin{array}{c}
N^+ \\
R_2
\end{array}
\end{array} : Y$$

wherein Y is a borate counter-anion and m can be 1, 2, 3, 4, or 5, depending on the selection of Y. Borate anions suitable for use herein include the dihydrogen borate anion, $\text{H}_2\text{BO}_3^-$; the hydrogen borate anion, $\text{HBO}_3^{2-}$; the borate anion, $\text{BO}_3^{3-}$; the tetraborate anion, $\text{B}_4\text{O}_7^{2-}$; the hydrogen tetraborate anion, $\text{HB}_4\text{O}_7^-$; $\text{B}_3\text{O}_5^-$; pentaborate, $\text{B}_5\text{O}_8^{2-}$; and $\text{BO}_2^-$. Thus, Y is suitably selected from $\text{H}_2\text{BO}_3^-$; $\text{HBO}_3^{2-}$; $\text{BO}_3^{3-}$; $\text{B}_4\text{O}_7^{2-}$; $\text{HB}_4\text{O}_7^-$; $\text{B}_3\text{O}_5^-$; $\text{B}_5\text{O}_8^{2-}$; and $\text{BO}_2^-$. It is preferred that Y is $\text{BO}_3^{3-}$, and m is 3.

[0007] The four carbon chains, i.e. $R_1$, $R_2$, $R_3$ and $R_4$, of the quats used in the present invention are independently selected from $i)$ substituted or unsubstituted alkyl groups or $ii)$
substituted or unsubstituted alkenyl groups, wherein if/\) or \(H\) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups. Alkyl and alkenyl groups suitable for use in the quats are those that contain in the range of from 1 to 20 carbon atoms. In preferred embodiments, \(R_i\) and \(R_2\) are independently chosen from alkenyl groups having in the range of from 1 to 3 carbon atoms, and \(R_3\) and \(R_4\) are independently chosen in the range of from 6 to 20 carbon atom-containing groups selected from \(i\) substituted or unsubstituted alkenyl groups or \(H\) substituted or unsubstituted alkenyl groups, wherein if \(i\) or \(H\) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups; and \(m\) is 1, 2, or 3. In a more preferred embodiment, \(R_1\) and \(R_2\) are methyl groups and \(R_3\) and \(R_4\) are independently selected from unsubstituted alkyl groups containing in the range of from 8 to 14 carbon atoms. In one embodiment, one of \(R_3\) or \(R_4\) is an unsubstituted alkyl group containing in the range of from 8 to 10 carbon atoms, and one of \(R_3\) or \(R_4\) is an unsubstituted alkyl group containing in the range of from 12 to 14 carbon atoms.

[0008] In other embodiments of the present invention, at least one, sometimes only one and in other embodiments only two, of the four carbon chains, i.e. \(R_i, R_2, R_3\) and \(R_4\), is selected from \(i\) substituted or unsubstituted alkyl groups that contain from 13 to 16, sometimes 14 to 16, sometimes 14, carbon atoms or \(u\) substituted or unsubstituted alkenyl groups that contain from 13 to 16, sometimes 14 to 16, sometimes 14, carbon atoms, wherein if \(i\) or \(u\) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups. These carbon chains can be saturated or unsaturated, preferably unsubstituted. In these embodiments, it is particularly preferred to select unsaturated substituted or unsubstituted, preferably unsubstituted, alkyl groups containing from 13 to 16, sometimes 14 to 16, sometimes 14, carbon atoms. In these embodiments, at least two, in some embodiments only two, and in other embodiments three, of \(R_i, R_2, R_3\) and \(R_4\) are independently chosen from alkyl groups having from 1 to 4, sometimes 1 to 3, in some embodiments 2 to 4, carbon atoms. In these embodiments, it is also contemplated that one of \(R_i, R_2, R_3\) and \(R_4\) be selected from \(i\) substituted or unsubstituted alkyl groups or \(u\) substituted or unsubstituted alkenyl groups, wherein if \(i\) or \(u\) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups. The alkyl and alkenyl groups are those that contain from 1 to 20 carbon atoms. In preferred embodiments, the one of \(R_i, R_2, R_3\) and \(R_4\) is chosen from 6 to 20 carbon atom-containing
groups selected from i) substituted or unsubstituted alkyl groups or ii) substituted or unsubstituted alkenyl groups, wherein if i) or ii) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups; and m is 1, 2, 3, 4, or 5, sometimes 1, 2, or 3. In some embodiments, it is selected from unsubstituted alkyl groups containing from 8 to 14 carbon atoms. In other embodiments, it is selected from unsubstituted alkyl group containing from 8 to 10 carbon atoms, and in other embodiments, it is selected from unsubstituted alkyl groups containing from 12 to 14 carbon atoms.

[0009] In some embodiments of the present invention, it is preferred that at least two of the four carbon chains be independently selected chosen from alkyl groups having from 1 to 4, sometimes 1 to 3, in some embodiments 2 to 4, carbon atoms, and two of the four carbon chains be independently chosen from 6 to 20 carbon atom-containing groups selected from i) substituted or unsubstituted alkyl groups or ii) substituted or unsubstituted alkenyl groups, wherein if i) or ii) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups; and m is 1, 2, 3, 4, or 5, sometimes 1, 2, or 3, wherein ranges as described above are contemplated and the two of the four carbon chains independently chosen from 6 to 20 carbon atom-containing groups contain different numbers of carbon atoms.

[0010] In other embodiments of the present invention, at least one, sometimes only one and in other embodiments only two, of the four carbon chains, i.e. Ri, R2, R3 and R4, is selected from i) substituted or unsubstituted alkyl groups that contain from 13 to 16, preferably 14 to 16, more preferably 14, carbon atoms or ii) substituted or unsubstituted alkenyl groups that contain from 13 to 16, preferably 14 to 16, more preferably 14, carbon atoms, wherein if i) or ii) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups. These carbon chains can be saturated or unsaturated, preferably unsubstituted. In these embodiment, it is particularly preferred embodiment, to select unsaturated substituted or unsubstituted, preferably unsubstituted, alkyl groups containing from 13 to 16, preferably 14 to 16, more preferably 14, carbon atoms. In these embodiments, at least two, in some embodiments only two, and in other embodiments three, of R1, R2, R3 and R4 are independently chosen from alkyl groups having from 1 to 4, preferably 1 to 3, in some embodiments 2 to 4, carbon atoms. In these embodiments, it is also contemplated that one of R1, R2, R3 and R4 be selected from i) substituted or unsubstituted alkyl groups or ii) substituted or unsubstituted alkenyl groups, wherein if i) or ii) is substituted, they have one or more substituent groups
selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups. The alkyl and alkenyl groups are those that contain from 1 to 20 carbon atoms. In preferred embodiments, the one of R1, R2, R3 and R4 is chosen from 6 to 20 carbon atom-containing groups selected from i) substituted or unsubstituted alkyl groups or ii) substituted or unsubstituted alkenyl groups, wherein if i) or ii) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups; and m is 1, 2, or 3. In some embodiments, it is selected from unsubstituted alkyl groups containing from 8 to 14 carbon atoms. In other embodiments, it is selected from unsubstituted alkyl group containing from 8 to 10 carbon atoms, and in other embodiments, it is selected from unsubstituted alkyl groups containing from 12 to 14 carbon atoms.

[0011] In another embodiment, m is 2, and one of the four organic radicals of a quat may be a "shared" radical with a second quat. It should be noted that while in this embodiment R4 is shown as the shared radical, the shared radical can be any of R1, R2, R3, or R4. In this embodiment, the quaternary ammonium compounds used in the practice of the present invention have the general formula:

\[ \text{Y} \]

\[ \text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4 \]

[0012] In this embodiment, R1, R2, R3, R4, are as described above including preferred embodiments, and Y is selected from those anions described above having an ionic charge of -2, in some embodiments a borate anion having an ionic charge of -2, in some embodiments, HBO3^-2.

[0013] In another embodiment when m is 2, and one of the four organic radicals of a quat may be a "shared" radical with a second quat, the quaternary ammonium compounds used in the present invention have the general formula:
[0014] In this embodiment, R₁, R₂, R₃, R₄ are as described above including preferred embodiments, and each Y is independently selected from borate anions having an ionic charge of -1, in other embodiments each Y is H₂BO₃⁻. It should be noted that while in this embodiment R₄ is shown as the shared radical, the shared radical can be any of R₁, R₂, R₃, or R₄.

[0015] In another embodiment m is 3, and one of the four organic radicals of a quat is a "shared" radical with a second quat. In this embodiment, the quaternary ammonium compounds used in the coating formulations of the present invention can have the general formula:

[0016] In this embodiment, R₁, R₂, R₃, and R₄ are as described herein including preferred embodiments, and one Y is independently selected from the borate counter-anions described above having an ionic charge of -2 and the other Y is selected from borate counter-anions having an ionic charge of -1. In some embodiments, one Y is selected from H₂BO₃⁻; HB₄O₇⁻; B₃O₆⁻; and BO₂⁻ and the other Y is selected from HBO₃⁻; B₄O₇⁻; and B₅O₈⁻². It should be
noted that while in this embodiment $R_4$ is shown as the shared radical, the shared radical can be any of $R_1$, $R_2$, $R_3$, or $R_4$.

[0017] In another embodiment when $m$ is 3, and one of the four organic radicals of a quat may be a "shared" radical with a second quat, the quaternary ammonium compounds used in the present invention have the general formula:

$$Y: \begin{array}{c}
R_1 \\
R_2 \\
R_3 \\
R_4
\end{array} : Y$$

[0018] In this embodiment, $R_1$, $R_2$, $R_3$, and $R_4$ are as described above including preferred embodiments, and each $Y$ is independently selected from those borate counter anions having a net ionic charge of -1. In some embodiments, each $Y$ is independently selected from $H_2BO_3^{-}$; $HB_4O_7^{-}$; $B_3(V$. It should be noted that while in this embodiment $R_4$ is shown as the shared radical, the shared radical can be any of $R_1$, $R_2$, $R_3$, or $R_4$.

[0019] In some embodiments, $m$ is 3 and $Y$ is $BO_3^{-3}$. In these embodiments, the quaternary ammonium compounds used in the present invention have the general formula:

$$\begin{array}{c}
R_1 \\
R_2 \\
R_3 \\
R_4
\end{array} BO_3^{-3}$$
In this embodiment, R₁, R₂, R₃, or R₄ are as described above including preferred embodiments. It should be noted that while in this embodiment R₄ and R₂ are shown as the shared radicals, the shared radicals can be independently any of Ri, R₂, R₃, or R₄ or any combinations thereof. For example, R₄ and R₁ can be the shared radicals, Ri and R₂ can be the shared radicals, etc. Also, all three nitrogen atoms can share the same radical group, independently selected from Rj, R₂, R₃, or R₄.

In some embodiments, one, in some embodiments more than one, quaternary ammonium compound(s) having the formula can be used:

\[
\begin{array}{c}
R' \quad N^+ \quad R_2 \\
R_3 \\
R_1 \\
\end{array}
\]

\[
[O \quad B \quad O] \\
R'' \\
R'' \\
\]

wherein R₁, R₂, R₃, Y, and m are as described above, R' is a hydrocarbon group having from 1-10 carbon atoms, in some embodiments in the range of from 1 to 5, in some embodiments in the range of from 1 to 3, and R" and R'" are independently selected from i) substituted or unsubstituted alkyl groups or ii) substituted or unsubstituted alkenyl groups, wherein if i) or ii) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups. In some embodiments R" and R'" are selected from unsubstituted alkyl groups having in the range of from 1 to 20 carbon atoms, in some embodiments in the range of from 1 to 15, and in other embodiments in the range of from 6 to 14.

The quats of the present invention can be prepared by any methods known in the art, exemplary methods include those described in commonly-owned co-pending applications PCT US2005/010162 and US 60/730,821, which are incorporated herein by reference in their entirety.

The processes used in the production of quats, such as those described in commonly-owned co-pending applications PCT US2005/010162 and US 60/730,821, typically produce quats in an aqueous solution. The aqueous solution typically comprises water, at least one
polar organic co-solvent, and one or more quats, as described herein. These aqueous solutions generally have a polar organic co-solvent to water ratio in the range of from about 10:90 up to about 99:1 (wt. co-solvent: wt. water based on the combination of the water and polar organic co-solvent), and the exact amount of the polar organic co-solvent and water is selected according to the selection of Ri, R2, R3 and R4. In general, it is preferred that the ratio of co-solvent : water, by weight and on the same basis, is within the range of from about 50:50 to about 99:1, about 60:40 to about 99:1 is more preferred, about 70:30 to about 98:2 is even more preferred, and about 80:20 to about 95:5 is yet more preferred.

[0024] It has generally been found that aqueous solutions having a higher ratio of co-solvent to water are preferred for quats containing very hydrophobic alkyl substituent groups, e.g., double tailed or twin tailed quats where the alkyl groups are C10 - C20, for example, while aqueous solutions having a lower ratio of co-solvent to water are preferred for boron-quats having less hydrophobic alkyl substituent groups, e.g., a (C2 - C6) alkyltrimethylammonium salt.

[0025] It should be understood that the aqueous solutions comprise water, at least one polar organic co-solvent and the quat(s) according to the present invention. However, when describing the amount of water and polar organic co-solvent in the aqueous solution above, these ratios were based on the amount of polar organic co-solvent and water. Thus, when considering the amounts of these components and the quat in the prophylactic solution, the mixture is a ternary composition comprising at least three major components, water, polar organic co-solvent, and the quat "salt". Thus, the ratio of the components of the aqueous solution can be represented as a ratio of wt. quat: wt. polar organic co-solvent: wt. water, based on the aqueous solution. By way of example, an aqueous solution formed by adding 25% by weight of a quat salt to a mixture comprising an 85:15 by weight mixture of methanol: water, would have a ternary composition, by weight, of 25:64:11, quat salt: methanol: water by weight, based on the aqueous solution.

[0026] Because of economic and/or process considerations these aqueous solutions generally have a concentration of quat(s) ranging from about 1 to about 50 wt.% quat, based on the aqueous solution.

[0027] Thus, in some embodiments, the quaternary ammonium betaine compositions are contained in an aqueous solution, as described above. In some embodiments, the aqueous solutions are metal coupler free. By metal coupler free, it is meant that the aqueous solutions do not contain metals such as copper, mercury, lead, cadmium, hexavalent chromium, arsenic, antimony, or zinc. These metals are commonly used for their biocidal properties.
However, these and other "heavy" metals pose certain environmental concerns, thus, it would be beneficial to use biocides without these heavy metals.

[0028] In the practice of the present invention, the quaternary ammonium borate compositions can be used as a biocide in any step of the papermaking process. For example, the quaternary ammonium borate compositions can be used as an effective biocide in the pulping area or in the wet end. It should be noted that the quaternary ammonium borate compositions of the present invention can also be applied to the paper sheet to provide the end paper product with desired characteristics, discussed below. In some embodiments, the quaternary ammonium borate compositions can be applied to the paper sheet at the size press. In some embodiments, the quaternary ammonium borate compositions can be applied to the paper sheet and used as a biocide in the wet end and/or in the pulping process.

[0029] The inventors hereof, while not wishing to be bound by theory, believe that the application of quaternary ammonium borates to the paper sheet or use of the same in the wet end can impart at least one of, preferably at least two of, more preferably substantially all of, the following properties to the final paper product: i) fungicidal properties, ii) mildewcidal properties, iii) biocidal properties, and iv) termite repellant properties. Further, in preferred embodiments, the quats of the present invention are effective at imparting some flame retardant properties to the treated paper. By "some flame retardant properties" it is meant that the paper containing the quaternary ammonium borate compositions does not ignite, and or burn when exposed to flame, as readily as paper that does not contain the quaternary ammonium borate compositions.

[0030] It should be noted that by "repelling termites", it is meant that the termites do not feed on the quat treated paper, will crawl across the quat-treated paper without feeding on it, and in essence resort to cannibalistic behavior for food instead of feeding on the quat treated paper. The inventors hereof, while not wishing to be bound by theory, believe that the termites do not recognize the paper as a food source.

[0031] In order to achieve these characteristics, the final paper product comprises an effective amount of the quaternary ammonium borate composition. By an effective amount, it is meant that the treated paper comprises in the range of from about 1 to about 30 wt.%, based on the weight of the treated paper sheet, of the quaternary ammonium borate composition. In preferred embodiments, the treated paper comprises from about 5 to about 10 wt.% of the quaternary ammonium borate composition, on the same basis.

[0032] If the quat is used as a biocide in the papermaking process, it is added until an effective mount of quat is present in the area where biocidal activity is desired. For example,
if the quat is used as a biocide in the white water, the amount of quat added is that amount necessary to provide for a quat concentration in the range of from about 10,000 to about 300,000 ppm of the quat is present in the white water, preferably in the range of from about 50,000 to about 100,000 ppm. Likewise, if the quat is used as a biocide in a pulp storage chest, the amount of quat present in the pulp storage chest is added is in the range of from about 10,000 to about 300,000 ppm of the quat is present in the chest, preferably in the range of from about 50,000 to about 100,000 ppm. Likewise, if the quat is used as a biocide in the pulping process, the amount ofquat added is that amount necessary to maintain a quat concentration in the range of from about 10,000 to about 300,000 ppm of the quat, preferably in the range of from about 50,000 to about 100,000 ppm. It should be noted that it is within the present invention to add the quaternary ammonium composition either batch-wise or continuously to maintain a satisfactory concentration of quat. However, it is preferred that the quat be continuously metered to maintain the concentration of quat.

[0033] The above description is directed to several embodiments of the present invention. Those skilled in the art will recognize that other embodiments, which are equally effective, could be devised for carrying out the spirit of this invention. It should also be noted that preferred embodiments of the present invention contemplate that all ranges discussed herein include ranges from any lower amount to any higher amount.

[0034] The following examples will illustrate the present invention, but are not meant to be limiting in any manner.
WHAT IS CLAIMED

1) The use of quaternary ammonium borate compositions as biocides in the manufacturing of paper and/or in the manufacture of wood pulp used in the manufacturing of paper, wherein said quaternary ammonium borate compositions have the formula:

\[
\begin{array}{c}
\text{R}_1 \\
\text{N}^+ \\
\text{R}_2 \\
\text{R}_3 \\
\text{R}_4 \\
m
\end{array}
\]

wherein \( Y \) is selected from \( \text{H}_2\text{BO}_3^-; \text{HBO}_3^{2-}; \text{BO}_3^{3-}; \text{B}_4\text{O}_7^{2-}; \text{HB}_4\text{O}_7^-; \text{B}_5\text{O}_5^3-; \text{B}_8\text{O}_{10}^{7-}; \) and \( \text{BO}_2^-; \) \( \text{R}_i, \text{R}_2, \text{R}_3 \) and \( \text{R}_4 \) are independently selected from \( i) \) substituted or unsubstituted alkyl groups or \( ii) \) substituted or unsubstituted alkenyl groups, wherein if \( i) \) or \( ii) \) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups; and \( m \) is 1, 2, or 3, depending on the selection of \( Y \).

2) The use according to claim 1 wherein said quaternary ammonium borate compositions are used to control mold, mildew, and fungus.

3) The use according to claim 2 wherein \( \text{R}_1 \) and \( \text{R}_2 \) are independently chosen from alkyl groups having in the range of from 1 to 3 carbon atoms, and \( \text{R}_3 \) and \( \text{R}_4 \) are independently chosen from 6 to 20 carbon atom-containing groups selected from \( i) \) substituted or unsubstituted alkyl groups or \( ii) \) substituted or unsubstituted alkenyl groups, wherein if \( i) \) or \( ii) \) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups.

4) The use according to claim 2 wherein \( \text{R}_i \) and \( \text{R}_4 \) are methyl groups and \( \text{R}_3 \) and \( \text{R}_4 \) are independently selected from unsubstituted alkyl groups containing from 8 to 14 carbon atoms.

5) The use according to claim 4 wherein one of \( \text{R}_3 \) or \( \text{R}_4 \) is an unsubstituted alkyl group containing in the range of from 8 to 10 carbon atoms, and one of \( \text{R}_3 \) or \( \text{R}_4 \) is an unsubstituted alkyl group containing in the range of from 12 to 14 carbon atoms.

6) The use according to claim 1 wherein \( Y \) is \( \text{BO}_3^{3-} \), and \( m \) is 3.
7) The use according to claim 1 wherein said quaternary ammonium borate compositions are used as a biocide in the wet end of the papermaking process or as an additive to the paper sheet, said additive optionally applied at the size press.

8) The use according to claim 7 wherein said use of said quaternary ammonium borate compositions impart to the paper product resulting from the paper making process at least one of the following properties: i) fungicidal properties, ii) mildewcidal properties, iii) biocidal properties, and iv) termite repellant properties.

9) The use according to claim 8 wherein said paper product resulting from the paper making process comprises in the range of from about 1 to about 30wt.% of said quaternary ammonium borate compositions, based on the total weight of the paper product resulting from the paper making process.

10) The use according to claim 1 wherein said quaternary ammonium borate compositions are used as a biocide in the wet end or in the pulping process, wherein the amount of quaternary ammonium borate composition used is that amount necessary to provide for a concentration of quaternary ammonium borate compositions in the range of from about 10,000 to about 300,000 ppm.

11) The use according to claim 10 wherein said quaternary ammonium borate compositions are continuously metered to maintain said concentration.

12) The use according to claim 10 wherein said quaternary ammonium borate compositions are added batchwise to maintain said concentration.

13) The use according to claim 1 wherein said quaternary ammonium composition has the formula:

\[
\begin{array}{c}
\text{\text{R}}_3 \overset{\text{N}^+}{\text{R}}_2 \\
\text{O} \overset{\text{R}'}{\text{B}} \overset{\text{O}}{\text{R}''}
\end{array}
\]

\[
\begin{align*}
\text{Y} & : \text{m}
\end{align*}
\]
wherein \( Y \) is selected from \( \text{H}_2\text{BO}_3^-; \text{HBO}_3^{2-}; \text{BO}_3^{3-}; \text{B}_4\text{O}_7^{2-}; \text{HB}_4\text{O}_7^-; \text{B}_3\text{O}_5^-; \text{B}_5\text{O}_8^{2-}; \text{BO}_2^-; \) \( R_1, R_2, R_3 \) and \( R_4 \) are independently selected from \( i) \) substituted or unsubstituted alkyl groups or \( ij) \) substituted or unsubstituted alkenyl groups, wherein if \( i) \) or \( U) \) is substituted, they have one or more substituent groups selected from aryl, heterocycl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups; and \( m \) is 1, 2, or 3, depending on the selection of \( Y \); \( R \) is a hydrocarbon group having from 1-10 carbon atoms, in some embodiments in the range of from 1 to 5, in some embodiments in the range of from 1 to 3, and \( R^" \) and \( R^" \) are independently selected from \( l) \) substituted or unsubstituted alkyl groups or \( ul) \) substituted or unsubstituted alkenyl groups, wherein if \( i) \) or \( if) \) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups.

14) Paper containing at least one quaternary ammonium borate composition, wherein said quaternary ammonium borate compositions have the formula:

\[
\begin{array}{c}
\text{N}^+ \\
\text{R}_1 \\
\text{R}_2 \\
\text{R}_3 \\
\text{R}_4 \\
\text{m}
\end{array}
\]

wherein \( Y \) is selected from \( \text{H}_2\text{BO}_3^-; \text{HBO}_3^{2-}; \text{BO}_3^{3-}; \text{B}_4\text{O}_7^{2-}; \text{HB}_4\text{O}_7^-; \text{B}_3\text{O}_5^-; \text{B}_5\text{O}_8^{2-}; \text{BO}_2^-; \) \( R_1, R_2, R_3 \) and \( R_4 \) are independently selected from \( i) \) substituted or unsubstituted alkyl groups or \( U\) substituted or unsubstituted alkenyl groups, wherein if \( i) \) or \( U) \) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups; and \( m \) is 1, 2, or 3, depending on the selection of \( Y \).

15) The paper according to claim 14 wherein said paper has at least one of the following properties: \( i) \) fungicidal properties, \( if) \) mildewcidal properties, \( iii) \) biocidal properties, and \( iv) \) termite repellant properties.

16) The paper according to claim 15 wherein said paper has some flame retardant properties.

17) The paper according to claim 14 wherein said quaternary ammonium composition has the formula:
wherein \( Y \) is selected from \( \text{H}_2\text{BO}_3^{\cdot} \); \( \text{HBO}_3^{2\cdot} \); \( \text{BO}_3^{3\cdot} \); \( \text{B}_4\text{O}_7^{2\cdot} \); \( \text{HB}_4\text{O}_7^{\cdot} \); \( \text{B}_3\text{O}_5^{\cdot} \); \( \text{B}_5\text{O}_8^{2\cdot} \); and \( \text{BO}_2^{\cdot} \); \( \text{R}_1 \), \( \text{R}_2 \), \( \text{R}_3 \) and \( \text{R}_4 \) are independently selected from \( i \) substituted or unsubstituted alkyl groups or \( H \) substituted or unsubstituted alkenyl groups, wherein if \( i \) or \( u \) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups; and \( m \) is 1, 2, or 3, depending on the selection of \( Y \); \( \text{R}' \) is a hydrocarbon group having from 1-10 carbon atoms, in some embodiments in the range of from 1 to 5, in some embodiments in the range of from 1 to 3, and \( \text{R}'' \) and \( \text{R}''' \) are independently selected from \( i \) substituted or unsubstituted alkyl groups or \( H \) substituted or unsubstituted alkenyl groups, wherein if \( j \) or \( H \) is substituted, they have one or more substituent groups selected from aryl, heterocyclyl, hydroxyl, ester, benzyl, carboxyl, halo, nitro, cyano, alkoxy or oxo groups.

18) The paper according to claim 17 wherein \( \text{R}'' \) and \( \text{R}''' \) are selected from unsubstituted alkyl groups having in the range of from 1 to 20 carbon atoms, in some embodiments in the range of from 1 to 15, and in other embodiments in the range of from 6 to 14.