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IMPROVEMENTS IN OR RELATING TO PRESERVATIVES AND/OR BIOCIDES
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- (56) Prior Art Documents
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- (57) Claim

1. A method of preparing a biocidal and/or preservative composition

comprising the steps of:

reacting an organic complexing agent selected from the group consisting of 1,2 diols, 1,3 diols, 1,3,5 triols and polyhydroxy macrolide-type compounds with a borate and/or boric acid to produce a borate organic complex ion;

and further reacting said complex ion with a cationic species selected from the group consisting of ions of copper, zinc, barium, magnesium, calcium, iron, manganese, cobalt, and nickel; alkyl (C₉ - C₁₆) dimethyl amines, dialkyl (C₇ - C₁₄) methyl amines, alkyl (C₉ - C₁₆) dimethyl benzyl ammonium, dialkyl (C₇ - C₁₄) dimethyl ammonium and biocidally active substituted triazole compounds.

11. A biocidal and/or preservative composition comprising a borate organic complex ion and a cationic species wherein said borate organic complex ion comprises a 1,2 diol, 1,3 diol, 1,3,5 triol or polyhydroxy macrolide-type organic moiety that has been complexed with a borate and/or boric acid and said

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cationic species is selected from the group consisting of ions of copper, zinc, barium, magnesium, calcium, iron, manganese, cobalt, and nickel; alkyl ($C_9 - C_{16}$) dimethyl amines, dialkyl ($C_7 - C_{14}$) methyl amines, alkyl ($C_9 - C_{16}$) dimethyl benzyl ammonium, dialkyl ($C_7 - C_{14}$) dimethyl ammonium and biocidally active substituted triazole compounds.

17. A composition comprising 2-chloro-4-(1,1,3,3-tetra methyl butyl)-6-methylol-phenol complexed with a borate and/or boric acid and further complexed with copper cations and dissolved in kerosene.

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COMPLETE SPECIFICATION

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Complete Specification for the invention entitled:

IMPROVEMENTS IN OR RELATING TO PRESERVATIVES AND/OR BIOCIDES.

The following statement is a full description of this invention including the best method of performing it known to me:-

This invention relates to a composition and/or a method of preparing a composition, having biocidal properties against certain microbiological or macrobiological organisms, or both, for example, against certain fungi, insects and molluscs, and which is intended particularly though not necessarily solely for use in the preservation of timber.

It is therefore an object of the present invention to provide a biocidal and/or preservative composition and/or a method of preparing a biocidal and/or preservative composition which will at least provide the public with a useful choice.

Accordingly, in one aspect the invention consists in a method of preparing a biocidal and/or preservative composition comprising the steps of:

reacting an organic complexing agent selected from the group consisting of 1,2 diols, 1,3 diols, 1,3,5 triols and polyhydroxy macrolide-type compounds with a borate and/or boric acid to produce a borate organic complex ion;

and further reacting said complex ion with a cationic species selected from the group consisting of ions of copper, zinc, barium, magnesium, calcium, iron, manganese, cobalt, and nickel; alkyl (C₉ - C₁₆) dimethyl amines, dialkyl (C₇ - C₁₄) methyl amines, alkyl (C₉ - C₁₆) dimethyl benzyl ammonium, dialkyl (C₇ - C₁₄) dimethyl ammonium and biocidally active substituted triazole compounds.

Preferably said organic complexing agent is selected from the group consisting of naphthalene diols, phenyl glycols, glycerol ethers, dihydroxy phenyl compounds, dihydroxy anthracene compounds, methylol phenols, methylol naphthols, methylol anthrols, aliphatic 1, 2 diols, aliphatic 1, 3 diols, and triol



monoesters.

The invention also consists in a biocidal and/or preservative composition comprising a borate organic complex ion and a cationic species wherein said borate organic complex ion comprises a 1,2 diol, 1,3 diol, 1,3,5 triol or
5 polyhydroxy macrolide-type organic moiety that has been complexed with a borate and/or boric acid and said cationic species is selected from the group consisting of ions of copper, zinc, barium, magnesium, calcium, iron, manganese, cobalt, and nickel; alkyl ($C_9 - C_{16}$) dimethyl amines, dialkyl ($C_7 - C_{14}$) methyl amines, alkyl ($C_9 - C_{16}$) dimethyl benzyl ammonium, dialkyl ($C_7 - C_{14}$) dimethyl
10 ammonium and biocidally active substituted triazole compounds.

The invention also consists in a compound comprising:-

- (i) copper cations and;
- (ii) anions formed by a complexing of 2-chloro-4-(1,1,3,3-tetra methyl butyl)-6-methylol-phenol with a borate and/or boric acid.

In a further aspect the invention also consists in a method of controlling
15 fungi, insects and/or molluscs which comprise applying to a locus where such control is required a biocidally effective amount of a compound or composition as described in the preceding two paragraphs.

To those skilled in the art to which the invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the scope of the invention as defined in the appended claims. The disclosures and the descriptions herein are purely illustrative and are not intended to be in any sense limiting.



Presently preferred forms of the invention will now be described with reference to specific examples.

By way of example, one part of 2-chloro-4(1,1,3,3-tetra methyl butyl)-6-methylol-phenol was dissolved in three parts of kerosene and this solution is contacted and agitated for a short time (1 to 2 minutes) with an equal amount of aqueous solution containing 3% Borax. After agitation ceases the aqueous and organic phases separate. The organic layer can be analysed for Boron prior to use as, for example, a fungicide/insecticide in an organic solvent timber preservative. The aqueous layer can be replenished with further Borax prior to reuse.

The organic layer can be reacted further to produce biocidally more effective compounds for example as follows.

The organic layer is separated from the original aqueous layer, said organic layer being further contacted and agitated for a short time (1 to 2 minutes) with an aqueous solution containing 3% of a copper salt, for example, copper sulphate. The transfer of the copper cation to the organic phase can be followed by a darkening of colour of the organic phase.

After agitation ceases the aqueous and organic phases separate. The organic layer can be analysed for Copper and boron prior to use as a biocide.

Depending on the hydrophobicity of the diols and triols or polyhydroxy compounds used or the complexes formed one or a mixture of a range of solvents can be chosen. Examples of such solvents include white spirits, kerosene, chlorinated solvents (including Freons), aromatic esters, phosphate esters or alcohols (having 4 to 17 carbon atoms per molecule).

High capacity can be achieved at ambient temperatures, that is to say up to about 20% boric acid.

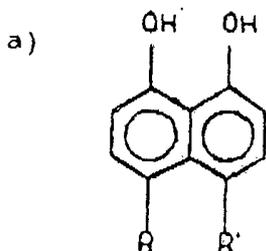
It has been shown that certain alcohols, eg. 1-octanol, have a synergistic effect in preparation of the complexes when used as a co-solvent.

Thus boric acid and borates can be seen to form complexsalts stable to a greater or lesser degree, with organic alcohols. The alcohols are preferably 1,2 or 1,3 diols or 1,3,5, triols but can include polyhydroxy macrolide type compounds.

Possible complexing agents include;

1. Naphthalene Diols

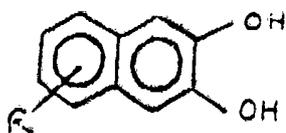
For example:



FORMULA I

where R,R' are independently selected from the group consisting of hydrogen, halogen and aliphatic radicals of 1 to 8 carbon atoms;

b)

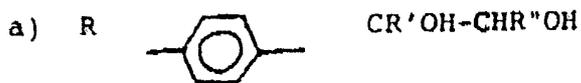


where R is defined as above;

FORMULA II

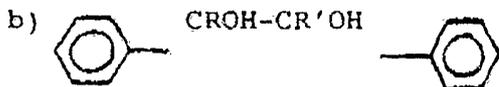
2. Phenyl Glycols

For example:



FORMULA III

where R is selected from the group consisting of hydrogen, halogen and aliphatic radicals of 1 to 15 carbon atoms; and R' is selected from the group consisting of hydrogen and aliphatic radicals of 1 to 8 carbon atoms and R'' is selected from the group consisting of hydrogen, and aliphatic radicals of 1 to 8 carbon atoms, and phenyl substituents;

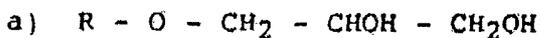


FORMULA IV

where R is selected from the group consisting of hydrogen and aliphatic radicals of 1 to 8 carbon atoms; and R' is selected from the group consisting of hydrogen and aliphatic radicals of 1 to 8 carbon atoms.

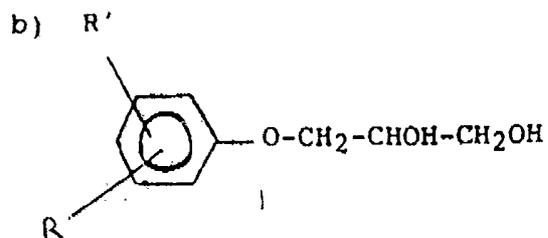
3. Glycerol Ethers

For example:



FORMULA V

where R is selected from the group consisting of saturated and unsaturated aliphatic radicals of 1 to 15 carbon atoms;

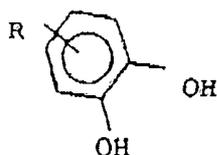


FORMULA VI

where R, R' are independently selected from the group consisting of hydrogen, halogen, aliphatic radicals of 1 to 10 carbon atoms and halogen substituted aliphatic radicals of 1 to 10 carbon atoms.

4. Dihydroxy Phenyl Compounds

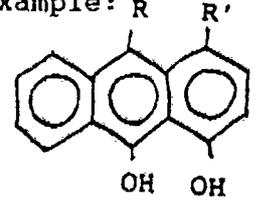
For example:

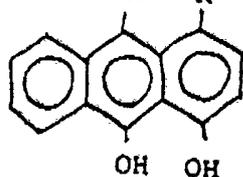


FORMULA VII

where R is an aliphatic radical of 1 to 15 carbon atoms, or is phenyl or cyclohexyl.

5. Dihydroxy Anthracene Compounds

For example: 

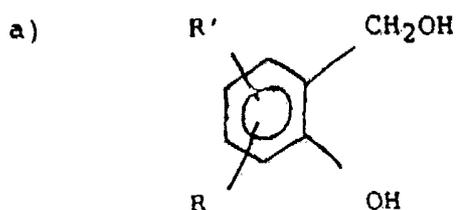


FORMULA VIII

where R, R' are independently selected from the group consisting of hydrogen, halogen and aliphatic radicals of 1 to 8 carbon atoms.

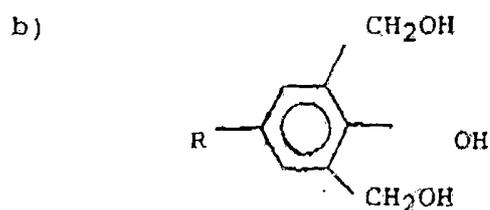
6. Methylol Phenols, Methylol Naphthols, Methylol Anthrols

For example:



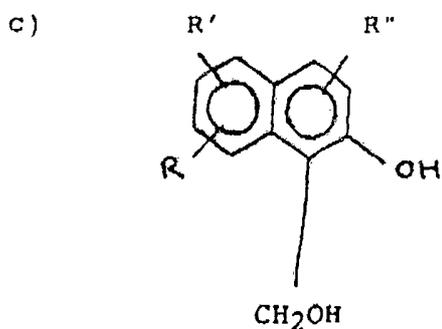
FORMULA IX

where R, R' are independently selected from the group consisting of hydrogen, halogen, cyclopentyl, cyclohexyl, phenyl and aliphatic radicals of 1 to 15 carbon atoms;



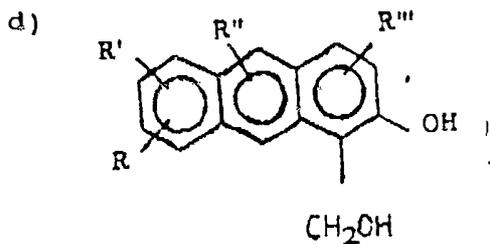
FORMULA X

where R is selected from the group consisting of aliphatic radicals of 1 to 15 carbon atoms, phenyl and cyclohexyl substituents;



FORMULA XI

where R, R', R'', are independently selected from the group consisting of hydrogen, halogen and aliphatic radicals of 1 to 8 carbon atoms;



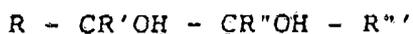
FORMULA XII

where R, R', R'', R''' are independently selected from the group consisting of hydrogen, halogen and aliphatic radicals of 1 to 8 carbon atoms.

atoms.

7. Aliphatic 1, 2 Diols

For example:

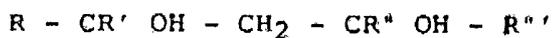


FORMULA XIII

where R, R', R'', R''' are independently selected from the group consisting of aliphatic radical of 1 to 8 carbon atoms, cyclohexyl and cyclopentyl substituents.

8. Aliphatic 1, 3 Diols

For example:

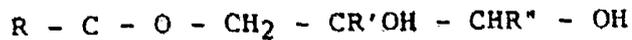


FORMULA XIV

where R, R', R'', R''' are independently selected aliphatic radicals of 1 to 8 carbon atoms.

9. Triol Monoesters

For example:

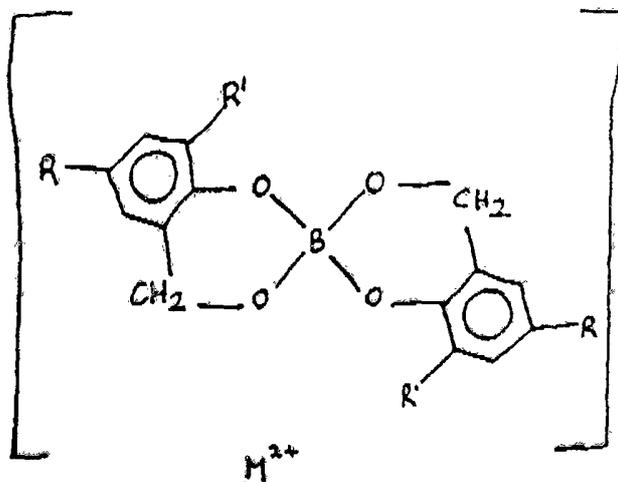


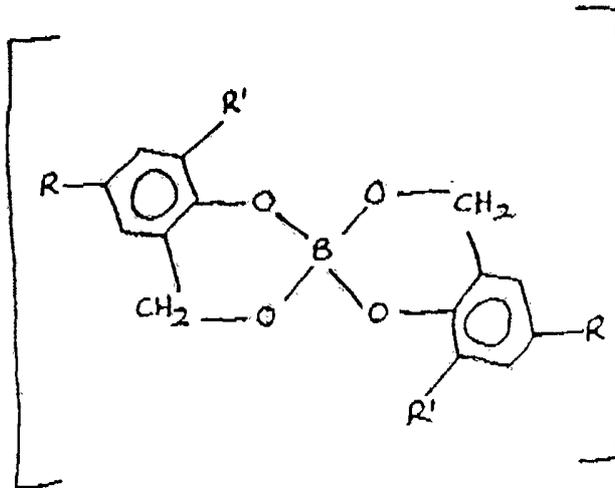
FORMULA XV

where R, R', R'' are independently selected aliphatic radicals of 1 to 15 carbon atoms.

The preferred biocidally active cationic species is, for example copper or zinc but other cations such as hydrogen, barium, sodium, potassium, magnesium, calcium, iron, manganese, cobalt or nickel can be used. Also other suitable inorganic or organic species may be used. The species may be introduced by shaking the solvent containing the alkali metal organic complex boron salt in contact with an aqueous solution of, for example, a copper salt, for example, copper sulphate, so that the alkali metal for example sodium in the organic complex is replaced by copper ions.

Where the metal ion can be characterised as M^{2+} then the complex could be

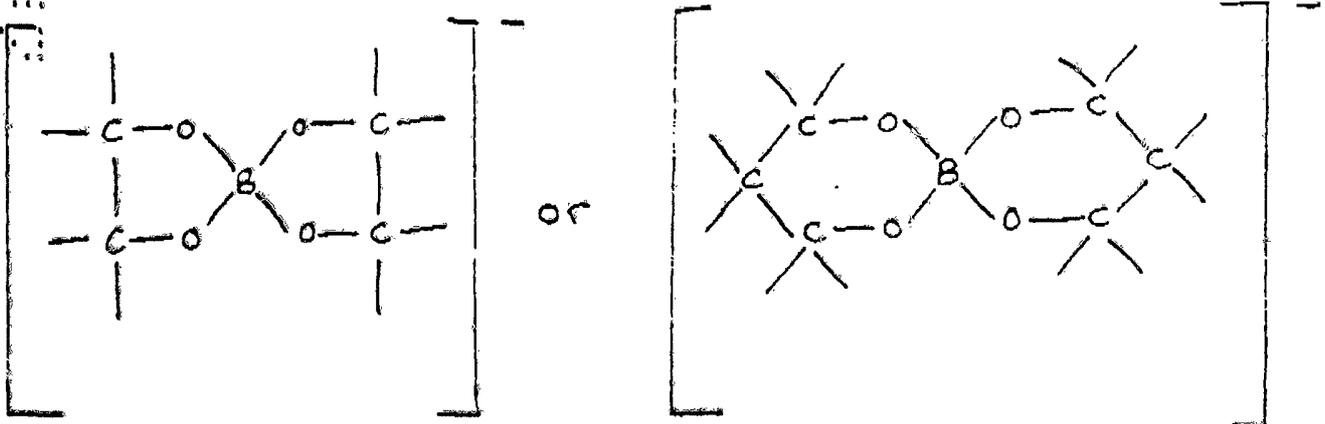




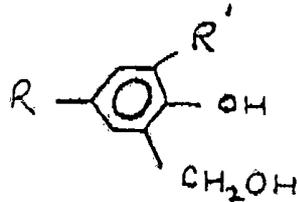
FORMULA XVI

where R, R' are independently selected from the group consisting of hydrogen, halogen, cyclopentyl, cyclohexyl, and phenyl substituents and aliphatic radicals of 1 to 15 carbon atoms.

Boron completes the octet of electrons in its outer shell by forming anionic complexes such as:



Many of the complexes described have very low solubility in water and therefore once distributed into for example a timber matrix should offer substantial resistance to leaching. An example of those with low solubility is a complex formed using the following diol:



FORMULA XVII

where R is an aliphatic radical with 4 to 15 carbon atoms. R' is halogen or an aliphatic radical with 1 to 15 carbon atoms.

The organic complex ion boron salts provided by the invention can be used for example to treat timber substantially in the known manners utilising vacuum pressure treatment or variations of this process or by diffusion into the timber.

In a further use the organic complex ion boron salt can be mixed with resins in solution or emulsion form to provide preservation of paint or to provide anti-fouling properties in marine paints or surface coatings for example to ships.

As a marine anti-fouling paint there would be little or no water contamination as copper and boron do not adversely effect sea water.

The organic complex ion boron salts may be used in agricultural applications to eliminate fungi, insects, molluscs or other organisms, which can restrict yields of produce.

Where aqueous carriers are preferred for a particular reason the complex ion boron salts may be utilised in the form of emulsions or micro emulsions which can be preferred for ease

of handling or to reduce expense by using a cheaper carrying solvent.

By way of example, one commercially important area of use of the complex ion boron salts is in the area of timber preservation.

Many chemicals used in timber preservation of the present time are unacceptable for environmental reasons and restrictions are being applied to their use. These chemicals include arsenic, pentachlorophenol and tri butyl tin compounds. Boron chemicals can be used in some situations as a replacement for these chemicals but due to high aqueous solubility these boron compounds are also less suitable as they readily leach out of the timber, reducing efficacy.

The organic complex ion boron salts provided by the present invention are preferable since they have reduced solubility in water.

To illustrate the use in timber preservation, solutions of an organic complex ion boron salt and an organic complex ion boron salt containing copper were separately used to treat matched samples of Pinus radiata wood. Treated samples and control samples were exposed to several fungal species and also were placed in a fungal cellar in contact with contaminated soil. Comparisons with other known wood preservative fungicides showing improved efficacy are given in Table I.

TABLE I

Toxic threshold values

<u>Fungus</u>	<u>Preservative Complex</u>	<u>Toxic Threshold % w/w</u>
<u>Coriolus versicolor</u>	Boron + Copper	<0.03
<u>Coriolus versicolor</u>	Boron only	0.10-0.13
<u>Coriolus versicolor</u>	TBTO	0.025-0.05
<u>Coniophora puteana</u>	Boron + Copper	0.1-0.13
<u>Coniophora puteana</u>	Boron only	0.1-0.13
<u>Coniophora puteana</u>	TBTO	0.025-0.05
<u>Gloeophyllum abietinum</u>	Copper + Boron	<0.03
<u>Gloeophyllum abietinum</u>	Boron only	0.06-0.1
<u>Gloeophyllum abietinum</u>	TBTO	<0.025
<u>Trametes lilacinoqilva</u>	Boron + Copper	<0.03
<u>Trametes lilacinoqilva</u>	Boron only	0.03-0.06
<u>Trametes lilacinoqilva</u>	TBTO	<0.025

Mean soundness figures after six months in a fungal cellar also showing the efficacy of the complexes, are given in Table II.

TABLE II

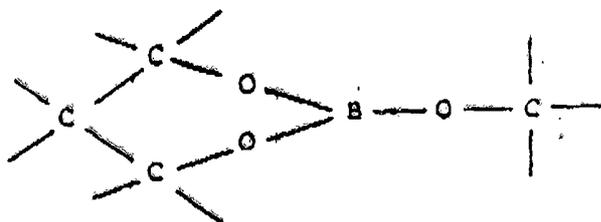
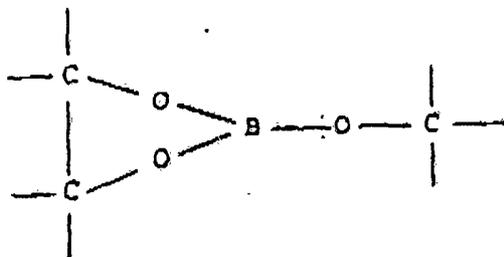
	<u>Retention % w/w</u>	<u>Soundness %</u>
Copper + Boron	0.08	94
Boron only	0.08	78
TBTO	0.08	78

Thus it can be seen that a method of treatment of timber and/or timber treated by such method are provided which have particular advantages.

Tests were carried out to determine efficacy against molluscs. Very weak solutions both in organic solvent and as an aqueous emulsion were applied to an inert surface (glass) and to plant surfaces and molluscs such as snails and slugs were encouraged to travel across the surfaces. In all cases sufficient biocide was assimilated to kill the molluscs. It was also shown that at the concentration used the biocide was not phytotoxic to the plants.

There are many chemicals known in the art which have biocidal properties. However in certain end uses the choice of chemical is restricted by factors including high cost, environmental limitations or difficulties in formulating the compositions to obtain the physical properties required or desired for a particular end use.

Organic boron esters of the type



have been proposed as timber preservatives. These compounds are non ionic and are very sensitive to hydrolysis, releasing free

boric acid which is easily leached reducing efficacy and usefulness in severe situations.

Boron compounds, which are relatively low in toxicity to humans but have good efficacy against lower forms of life, are incorporated into the compounds of the present invention, with the option of incorporating biocidally active cations as described hereinabove, copper, zinc, and other metallic cations and suitable including cationic organic species, in an organic complex ion salt, thus combining the benefits of the biocidally active components while obviating some or all of the disadvantages associated with earlier proposed formulations.

The present compounds have potential for use in many areas including replacement of, for example, tri butyl tin compounds in antifouling paints or timber preservatives, where said tin compounds are becoming environmentally unacceptable, and copper naphthenate in timber preservatives where the strong colour of the copper naphthenate may be a disadvantage. It is believed there is potential for use in preservation in wide ranging areas where insecticidal, fungicidal, molluscicidal, crustacacidal or the like properties are required.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of preparing a biocidal and/or preservative composition comprising the steps of:

reacting an organic complexing agent selected from the group consisting of 1,2 diols, 1,3 diols, 1,3,5 triols and polyhydroxy macrolide-type compounds with a borate and/or boric acid to produce a borate organic complex ion;

and further reacting said complex ion with a cationic species selected from the group consisting of ions of copper, zinc, barium, magnesium, calcium, iron, manganese, cobalt, and nickel; alkyl (C₉ - C₁₆) dimethyl amines, dialkyl (C₇ - C₁₄) methyl amines, alkyl (C₉ - C₁₆) dimethyl benzyl ammonium, dialkyl (C₇ - C₁₄) dimethyl ammonium and biocidally active substituted triazole compounds.

2. A method as claimed in Claim 1 wherein said organic complexing agent is selected from the group consisting of naphthalene diols, phenyl glycols, glycerol ethers, dihydroxy phenyl compounds, dihydroxy anthracene compounds, methylol phenols, methylol naphthols, methylol anthrols, aliphatic 1,2 diols, aliphatic 1,3 diols, and triol monoesters.

3. A method as claimed in Claim 1 or Claim 2 wherein said organic complexing agent comprises a methylol phenol.

4. A method as claimed in any one of the preceding claims wherein said

cationic species comprises ions of copper, zinc or barium.

5. A method as claimed in Claim 4 wherein said cationic species comprises ions of copper.

6. A method as claimed in any one of the preceding claims wherein said organic complexing agent is dissolved in a solvent prior to the step of reacting said organic complexing agent with said borate and/or boric acid, said solvent being selected according to the hydrophobicity of said organic complexing agent and/or said borate organic complex ion.

7. A method as claimed in Claim 6 wherein said solvent is selected from the group consisting of white spirits, kerosene, chlorinated solvents (including Freons), aromatic esters, phosphate esters and alcohols (having 4 to 27 carbon atoms per molecule).

8. A method as claimed in Claim 6 or Claim 7 wherein said organic complexing agent is dissolved in said solvent and a co-solvent.

9. A method as claimed in Claim 8 wherein said co-solvent comprises 1-octanol.

10. A method of preparing a biocidal and/or preservative composition comprising the steps of:



dissolving an organic complexing agent comprising 2-chloro-4-(1,1,3,3-tetra methyl butyl)-6-methyl-phenol in kerosene and reacting said organic complex agent with a borate and/or boric acid to form a borate organic complex ion and further reacting said organic complex ion with an aqueous solution of a copper salt.

11. A biocidal and/or preservative composition comprising a borate organic complex ion and a cationic species wherein said borate organic complex ion comprises a 1,2 diol, 1,3 diol, 1,3,5 triol or polyhydroxy macrolide-type organic moiety that has been complexed with a borate and/or boric acid and said cationic species is selected from the group consisting of ions of copper, zinc, barium, magnesium, calcium, iron, manganese, cobalt, and nickel; alkyl ($C_9 - C_{16}$) dimethyl amines, dialkyl ($C_7 - C_{14}$) methyl amines, alkyl ($C_9 - C_{16}$) dimethyl benzyl ammonium, dialkyl ($C_7 - C_{14}$) dimethyl ammonium and biocidally active substituted triazole compounds.

12. A composition as claimed in Claim 11 wherein said organic complexing agent is selected from the group consisting of naphthalene diols, phenyl glycols, glycerol ethers, dihydroxy phenyl compounds, dihydroxy anthracene compounds, methylol phenols, methylol naphthols, methylol anthrols, aliphatic 1,2 diols, aliphatic 1,3 diols, and triol monoesters.

13. A composition as claimed in claim 12 wherein said organic complexing



agent comprises a methylol phenol.

14. A composition as claimed in any one of Claims 11 to 13 wherein said cationic species comprises copper, zinc or barium.
15. A composition as claimed in any one of Claims 11 to 14 dissolved in a solvent selected from the group consisting of white spirits, kerosene, chlorinated solvents (including Freons), aromatic esters, phosphate esters and alcohols (having 4 to 27 carbon atoms per molecule).
16. A composition as claimed in Claim 15 dissolved in a co-solvent comprising 1-octanol.
17. A composition comprising 2-chloro-4-(1,1,3,3-tetra methyl butyl)-6-methylol-phenol complexed with a borate and/or boric acid and further complexed with copper cations and dissolved in kerosene.
18. A biocidal and/or preservative composition comprising:
- (i) copper cations and
 - (ii) anions formed by a complexing of 2-chloro-4-(1,1,3,3-tetra methyl butyl)-6-methylol-phenol with a borate and/or boric acid.
19. An anti-fouling paint including the composition as claimed in any one of



Claims 11 to 17 or the compound as claimed in Claim 18.

20. Use of a composition as claimed in any one of Claims 11 to 17 or a use of a compound as claimed in Claim 18 as a preservative and/or biocidal agent.

21. Use as claimed in Claim 20 wherein said compound or composition is used to treat timber.

22. A method of controlling fungi, insects and/or molluscs which comprises applying to locus where such control is required a biocidally effective amount of a composition as claimed in any one Claims 11 to 17 or a compound as claimed in Claim 18.

23. A method of preparing a biocidal and/or preservative composition as claimed in any one of Claims 1 to 10 and substantially as hereinbefore described with reference to the examples.

24. A biocidal and/or preservative composition as claimed in any one of claims 11 to 17 and substantially as hereinbefore described with reference to the examples.

25. Use biocidally and/or as a preservative of a composition as claimed in Claim 20 or Claim 21 and substantially as hereinbefore described with reference



to the examples.

26. A biocidal and/or preservative compound as claimed in Claim 18 and substantially as hereinbefore described with reference to the examples.

DATED THIS 16TH DAY OF JULY 1992

Nigel Paul MAYNARD

By his Patent Attorney:

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