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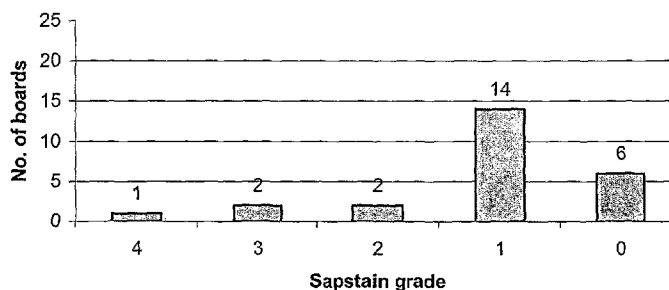
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(54) Title: WOOD PRESERVATIVE FORMULATIONS

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(57) **Abstract:** The invention provides formulations comprising an amine oxide, an azole and a compound of formula (I): $R^1-A-NR_p^2$ Wherein: R^1 denotes an alkyl group which contains from 6 to 24 carbon atoms, benzyl or substituted benzyl, or $(CH_2-CH_2O)_nH$ where $n = 1-20$; A is absent or denotes a linker group that may be $C=O$ or $-C=ONH(CH_2)_s-$ where $s = 1-3$; $P = 2$ or 3 ; and each R^2 , which are the same or different, denotes H , CH_3 , C_2H_5 , $(CH_2-CH_2O)_nH$ where $n = 1-20$, an alkyl group which contains from 6 to 24 carbon atoms, $(CH_2)_mCOOH$, $(CH_2)_mCOO^-$, $(CHX)_mSO_3H$ or $(CHX)_mSO_3^-$ where $m = 1$ to 3 and X denotes H or OH; and wherein if the compound is charged it is accompanied by a counterion X. The formulations of the invention are surprisingly effective at protecting wood and other cellulosic substrates, in particular at providing antisapstain activity. The invention also provides methods for treating wood and other cellulosic substrates with said formulations.

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Wood Preservative Formulations

The present invention relates to formulations for protecting wood and other cellulosic substrates against moulds, staining and other defacing organisms, and in particular to antisapstain applications.

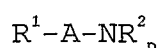
Antisapstain chemicals are used to protect timber, in particular freshly felled or sawn timber, from attack by moulds, sapstain and decay fungi which would otherwise discolour the timber and so reduce its value.

Commonly used chemicals in antisapstain formulations include 3-iodo-2-propynyl-butyl-carbamate (IPBC), quaternary ammonium compounds such as didecyldimethylammonium chloride (DDAC) and benzalkonium chloride (BAC), borates (such as Borax), triazoles, copper 8-hydroxyquinoline, alkyl amines and their salts, and fenpropimorph.

Combinations of IPBC, triazoles and quaternary ammonium compounds have been used commercially. Formulations containing boron, for example Antiblu Select (Arch Timber Protection, Ltd.) which contains BAC, IPBC and boric acid are also known. Amine oxides have also been described for use in antisapstain formulations (WO 2001/0189779, WO 2000/0071312).

However, there remains a need for alternative and improved wood preservative formulations, to address environmental concerns and customer pressure for ever more effective and competitive products. Improved azole containing formulations are of particular interest.

The present inventors have found that formulations comprising an amine oxide, an azole and a compound of formula (I)



(I)

wherein

- 2 -

R^1 denotes an alkyl group which contains from 6 to 24 carbon atoms, benzyl or substituted benzyl, or $(CH_2-CH_2O)_nH$ where $n = 1-20$;

A is absent or denotes a linker group that may be
 5 $C=O$ or $-C=ONH(CH_2)_s-$ where $s = 1-3$;

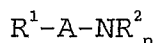
$p = 2$ or 3 ;

and each R^2 , which may be the same or different, denotes H, CH_3 , C_2H_5 , $(CH_2-CH_2O)_nH$ where $n = 1-20$, an alkyl group which contains from 6 to 24 carbon atoms,
 10 $(CH_2)_mCOOH$, $(CH_2)_mCOO^-$, $(CHX)_mSO_3H$ or $(CHX)_mSO_3^-$ where $m = 1$ to 3 and X denotes H or OH;

and wherein if the compound is charged it is accompanied by a suitable counterion X^-

are surprisingly effective at protecting wood, in
 15 particular at providing antisapstain activity.

Thus the present invention provides an antisapstain composition comprising an amine oxide compound, an azole compound and compound of formula (I)



20

(I)

wherein

R^1 denotes an alkyl group which contains from 6 to 24 carbon atoms, benzyl or substituted benzyl, or $(CH_2-CH_2O)_nH$ where $n = 1-20$;

25 A is absent or denotes a linker group that may be $C=O$ or $-C=ONH(CH_2)_s-$ where $s = 1-3$;

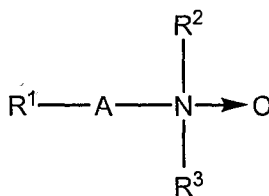
$P = 2$ or 3 ;

and each R^2 , which may be the same or different, denotes H, CH_3 , C_2H_5 , $(CH_2-CH_2O)_nH$ where $n = 1-20$, an alkyl
 30 group which contains from 6 to 24 carbon atoms, $(CH_2)_mCOOH$, $(CH_2)_mCOO^-$, $(CHX)_mSO_3H$ or $(CHX)_mSO_3^-$ where $m = 1$ to 3 and X denotes H or OH;

and wherein if the compound is charged it is accompanied by a suitable counterion X^- .

35 Preferably, the amine oxide is represented by the general formula (II)

- 3 -



(II)

wherein

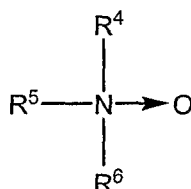
R^1 , R^2 and R^3 are independent and can be hydrogen, optionally substituted poly(oxyalkylene) or a linear, branched, cyclic, aromatic or any combination thereof of a saturated or unsaturated, substituted or unsubstituted C_1 to C_{40} group, preferably C_1 to C_{20} , or alternatively R^2 and R^3 together form a substituted or unsubstituted cyclic group;

A is absent or denotes a linker group that may be $-\text{C}=\text{ONH}(\text{CH}_2)_s-$ where $s = 1-3$;

wherein any of the carbon atoms other than those bound to the nitrogen atom shown in formula (II) may be replaced with a hetero atom, or alternatively any methyl group that forms part of R^1 , R^2 or R^3 other than one which is bound directly to the nitrogen atom shown in formula (II) may be replaced with a dimethyl amine oxide.

The amine oxide compound may be a trialiphatic substituted amine oxide, an *N*-alkylated cyclicamine oxide, a dialkylpiperazine di-*N*-oxide, an alkyl-di(poly(oxyalkylene))amine oxide, a dialkylbenzylamine oxide, a fatty amidopropyl dimethyl amine oxide, a diamine oxide, a triamine oxide, or any combination of any of the foregoing. Preferably, the amine oxide includes at least one C_8 - C_{18} alkyl moiety.

Preferred trialiphatic substituted amine oxides are represented by the general formula (III)



- 4 -

(III)

wherein R^4 , R^5 and R^6 are independent and can be linear, branched, cyclic, aromatic or any combination thereof of a saturated or unsaturated C_1 to C_{40} group
5 wherein any of the carbon atoms other than those bound to the nitrogen atom shown in formula (III) may be replaced with a hetero atom, particularly oxygen, sulphur or nitrogen. R^4 , R^5 and R^6 independently may be alkyl, alkenyl, or alkynyl groups. More preferably, R^4
10 is a linear, branched, cyclic or any combination thereof C_8 to C_{22} saturated or unsaturated group, such as coco, hydrogenated tallow, soya, decyl, hexadecyl, and oleyl; and R^5 and R^6 independently are linear, branched, or any combination thereof C_1 to C_{22} saturated or unsaturated
15 groups, such as coco, hydrogenated tallow, soya, decyl, and hexadecyl.

A preferred trialiphatic substituted amine oxide is dialkylmethylamine oxide having the formula $R^4R^5CH_3N \rightarrow O$, where R^4 and R^5 are defined as above. Another preferred
20 trialiphatic substituted amine oxide is an alkyl dimethylamine oxide having the formula $R^4(CH_3)_2N \rightarrow O$, where R^4 is defined as above. More preferred alkyl dimethylamine oxides have the formula $R^{22}(CH_3)_2N \rightarrow O$, where R^{22} is a linear or branched C_8 - C_{18} alkyl or alkenyl.
25 Preferably, R^{22} is a linear or branched C_8 - C_{16} alkyl. Alkyl dimethylamine oxides are non-toxic and non-mutagenic surfactants. Suitable alkyl dimethylamine oxides include, but are not limited to, a C_{10} alkyl dimethylamine oxide, a C_{10} - C_{14} alkyl dimethylamine
30 oxide, a C_{12} - C_{16} alkyl dimethylamine oxide, a C_{16} - C_{18} alkyl dimethylamine oxide, and any combination of any of the foregoing.

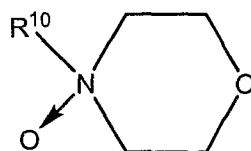
Preferred *N*-alkylated cyclicamine oxides have the formula $R^7R^8R^9N \rightarrow O$ where R^7 is defined as R^4 above. and R^8
35 and R^9 are linked to form a cyclic group. The cyclic group typically contains from 4 to 10 carbon atoms and

- 5 -

may optionally contain oxygen, sulphur, nitrogen, or any combination of any of the foregoing. More preferred *N*-alkylated cyclicamine oxides include, but are not limited to, an alkylmorpholine *N*-oxide, a

5 dialkylpiperazine di-*N*-oxide, and any combination of any of the foregoing.

Preferred alkylmorpholine *N*-oxides have the general formula (IV):



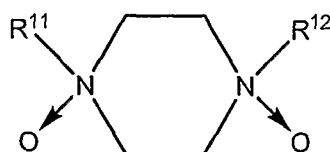
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(IV)

where R^{10} is defined as R^4 above. According to a more preferred embodiment, R^{10} is a linear or branched C_8 to C_{16} alkyl. Examples of preferred alkylmorpholine *N*-oxides include, but are not limited to, cetyl morpholine *N*-oxide and lauryl morpholine *N*-oxide.

15

Preferred dialkylpiperazine di-*N*-oxides have the general formula (V):

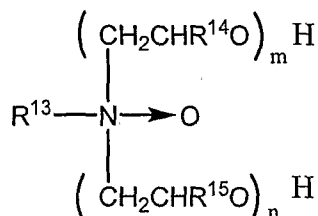


(V)

20 where R^{11} is defined as R^4 above and R^{12} is defined as R^5 above.

Preferred alkyl-di(poly(oxyalkylene))amine oxides have the general formula (VI):

- 6 -



(VI)

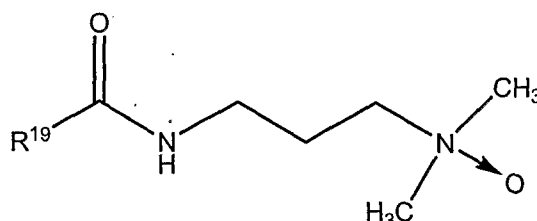
where R^{13} is defined as R^4 above; R^{14} and R^{15} independently are H or CH_3 ; and m and n independently are integers from about 1 to about 10.

5 Preferred dialkylbenzylamine oxides have the formula $\text{R}^{16}\text{R}^{17}\text{R}^{18}\text{N} \rightarrow \text{O}$, where R^{16} is defined as R^4 above; R^{17} is defined as R^5 above; and R^{18} is benzyl. More preferred dialkylbenzylamine oxides include, but are not limited to, alkylbenzylmethanamine oxides having the formula

10 $\text{R}^{16}\text{R}^{17}\text{CH}_2\text{N} \rightarrow \text{O}$ where R^{16} and R^{17} are defined as above. According to a more preferred embodiment, R^{16} is a linear or branched C_8 - C_{12} alkyl.

Preferred fatty amidopropyldimethylamine oxides have the general formula (VII):

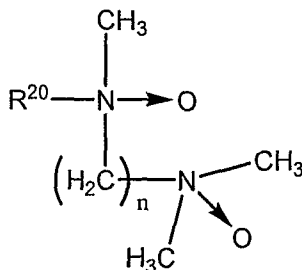
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(VII)

where R^{19} is defined as R^4 above.

Preferred diamine oxides have the general formula (VIII):



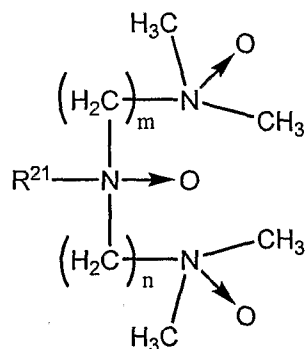
20

(VIII)

- 7 -

where R^{20} is defined as R^4 above; and n is an integer from about 1 to about 10.

Preferred triamine oxides have the general formula (IX) :



5

(IX)

where R^{21} is defined as R^4 above; and m and n independently are integers from about 1 to about 10.

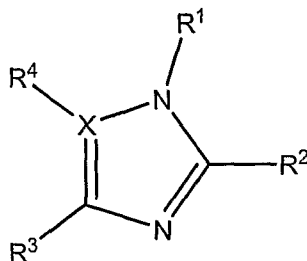
Particularly preferred amine oxides are alkyl dimethyl amine oxides such as decyl dimethyl amine oxide, lauryl dimethyl amine oxide, isoalkyl dimethyl amine oxide, myristyl dimethyl ethyl amine oxide, cetyl dimethyl amine oxide, stearyl dimethyl amine oxide and octyl dimethyl amine oxide. Particularly preferred is N-alkyl(C_{12} - C_{16})-N,N-dimethylamine oxide (ADO).

In addition a mixture of two or more amine oxides may be used, with a mixture, e.g. an equimolar mixture of C_{12} -N,N-dimethylamine oxide and C_{16} -N,N-dimethylamine oxide being especially preferred.

The formulations of the present invention comprise one or more azole compounds, i.e. a compound comprising an azole group. The azole compound may be an imidazole or a 1,2,4-triazole and is preferably represented by the general formula (X)

25

- 8 -



(X)

wherein

X denotes C or N;

- 5 R¹ denotes hydrogen or a linear, branched, cyclic, aromatic or any combination thereof of a saturated or unsaturated, substituted or unsubstituted C₁ to C₄₀ group wherein any of the carbon atoms other than those bound to the nitrogen atom shown in formula (X) may be
10 replaced with an optionally substituted hetero atom;

R² denotes hydrogen, C₁-C₈ alkyl, C₂-C₈ alkenyl, C₆-C₁₀ aromatic, C₅-C₁₀ heteroaromatic or C₁-C₄ alkyl carbamate;

R³ denotes hydrogen; or

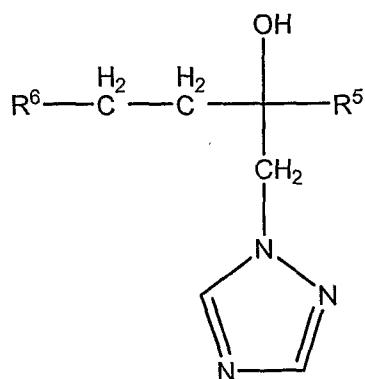
- 15 when X is C together with R⁴ may provide a benzimidazole group.

- The imidazole compound incorporates a five-membered diunsaturated ring composed of three carbon atoms and two nitrogen atoms at non-adjacent positions. The imidazole compound may be a benzimidazole. Preferred
20 compounds include thiabendazole, imazalil, carbendazim and prochloraz.

- The 1,2,4-triazole compound incorporates a five-membered diunsaturated ring composed of three nitrogen atoms and two carbon atoms at non-adjacent
25 positions.

Preferred triazole compounds include a triazole compound selected from compounds of formula (XI):

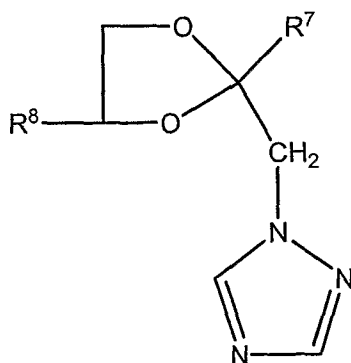
- 9 -



(XI)

wherein R⁵ represents a branched or straight chain C₁₋₅ alkyl group (e.g. t-butyl) and R⁶ represents a phenyl group optionally substituted by one or more substituents selected from halogen (e.g. chlorine, fluorine or bromine) atoms or C₁₋₃ alkyl (e.g. methyl), C₁₋₃ alkoxy (e.g. methoxy), phenyl or nitro groups.

Alternatively, the triazole compound is advantageously selected from compounds of formula (XII):



(XII)

wherein R⁷ is as defined for R⁶ above and R⁸ represents a hydrogen atom or a branched or straight chain C₁₋₅ alkyl group (e.g. n-propyl).

Particularly preferred triazoles include but are not limited to, triadimefon, triadimenol, triazbutil, propiconazole, cyproconazole, difenoconazole, fluquinconazole, tebuconazole, flusilazole, uniconazole, diniconazole, bitertanol, hexaconazole, azaconazole,

- 10 -

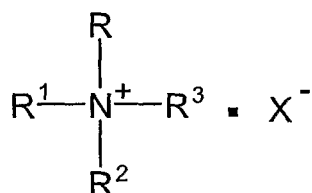
flutriafol, epoxyconazole, tetraconazole, penconazole, and mixtures thereof.

Most preferred triazoles are propiconazole, azaconazole, hexaconazole, tebuconazole, cyproconazole,
 5 triadimefon and mixtures thereof.

The compound of formula (I) may optionally be a quaternary ammonium compound, an amine or amine salt, a betaine or an amphoteric betaine compound. When the linker group A is absent, the R¹ group is directly bonded
 10 to the nitrogen.

Where the compound of formula (I) is positively charged, it is accompanied by an anion X⁻ which is chosen to allow ready water solubility. Examples of suitable anions include chloride, bromide, sulphate, acetate,
 15 propionate, lactate, citrate, methosulphate, hydroxide, carbonate and bicarbonate.

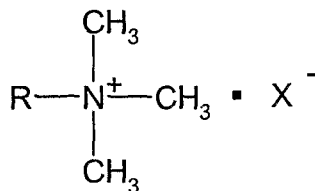
The compound of formula (I) may preferably be a quaternary ammonium compound, i.e. a compound derived from ammonium with all four hydrogen atoms replaced by
 20 organic groups and having the general formula (XIII):



(XIII)

Of the quaternary ammonium compounds which may be used in the compositions and methods of the present invention, suitable compounds include:

25 1. Monoalkyltrimethyl ammonium salts of formula (XIV):



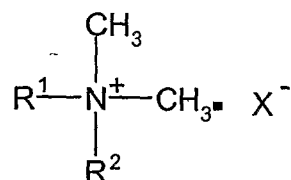
(XIV)

- 11 -

wherein R is an alkyl group having from 6 to 22 carbon atoms, preferably from 12 to 14 carbon atoms, and X⁻ is an anion chosen to allow ready water solubility of the quaternary ammonium salt. Examples being : chloride, bromide, sulphate, acetate, propionate, lactate, citrate, methosulphate, carbonate and bicarbonate.

Preferred examples include Cocotrimethyl ammonium chloride in which the alkyl group R consists of a mixture of predominantly C₁₂ and C₁₄.

2. Dialkyl dimethyl ammonium salts of formula (XV):

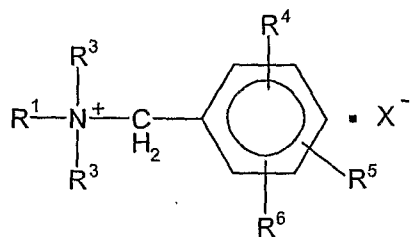


(XV)

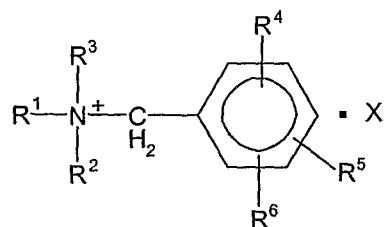
wherein R¹ and R² are alkyl groups which may be the same or different and which contain from 6 to 22 carbon atoms, preferably from 8 to 10 carbon atoms, and X⁻ is an anion of the type previously described.

Preferred examples include Didecyl dimethyl ammonium chloride, didecyl dimethyl ammonium carbonate, didecyl dimethyl ammonium bicarbonate, dioctyl dimethyl ammonium chloride and octyl decyl dimethyl ammonium chloride either individually or as a mixture containing two or three of these.

3. Alkyl dimethyl or diethyl benzyl ammonium salts and dialkyl methyl or ethyl benzyl ammonium salts of formulae (XVI) or (XVII):



and

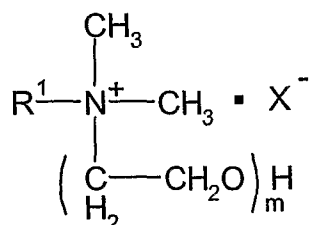


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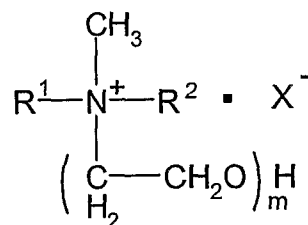
wherein R^1 and R^2 are alkyl groups which can be the same or different and which contain from 6 to 22 carbon atoms, preferably from 8 to 10 carbon atoms in a dialkyl compound and from 10 to 14 carbon atoms in a monoalkyl compound; R^3 is methyl or ethyl; R^4 , R^5 and R^6 are hydrogen or C_{1-8} alkyl groups; and X^- is an anion of the type previously described.

Preferred examples include Coco benzyl dimethyl ammonium chloride and dicoco benzyl methyl ammonium chloride in which the alkyl groups are predominantly C_{12} and C_{14} .

4. Alkyl and dialkyl oxyethylene methyl ammonium salts of formulae (XVIII) or (XIX):



(XVIII)



(XIX)

wherein R^1 and R^2 are alkyl groups which may be the same or different and which contain from 6 to 22 carbon atoms, preferably from 8 to 10 carbon atoms in a dialkyl compound and from 10 to 14 carbon atoms in a monoalkyl compound, most preferably 10 carbon atoms. m is a number from 1 to 20 typically from 1 to 8, preferably from 3 to 5. X^- is an anion of the type previously described, preferably propionate or lactate.

Preferred examples include N,N-didecyl-N-methyl-poly(oxyethyl) ammonium propionate (Bardap 26) or N,N-didecyl-N-methyl-poly(oxyethyl) ammonium lactate.

Benzalkonium chloride and benzalkonium hydroxide are especially preferred.

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Alternatively, the compound of formula (I) may preferably be a betaine. Betaines are advantageous as they are amphoteric and hence remove the need to have a potentially corrosive counterion.

5 Preferably, the betaine is selected from the group consisting of coco amido propyl dimethyl betaine; cetyl betaine((carboxylatomethyl) hexadecyldimethylammonium); C12 amine dipropionate; and coco amido propyl dimethyl
10 sultaine (cocoamidopropyl-N, N-dimethyl-N-2-hydroxypropyl sulfobetaine).

The betaine is, e.g. of the formula $R-N^+(CH_3)_2-CH_2-COO^-$; or $R-C(=O)N^+(CH_3)_2-CH_2-COO^-$ or a salt thereof where R is a straight chain C_6-C_{24} alkyl group, or a C_8-C_{18} alkyl group, or R is a straight chain $C_{12}-C_{16}$ alkyl group.

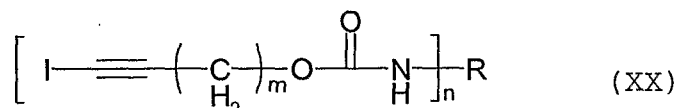
15 The betaine in one embodiment is a cocamidopropylbetaine of formula: $RC(=O)NH(CH_2)_3-N^+(CH_3)_2-CH_2-COO^-$ wherein R is a $C_{11}-C_{13}$ straight chain alkyl group.

The compound of formula (I) may be a dimethylalkylamine or salt thereof. A

20 dimethylalkylamine is an N,N-dimethyl-N-alkylamine where alkyl represents an alkyl chain with 6 to 20 carbon atoms, preferably 12 to 14 carbon atoms. In addition to pure dimethylalkylamines, it is also possible to use mixtures, for example dimethyl- C_{12} -alkylamine and
25 dimethyl- C_{14} alkylamine (dimethyl- C_{12}/C_{14} -alkylamine).

The compositions typically comprise one or more further active ingredients. Halopropynyl compounds are particularly preferred examples of additional active ingredients.

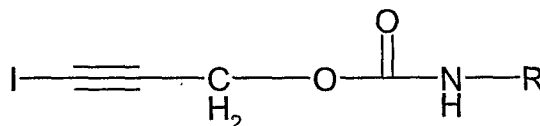
30 Preferred halopropynyl compounds are iodopropynyl carbamate compounds. The iodopropynyl carbamate compound is an ester or salt of carbamic acid. This class of compounds includes compounds of the general formula (XX):



- 14 -

wherein R is selected from the group consisting of hydrogen, substituted and unsubstituted alkyl groups having from 1 to 20 carbon atoms, substituted and unsubstituted aryl, alkyl aryl, and aralkyl groups having from 6 to 20 carbon atoms and from substituted and unsubstituted cycloalkyl and cycloalkenyl groups of 3 to 10 carbon atoms, and m and n are independently integers from 1 to 3, i.e., m and n are not necessarily the same.

Preferred are compounds where m is 1 and n is 1 having the following formula (XXI):



(XXI)

Suitable R substituents include alkyls such as methyl, ethyl, propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, octadecyl, cycloalkyls such as cyclohexyl, aryls, alkaryl and aralkyls such as phenyl, benzyl, tolyl, cumyl, halogenated alkyls and aryls, such as chlorobutryl and chlorophenyl, and alkoxy aryls such as ethoxyphenyl and the like.

Compounds of this formula include iodopropargyl carbamates such as 3-iodo-2-propynyl propyl carbamate, 3-iodo-2-propynyl butyl carbamate, 3-iodo-2-propynyl hexyl carbamate, 3-iodo-2-propynyl cyclohexyl carbamate, 3-iodo-2-propynyl phenyl carbamate, and mixtures thereof. Most preferred is 3-iodo-2-propynyl butyl carbamate (IPBC).

The inventors have shown that the efficacy of the formulations described is surprisingly greater than would be expected based on an additive effect. Therefore synergy is taking place. Thus preferred compositions comprise, in synergistic proportions, an

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azole compound, an amine oxide compound and a compound of formula (I).

Particularly effective ratios of the azole to amine oxide have been identified and include amine oxide:azole ratios of 4:1 to 1:20, preferably 4:1 to 1:10, preferably 2:1 to 1:5, more preferably 1.5:1 to 1:2.

Particularly effective ratios of compound (I) to amine oxide have been identified and include compound (I):amine oxide ratios of greater than 2:1, preferably greater than 4:1, more preferably greater than 5:1 or 6:1 e.g. greater than 8:1 or 10:1, such as 2:1 to 100:1, or 2:1 to 50:1, or 4:1 to 30:1 preferably 10:1 to 25:1, preferably 15:1 to 25:1.

Particularly preferred formulations are those in which the compound of formula (I) is a quaternary ammonium compound. Typically these formulations will have a quaternary ammonium compound:amine oxide ratio of greater than 2:1, preferably greater than 4:1, more preferably greater than 5:1 or 6:1 e.g. greater than 8:1 or 10:1, such as 2:1 to 50:1, or 4:1 to 30:1 preferably 10:1 to 25:1, preferably 15:1 to 25:1.

Particularly effective ratios of compound (I) to azole have been identified and include compound (I):azole ratios of greater than 2:1, preferably greater than 4:1, such as 2:1 to 20:1, or 3:1 to 15:1, or 4:1 to 12:1, preferably 5:1 to 10:1.

Preferred formulations contain a mixture of azoles, preferably a mixture of 1,2,4-triazoles and imidazoles. Typically these formulations will have a triazole:imidazole ratio of 10:1 to 1:10, preferably 10:1 to 1:2, more preferably 10:1 to 1:1, most preferred is 10:1 to 2:1. Alternatively, the triazole:imidazole ratio is preferably 2:1 to 1:10, more preferably 1:1 to 1:10, most preferred being 1:2 to 1:10.

Preferably C12 amine oxides are used, or alternatively a mixture of C12 and C16 amine oxides,

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preferably with a ratio of 3:1 to 1:3, preferably 2:1 to 1:2, most preferred is about 1:1.

Further preferred formulations contain a halopropynyl compound. Typically these formulations will have a halopropynyl:amine oxide ratio of 4:1 to 1:10, preferably 2:1 to 1:5, more preferably 1.5:1 to 1:2. Thus, the formulations have a preferred compound (I) to halopropynyl compound ratio of 20:1 to 4:1, preferably 15:1 to 5:1, most preferably about 10:1.

All of the above ratios refer to weight percent as a percentage of the total weight of the composition. Thus, a ratio of 1:1 will refer to two components being present in equal weight percents in a composition.

Thus, especially preferred formulations according to the present invention comprise, an imidazole compound, an amine oxide compound, a triazole compound, a quaternary ammonium compound and a halopropynyl compound, all as defined above and preferably at the ratios specified above. Suitable examples of such formulations include benzalkonium chloride or didecyldimethylammonium chloride or carbonate or bicarbonate, IPBC, propiconazole or tebuconazole, thiabendazole or imazalil and a C₁₆ and/or C₁₂ dimethyl amine oxide. Each of the ingredients are also preferred in their own right and may be combined with other ingredients to form further preferred formulations according to the invention.

The concentration of the formulation required for preservative treatment depends on the ratio of particular active agents selected, the method of treatment employed, the timber species, the level of protection required and the nature and quantity of any other biocides present. The amounts necessary can be determined readily by one skilled in the art.

The compositions according to the invention may additionally, comprise other active ingredients such as

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termiticides, insecticides, bacteriocides and other fungicides. Suitable additional fungicides would be apparent to one skilled in the art and will vary according to the application. In particular, additional
5 fungicides which extend the spectrum of activity of the formulation may be chosen, such as fungicides active against bluestain fungi, white rots, brown rots, dry rots and moulds. Suitable additional fungicides include for example, dichlofluanid, acypetacs, including copper
10 and zinc salts, isothiazolones, tolyfluanid, chlorothanonil, fenpropimorph, sorbic acid and salts thereof, borates, guazatine and salts thereof, benzoic acid and its salts, oxathiazines, TCMTB, MBT, PCP and its salts, N-(3-aminopropyl)-N-dodecylpropane-1,3-
15 diamine, Dazomet, (E)-1-(2-chloro-1,3-thiazol-5-ylmethyl-2-nitroguanadine, as well as metal compounds such as copper, Cu-oxide, copper naphthenate, copper carbonate, copper oxine, copper hydroxide, copper dihydroxide, Cu-HDO, potassium-HDO, also iron and zinc
20 and salts, compounds and soaps thereof.

Suitable insecticides would also be apparent to the skilled man depending upon the intended application, and include, for example, chlorpyrifos, cypermethrin, fenvalerate, fipronil, farox, tetramethrin, isofenphos,
25 permethrin, silafluofen, deltamethrin, bifenthrin, cyfluthrin, chlorfenapyr, thiachloprid, etofenprox, chlothianidin, thiamethoxam and imidacloprid, and benzoylureas such as lufenuron, hexaflumuron and flufenoxuron and in particular, flurox.

30 The compositions according to the invention may additionally comprise other components which may act to improve the characteristics of the wood treated with these biocides. Such compounds could include water repellents based on waxes, silicones and polysiloxanes,
35 latex, fluorocarbon, organic carboxylate/metals, paper sizing agents or amine oxides, or combinations thereof;

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resins or crosslinking agents based on alkyds, acrylics, polyurethanes, formaldehydes, dimethylol, and epichlorohydrin or combinations thereof. Oils may also be used as may UV absorbers, corrosion inhibitors,

5 penetrating aids including glycols, bactericides eg PHMB, colouring agents, antioxidants, metal chelators especially iron chelators, optical brightening agents, defoamers, pH buffers or other stabilisers.

In concentrate form the wood treatment composition will
10 typically comprise as active ingredients 1-20%, preferably 1-10%, e.g. 1-5% w/w amine oxide, 0.5-20%, preferably 1-12%, e.g. 2-10% w/w of azole and 5-70%, preferably 10-60% w/w compound (I). When compound (I) is a quaternary ammonium compound, the wood treatment
15 will typically comprise as active ingredient 10-70%, preferably 20-60% w/w quaternary ammonium compound. Typically these concentrates will be diluted prior to application to the wood. Dilution will preferably be with water, e.g. at a ratio, water:concentrate v/v of
20 15:1 to 250:1 e.g. 75:1 to 150:1. The appropriate dilution level can be determined by one skilled in the art dependent upon cost, the type of wood to be treated, environmental conditions and the length of time protection is required.

25 In a further aspect, the invention provides a method of preserving wood or other cellulosic substrates which comprises applying to the wood or other cellulosic substrate a formulation of the invention as described above or applying the individual components to the
30 wood/substrate such that the wood/substrate effectively receives a formulation as described.

Types of wood which can benefit from treatment with the formulations of the invention include sawn timber, logs, glulam, plywood, laminated veneer lumber, wood
35 based composite products such as oriented strandboard,

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medium density fibreboard, fibreboard, hardboard and particle board

Other materials which can benefit from treatment with the formulations of the invention are

5 lignocellulosic substrates, wood plastic composites, cardboard and cardboard faced building products such as plasterboard, and cellulosic material such as cotton. Also, leather, textile materials and even synthetic fibres, hessian, rope and cordage as well as composite
10 wood materials. For convenience, the invention is described with reference to the treatment of wood but it will be appreciated that other materials may be treated analogously. Preferably, though not exclusively, the formulations are applied to unseasoned timber.

15 Conveniently, the compositions of the present invention are applied as a liquid composition. They may also be applied as a solid implant or paste. Preferably, the compositions are applied as a liquid composition, e.g. in the form of an emulsion made up of
20 solubilised liquid droplets. These emulsions do not contain any biocides in a solid, particulate form. Preferably, the emulsions are in the form of a micro-emulsion. The person skilled in the art of making emulsions knows how to make an emulsion according to the
25 invention by the use of suitable solvents and emulsifying agents.

Preferably, when applied in liquid form, this is in an aqueous solution, but one or more organic solvents or a mixture of water and an organic solvent could also be
30 used. Suitable organic solvents include both aromatic and aliphatic hydrocarbon solvents such as white spirit, petroleum distillate, kerosene, diesel oils and naphthas. Also, benzyl alcohol, 2-phenoxy ethanol, methyl carbitol, propylene carbonate, benzyl benzoate,
35 ethyl lactate and 2-ethyl hexyl lactate.

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The application of these compositions may be by one or more of dipping, deluging, spraying, brushing or other surface coating means or by impregnation methods, e.g. high pressure or double vacuum impregnation into the body of the wood or other material, all being techniques well known to the man skilled in the art. Impregnation under pressure is particularly advantageous when the substrate is wood or a wood composite material which is made to become wet during its life, for example, wood for window frames, timber used above ground in exposed environments such as decking and timber used in ground contact or fresh water or salt water environments.

Substrates made of wood or cellulosic material which have been treated with a composition or by a method according to the invention as described herein, comprise further aspects of the present invention.

Preferably, the compositions are applied to timber components before they are used but they can also be used remedially as a curative action in preventing continued wood defacement.

The invention will be further described with reference to the following non-limiting Examples and Figures in which:

Figure 1 is a graph showing the extent of sapstain present on the untreated boards used in Example 1.

Figure 2 is a graph showing the performance of AT6 applied at 1.35% v/v during the test of Example 1.

Figure 3 is a graph showing the performance of AT7M (AT6 plus thiabendazole and equal amounts of C12 and C16 amine oxides) applied at 1.15% v/v during the test of Example 1.

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Figure 4 is a graph showing the extent of sapstain present on the untreated Scots pine after 4 months' exposure, as described in Example 2.

- 5 Figure 5 is a graph showing the performance of AT6A applied at 1.02% v/v during the test of Example 2.

- Figure 6 is a graph showing the performance of AT7M (AT6A plus thiabendazole and mixed C12/C16 amine oxides)
10 applied during the test of Example 2.

- Figure 7 is a graph showing the performance of AT26 (AT6A plus Imazalil) applied during the test of Example
15 2.

- Figure 8 is a graph showing the performance of AT27M (AT26 plus mixed C12/C16 amine oxides) applied during
the test of Example 2.

- 20 Figure 9 is a graph showing the performance of AT15M (AT6A plus thiabendazole, prochloraz and mixed C12/C16 amine oxides) applied during the test of Example 2.

- Figure 10 is a graph showing the performance of AT29M
25 (AT6A plus thiabendazole, imazalil and mixed C12/C16 amine oxides) applied during the test of Example 2.

- Figure 11 is a graph showing the extent of sapstain present on the untreated boards after 4 months exposure,
30 as described in Example 3.

Figure 12 is a graph showing the performance of AT6 applied at 0.69% applied during the test of Example 3.

- 35 Figure 13 is a graph showing the performance of AT6 applied at 1.03% applied during the test of Example 3.

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Figure 14 is a graph showing the performance of AT9 (AT6 plus C16 amine oxide) applied at 0.62% applied during the test of Example 3.

5

Figure 15 is a graph showing the performance of AT9 (AT6 plus C16 amine oxide) applied at 0.93% applied during the test of Example 3.

10 Figure 16 is a graph showing the extent of sapstain present on the untreated boards after 2 months' exposure, as described in Example 4.

Figure 17 is a graph showing the performance of AT6A applied during the test of Example 4

15

Figure 18 is a graph showing the performance of AT7A (a diluted form of AT6A plus thiabendazole and C12 Amine oxide) applied during the test of Example 4.

20

Figure 19 is a graph showing the performance of ATF1 (AT7A with DDAC used in place of the BAC, and no thiabendazole) applied during the test of Example 4.

25 Figure 20 is a graph showing the performance of ATF2 (ATF1 without the IPBC) applied during the test of Example 4.

Figure 21 is a graph showing the performance of ATF3 applied during the test of Example 4.

30

Figure 22 is a graph showing the performance of ATF4 (ATF3 without the IPBC) applied during the test of Example 4.

35

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Figure 23 is a graph showing the performance of ATF5 applied during the test of Example 4.

Figure 24 is a graph showing the performance of ATF6
5 (ATF5 without the imazalil and IPBC) applied during the test of Example 4.

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Examples

Typically, the following formulations were made by first mixing the azoles and/or imidazoles plus the
5 halopropynyl compound (if present) with the Dowanol DPM® solvent for 30 minutes. After this time, the compound of formula (I) (and ethoxylated castor oil if required) was added and the formulation mixed until all the solids
10 dissolved. Water, amine oxides and defoamer were then added and mixed until a clear homogenous product was obtained.

Example 1

15 Two anti-sapstain formulations were tested in an accelerated field trial in Florida.

The formulations were as follows:

20 **AT6 (Comparative Formulation)**

	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
25	Defoamer	0.2
	Dowanol DPM®	10.0
	Water	12.2

AT7M

30

	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
	Thiabendazole (99% a.i.)	1.01
35	C16 amine oxide (30% a.i.)	4.0
	C12 amine oxide (30% a.i.)	4.0

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Defoamer	0.2
Dowanol DPM®	10.0
Water	3.19

5 Both formulations contained the same levels of IPBC, propiconazole and benzalkonium chloride, but AT7M additionally contained thiabendazole and C12 and C16 amine oxides.

10 The formulations were tested at solution strengths (diluted with water) chosen such that the cost of product in the treated wood was the same

AT6 1.35% v/v

15 AT7M 1.15%

The wood used for the trial was freshly sawn Southern Yellow Pine obtained locally in Florida. For each formulation a total of 25 boards each measuring 25mm x
20 100mm x 600mm were tested.

An accelerated field test method was used. After dipping boards for 1 minute in treatment solution and allowing excess liquid to run off, the boards were
25 stacked in blocks of 25, five boards wide by five boards high with no separation between layers or rows. Finally each stack was covered in polythene to maintain the moisture content at a high level.

30 The stacks were stored for the duration of the trial in the open sawmill yard.

After three weeks the boards were inspected for visual colonisation by sapstain and mould fungi. Each board
35 was assigned a grade according to the 0-4 scale given in CEN/TS 15082 'Wood Preservatives - Determination of the

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Preventive Effectiveness Against Sapstain Fungi on
Freshly Sawn Timber - Field Test'.

Grade	Description
0	"clean" timber with 0% surface stain coverage
1	"slight" staining with less than 10% surface stain coverage
2	"medium" staining with 10%-25% surface stain coverage
3	"heavy" staining with 26%-50% surface stain coverage
4	"severe" staining with >50% surface stain coverage

5 Table 1: Scale for estimation of sapstain coverage

The sapstain ratings (grades) for each board and each product as well as untreated control boards are presented graphically in Figures 1 to 3.

10

Figure 1 shows the extent of sapstain present on the untreated boards. All 25 boards have achieved either Grade 3 (heavy staining) or Grade 4 (severe staining) indicating a very high fungal activity during the test.

15 Grade 2 or higher is generally accepted as representing a failure to sapstain in commercial terms, hence a 100% failure rate has been achieved.

Figure 2 shows how AT6 performed at 1.35% v/v during the test. Performance is rather poor in this test as 5 boards have reached a Grade 2 or higher. Hence 25% of the boards treated with AT6 have failed the test.

Figure 3 shows the effect of incorporating both
25 thiabendazole and equal amounts of C12 and C16 amine

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oxides into AT6 to give a formulation called AT7M,
applied at 1.15% v/v such that the cost in the wood is
the same as 1.35% AT6. It is immediately clear that the
performance is now much improved over AT6 with only a 4%
5 failure rate as shown by only 1 of the 25 boards
reaching a grade 2.

Example 2

10 A number of anti-sapstain formulations were tested in a
field trial in Polnica, North-Eastern Poland.

All formulations contained the same levels of IPBC,
propiconazole and benzalkonium chloride but were
15 modified by the addition of other biocides; alone, in
combinations and with mixed C12/C16 amine oxides.

The formulations were as follows

20 **AT6A (Comparative Formulation)**

	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
25	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	11.2

30 **AT7M**

	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
35	Thiabendazole (99% a.i.)	1.01
	C16 amine oxide (30% a.i.)	4.0

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	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
5	Water	2.19

AT15M

	Benzalkonium chloride (80% a.i.)	62.5% w/w
10	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
	Prochloraz (99% a.i.)	2.02
	Thiabendazole (99% a.i.)	1.01
	C16 amine oxide (30% a.i.)	4.0
15	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	0.17
20		

AT26 (Comparative Formulation)

	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
25	Propiconazole (50% a.i.)	10.0
	Imazalil (99% a.i.)	2.02
	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
30	Water	9.18

AT27M

	Benzalkonium chloride (80% a.i.)	62.5% w/w
35	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0

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	Imazalil (99% a.i.)	2.02
	C16 amine oxide (30% a.i.)	4.0
	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
5	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	1.18

AT29M

10		
	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
	Imazalil (99% a.i.)	2.02
15	Thiabendazole (99% a.i.)	1.01
	C16 amine oxide (30% a.i.)	4.0
	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
	Dowanol DPM®	8.0
20	Propionic acid	3.0
	Water	0.17

The wood used for the trial was freshly sawn Scots pine obtained locally in Poland with moisture contents between 40 and 60%. For each formulation a total of 60 boards each were used, each board measuring 22mm x 125mm x 1000mm.

The boards were treated by dipping in open tanks containing 40 liters of solution. The samples were immersed in the bath for 1 min. Next the treated wood was stored for 10 min in a special stand in order to allow draining of excess product. 60 samples were dipped for each product and concentration. The wood was stored in 48 cm wide stacks (5 samples were stored parallel in a single layer). 40 samples were stored

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without stickers (close stacked) while the other 20 pieces were stored with stickers (open stacked) to reflect common commercial practices. The stickers used were 8mm thick and were dipped in the same product as
5 the stack to which they were allocated. Separate stacks were formed for each product in order to prevent any unwanted interactions. A control stack of untreated timber was also included.

10 All the stacks were covered by a layer of untreated boards and were stored for the duration of the trial in the open yard exposed to the weather.

This test methodology is broadly as described in CEN/TS
15 15082 "Wood Preservatives-Determination of the Preventive Effectiveness Against Sapstain Fungi on Freshly Sawn Timber-Field Test".

The stacks of treated boards were inspected after 4
20 months. Each individual board was assigned a visual grade according to the 0-4 scale also given in CEN/TS 15082 and described in Table 1 of Example 1.

The sapstain ratings (grades) for each board and each
25 product as well as untreated control boards are presented graphically in Figures 4 to 8.

Since a closed stack configuration represents the more severe hazard and shows up differences between
30 formulations more quickly and reliably, all data presented herein refers to this closed stacked arrangement. No data is presented for timber stored open stacked.

35 Figure 4 shows the data for untreated Scots pine after 4 months exposure

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Figure 5 shows how AT6A performed at 1.02% v/v during the test. The performance is poor, with 28% of the boards having grade 2 or above.

5

Figure 6 shows the effect of including thiabendazole and mixed C12/C16 amine oxides. AT7M is AT6A plus both 1% Thiabendazole and 8% mixed amine oxides.

10 Figure 7 shows the data for including Imazalil in AT6A. AT26 is AT6A plus 2% Imazalil.

Figure 8 shows the effect of including Imazalil and mixed C12/C16 amine oxides. AT27M is AT6A plus both 2%
15 imazalil and 8% mixed C12/C16 amine oxides.

Figure 9 shows the effect of including thiabendazole, prochloraz and mixed C12/C16 amine oxides. AT15M is AT6A plus thiabendazole, prochloraz and mixed C12/C16
20 amine oxides.

Figure 10 shows the effect of including thiabendazole, imazalil and mixed C12/C16 amine oxides. AT29M is AT6A plus thiabendazole, prochloraz and mixed C12/C16 amine
25 oxides.

AT7M with both 1% Thiabendazole and 8% mixed amine oxides performs better than AT6A, with only 3% failure rate and 75% of the boards being completely clean (Grade
30 0).

Figure 7 shows the addition of 2% Imazalil to AT6A to give formulation AT26, has a slightly detrimental effect on anti-sapstain performance with an increase in the
35 number of failing boards from 28% to 30% combined with a reduction in the number of clean (Grade 0) boards.

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However the combined addition of 2% Imazalil and 8% mixed C12/C16 amine oxides to give formulation AT27M, gives markedly improved anti-sapstain performance over
5 AT6A. As shown in Figure 8, the number of failures is reduced to 13% although the number of clean boards is rather similar.

AT15M with 2% prochloraz, 1% thiabendazole and 8% mixed
10 amine oxides performs better than AT6A, with only a 3% failure rate and 58% of the boards being completely clean (Grade 0).

AT29M with 2% imazalil, 1% thiabendazole and 8% mixed
15 amine oxides performs better than AT6A, with only a 5% failure rate.

Example 3

20 This example shows the results of a field trial conducted in Portugal. In this example, C16 amine oxide was used and incorporated in to the base formulation AT6 as used in Example 1 at 10% such that the add-on cost to the formulation was also around 10%. The formulation
25 was labeled as AT9.

AT9

	Benzalkonium chloride (80% a.i.)	62.5% w/w
30	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
	C16 amine oxide (30% a.i.)	10.0
	Defoamer	0.2
	Dowanol DPM®	10.0
35	Water	2.2

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The wood used in the trial was freshly sawn maritime pine (*Pinus pinsaster*) with moisture content in the region 40-60%.

- 5 Each board used in the trial was 1000mm x 95mm x 18mm and composed predominantly of sapwood.

AT6 and AT9 were used at two concentrations each:

- 10 AT6: 1.03% and 0.69% v/v
AT9: 0.93% and 0.62% v/v

- The solution strengths used were confirmed as correct by laboratory analysis. The strengths were chosen to match
15 the costs of the solutions as the same for each comparative test.

- The dipping was performed in open tanks containing 40 liters of solution. The samples were immersed in the
20 bath for 1 min. Next, wood was stored for 10 min in a special stand in order to allow draining of excess product. 30 samples were dipped for each product and concentration. The wood was stored in 48cm wide stacks (5 samples were stored parallel in a single layer). The
25 samples were stored without stickers (closed stacked). Separate stacks were formed for each product in order to prevent any unwanted interactions.

- All the stacks were covered by a layer of untreated
30 boards and were stored for the duration of the trial in the open yard exposed to the weather.

- This test methodology is broadly as described in CEN/TS 15082 "Wood Preservatives-Determination of the
35 Preventive Effectiveness Against Sapstain Fungi on Freshly Sawn Timber-Field Test".

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The stacks of treated boards were inspected after 4 months. Each individual board was assigned a visual grade according to the 0-4 scale also given in CEN/TS 15082 and described in Table 1 of Example 1.

The amount of sapstain present on each board is shown graphically in figures 11 to 15.

The extent of staining on the untreated boards after 4 months is shown in Figure 11. Boards showing sapstain grades of 2 or higher are generally taken to indicate failures to sapstain in commercial terms, hence all 30 boards (i.e. 100% of the boards) have failed. The results give validity to the trial.

Figures 12 to 15 show that at the solution strengths tested the formulations with the C16 amine oxide gave better performance. In commercial terms, the two tests of AT9 show a 0% failure rate as there were no boards with a sapstain grade of 2 or above. In contrast, the AT6 formulations show a commercial failure rating of 13% and 40% for 1.03% and 0.69% v/v respectively.

The levels of active ingredients (BAC, propiconazole and IPBC) in the wood are very close for each product at the two solution strengths tested. That is to say that 1.03% AT6 treated timber has rather similar levels of actives to 0.93% AT9 and so on. In fact the levels in the AT9 treated wood are slightly lower than in the AT6 due to the added cost of the C16 amine oxide and the desire to compare performance of the two formulations at equivalent cost in the wood.

It would be expected therefore that, if amine oxide was not having an effect on antisapstain performance, 0.62%

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AT9 would perform very similarly or slightly worse than 0.69% AT6. In fact, comparison of figures 12 to 15 and the failure rates quoted above shows the reverse with the amine oxide-containing variant far out-performing the base product despite the slightly lower active ingredient levels in the wood.

These two results suggest C16 amine oxide is enhancing the performance of the formulation.

Example 4

A number of anti-sapstain formulations were tested in a field trial in Polnica, North-Eastern.

The formulations were as follows:

AT7A

20	Benzalkonium chloride (50% a.i.)	48% w/w
	IPBC (98% a.i.)	2.45
	Propiconazole (50% a.i.)	4.8
	Thiabendazole (99% a.i.)	0.51
	C12 amine oxide (30% a.i.)	6.0
25	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	27.04

ATF1

	Dimethyldidecylammonium chloride (80% a.i.)	30% w/w
	IPBC (98% a.i.)	2.45
	Propiconazole (50% a.i.)	4.8
35	C12 amine oxide (30% a.i.)	6.0
	Defoamer	0.2

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	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	45.55
5	ATF2	
	Dimethyldidecylammonium chloride (80% a.i.)	30% w/w
	Propiconazole (50% a.i.)	4.8
	C12 amine oxide (30% a.i.)	6.0
10	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	48.0
15	ATF3	
	DDACarbonate* (50% a.i.)	48% w/w
	IPBC (98% a.i.)	2.45
	Azaconazole (98% a.i.)	2.45
20	C12 amine oxide (30% a.i.)	6.0
	Défoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	29.9
25	*DDACarbonate is didecyldimethylammonium carbonate/bicarbonate	
	ATF4	
30	DDACarbonate (50% a.i.)	48% w/w
	Azaconazole (98% a.i.)	2.45
	C12 amine oxide (30% a.i.)	6.0
	Defoamer	0.2
35	Dowanol DPM®	8.0
	Propionic acid	3.0

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Water	32.35
-------	-------

ATF5

5	DDACarbonate (50% a.i.)	48% w/w
	IPBC (98% a.i.)	2.45
	Hexaconazole (75% a.i.)	3.20
	Imazalil (99% a.i.)	0.75
	C12 amine oxide (30% a.i.)	6.0
10	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	28.4

15 **ATF6**

	DDACarbonate (50% a.i.)	48% w/w
	Hexaconazole (75% a.i.)	3.20
	C12 amine oxide (30% a.i.)	6.0
20	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	31.6

25 The formulations were tested at solution strengths
(diluted with water) chosen such that the cost of
product and amount of active components (namely the
amine oxide, azole and compound of formula (I)) in the
treated wood was approximately the same. Thus, ATF6A was
30 diluted to 0.58 % v/v, while the other compositions were
diluted to 1.2 % v/v.

The wood used for the trial was freshly sawn Scots pine
obtained locally in Poland with moisture contents
35 between 40 and 60%. For each formulation a total of 35

- 38 -

boards each were used, each board measuring approx. 22mm x 125mm x 1000mm.

The dipping was performed in open tanks containing 40
5 liters of solution. The samples were immersed in the bath for 1 minute and then the treated wood stored for 10 min in a special stand in order to allow draining of excess product. 35 samples were dipped for each product at the required concentration. The wood was stored in 63
10 cm wide stacks (5 samples were stored in parallel in a single layer). All 35 samples were stored in a five by seven board stack without stickers (close stacked) to reflect common commercial practice.

15 Separate stacks were formed for each product in order to prevent any unwanted interactions. A control stack of untreated timber was also included.

All the stacks were covered by a layer of untreated
20 boards and were stored for the duration of the trial in the open yard exposed to the weather

This test methodology is broadly as described in CEN TS 15082 "Wood Preservatives-Determination of the
25 Preventive Effectiveness Against Sapstain Fungi on Freshly Sawn Timber-Field Test".

The stacks of treated boards were inspected after 2 months. Each individual board was assigned a visual
30 grade according to the 0-4 scale also given in CEN TS 15082, as described in Table 1 of Example 1.

The sapstain ratings (grades) for boards treated with each product as well as untreated control boards are
35 presented graphically in Figures 16 to 24.

- 39 -

Figure 16 shows the data for untreated Scots pine after 2 months' exposure. All 35 of the 35 boards have achieved at least a Grade 2 (medium staining), with 34 reaching Grade 4 (severe staining) indicating a very high fungal activity during the test. Grade 2 or higher is generally accepted as representing a failure to sapstain in commercial terms, hence a 100% failure rate has been achieved for the untreated control boards. This result establishes the validity of the trial.

10

Figure 17 shows the performance of the control benzalkonium chloride, propiconazole and IPBC formulation (AT6A) and as such establishes the criteria by which the alternatives are judged. Details of this formulation are given in Example 2. 7 boards out of 35 have reached Grade 2 or above, hence the failure rate is 20%.

20 Figure 18 shows the performance of AT7A, which has the same combination of actives as AT6A but includes thiabendazole and C12 amine oxide. This formulation is similar to AT7M used in Examples 1 and 2, but does not contain a mixture of amine oxides. Furthermore, the A suffix in AT7A denotes a less concentrated version of the formulation, for ease of handling. This less concentrated material is used at a lesser dilution but active levels in the timber are the same.

30 The addition of thiabendazole and C12 amine oxide to AT6A reduces the failure rate to less than 3% with only one board reaching Grade 2. This gives clear confirmation of the synergism of this combination as demonstrated in Examples 1 and 2 as the costs of the product in the wood are the same. The failure rate of AT7A is comparable to that of AT7M from Examples 1 and

35

- 40 -

2, demonstrating that mixed amine oxides are not required to provide this synergism.

Figure 19 shows the effect of changing the benzalkonium chloride in AT7A for an equivalent amount of an alternative quaternary ammonium chloride, in this case dimethyldidecylammonium chloride (DDAC). Additionally the thiabendazole is omitted. This is referred to as formulation ATF1.

10

4 out of the 25 boards have reached Grade 2 ('medium' staining) and hence are classed as failures. However this represents only 11%, compared to 25% for AT6A, demonstrating that the improvement in performance from amine oxide inclusion is maintained when an alternative quaternary ammonium compound is used. Furthermore, the presence of both a triazole and an imidazole is not a requirement for synergism.

20

Figure 20 shows the effect of omitting the IPBC from ATF1 to give ATF2. Omission of the IPBC from ATF1 has not resulted in an increase in failures over AT6A, in fact a 0% failure rate is observed. This result demonstrates that IPBC is not a required co-formulant of the synergistic mixture.

25

Figure 21 shows the effect of changing the benzalkonium chloride in AT7A for an equivalent amount of an alternative quaternary ammonium compound, in this case dimethyldidecylammonium carbonate/bicarbonate. Additionally the propiconazole in AT7A has been substituted by azaconazole, and the thiabendazole has been omitted. This is formulation ATF3.

30

35

Changing the azole, quaternary ammonium compound and counter ion plus omitting thiabendazole has not resulted

- 41 -

in a loss of synergy with only 11% failure rate versus the 25% of the base system at the same active ingredient levels.

- 5 Figure 22 shows the effect of omitting the IPBC from ATF3 to give ATF4. The failure rate of only 9% clearly shows that omitting the IPBC from ATF3 is not detrimental to the synergistic improvement in performance of the amine oxide containing combination.
- 10 This result demonstrates that IPBC is not a required co-formulant of the synergistic mixture.

- Figure 23 shows the performance of a composition wherein the quaternary ammonium compound, triazole and imidazole of AT7A have been replaced with dimethyldidecylammonium carbonate/bicarbonate, hexaconazole and imazalil respectively. This is example ATF5. The lack of failures to sapstain clearly shows the suitability of this azole, imidazole and quaternary ammonium compound
- 15 for the synergistic mixture.
- 20

- Figure 24 shows the effect of omitting both the IPBC and imazalil from ATF5 to give formulation ATF6. The lack of failures in this example demonstrates that IPBC is
- 25 not required to provide excellent antisapstain activity.

Example 5

- The following formulations within the scope of the
- 30 invention are also described:

Formulation 1

- | | |
|---|----------|
| C12 amine oxide (30% a.i.) | 6.0% w/w |
| 35 Wocosen 50TK® (50% a.i. Propiconazole) | 4.8 |
| DDAC (80% a.i.) | 30.0 |

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	IPBC (98% a.i.)	2.45
	Dowanol DPM®	15.0
	Propionic acid	1.0
	Water	40.75
5		

Formulation 2

	C12 amine oxide (30% a.i.)	6.0% w/w
10	Wocosen 50TK® (50% a.i. Propiconazole)	4.8
	DDAC (80% a.i.)	30.0
	Dowanol DPM®	15.0
	Propionic acid	1.0
	water	43.2
15		

Formulation 3

	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen 50TK® (50% a.i. Propiconazole)	4.8
20	C12 dimethylamine	17.75
	Propionic acid	6.25
	IPBC (98% a.i.)	2.45
	Dowanol DPM®	15.0
	40 mole ethoxylated castor oil	10.0
25	water	37.75

Formulation 4

30	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen® 50TK(50% a.i. Propiconazole)	4.8
	C12 dimethylamine	17.75
	Propionic acid	6.25
	Dowanol DPM®	15.0
35	40 mole ethoxylated castor oil	10.0
	water	40.2

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Formulation 5

	C12 amine oxide (30% a.i.)	6.0% w/w
5	Wocosen 50TK® (50% a.i. Propiconazole)	4.8
	C12 dimethylamine	17.75
	Propionic acid	6.25
	IPBC (98% a.i.)	2.45
	Thiabendazole (99% a.i.)	0.5
10	Dowanol DPM®	15.0
	40 mole ethoxylated castor oil	10.0
	water	37.25

Formulation 6

15	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen 50TK® (50% a.i. Propiconazole)	4.8
	C12 dimethylamine	17.75
	Propionic acid	6.25
20	Thiabendazole (99% a.i.)	0.5
	Dowanol DPM®	15.0
	40 mole ethoxylated castor oil	10.0
	water	39.7

25 Formulation 7

	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen® 50TK(50% a.i. Propiconazole)	4.8
	C12 amine dipropionate (30% a.i.)	50.0
30	IPBC (98% a.i.)	2.45
	Dowanol DPM®	15.0
	Propionic acid	1.0
	40 mole ethoxylated castor oil	20.0
	water	0.75

35

Formulation 8

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	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen 50TK® 50% a.i. Propiconazole)	4.8
	C12 amine dipropionate (30% a.i.)	50.0
5	Dowanol DPM®	15.0
	Propionic acid	1.0
	40 mole ethoxylated castor oil	20.0
	water	3.2
10	Formulation 9	
	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen 50TK® (50% a.i. Propiconazole)	4.8
	C12 amine dipropionate (30% a.i.)	50.0
15	IPBC (98% a.i.)	2.45
	Imazalil (99% a.i.)	0.75
	Dowanol DPM®	15.0
	Propionic acid	1.0
	40 mole ethoxylated castor oil	20.0
20	Formulation 10	
	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen 50TK® (50% a.i. Propiconazole)	4.8
25	C12 amine dipropionate (30% a.i.)	50.0
	Imazalil (99% a.i.)	0.75
	Dowanol DPM®	15.0
	Propionic acid	1.0
	40 mole ethoxylated castor oil	20.0
30	water	2.45
	Formulation 11	
	C12 amine oxide (30% a.i.)	6.0% w/w
35	Azaconazole (98% a.i.)	2.45
	DDACarbonate* (50% a.i.)	48.0

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IPBC (98% a.i.)	2.45
Dowanol DPM®	15.0
water	26.1

- 5 *DDACarbonate is didecyldimethylammonium carbonate/bicarbonate

Formulation 12

10 C12 amine oxide (30% a.i.)	6.0% w/w
Azaconazole (98% a.i.)	2.45
DDACarbonate (50% a.i.)	48.0
Dowanol DPM®	15
water	28.55

15

Formulation 13

C12 amine oxide (30% a.i.)	6.0% w/w
Hexaconazole (75% a.i.)	3.2
20 DDACarbonate (50% a.i.)	48.0
IPBC (98% a.i.)	2.45
Imazalil(99% a.i.)	0.75
Dowanol DPM®	15.0
water	24.6

25

Formulation 14

C12 amine oxide (30% a.i.)	6.0% w/w
Hexaconazole (75% a.i.)	3.2
30 DDACarbonate (50% a.i.)	48.0
Dowanol DPM®	15.0
water	27.8

Formulation 15

35 C12 amine oxide (30% a.i.)	6.0% w/w
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	Wocosen 50TK® (50% a.i. propiconazole)	4.8
	Cocoamidopropyl betaine (30% a.i.)	50.0
	IPBC (98% a.i.)	2.45
	Dowanol DPM®	15.0
5	Propionic acid	1.0
	40 mole ethoxylated castor oil	20.0
	water	0.75

Formulation 16

10		
	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen 50TK® (50% a.i. propiconazole)	4.8
	Cocoamidopropyl betaine (30% a.i.)	50.0
	Dowanol DPM®	15.0
15	Propionic acid	1.0
	40 mole ethoxylated castor oil	20.0
	water	3.2

Formulation 17

20		
	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen 50TK® (50% a.i. propiconazole)	4.8
	C12 dimethylamine	24.0
	Dowanol DPM®	15.0
25	40 mole ethoxylated castor oil	20.0
	Water	30.2

Formulation 18

30	C12 amine oxide (30% a.i.)	6.0% w/w
	Wocosen 50TK® (50% a.i. Propiconazole)	4.8
	Methyl C12 bis(glycol ether) quarternary ammonium chloride	30.0
	IPBC (98% a.i.)	2.45
35	Dowanol DPM®	15.0
	Propionic acid	1.0

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Water	40.75
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AT9M

5	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
	C16 amine oxide (30% a.i.)	4.0
	C12 amine oxide (30% a.i.)	4.0
10	Defoamer	0.2
	Dowanol DPM®	10.0
	Water	4.2

AT9MA

15	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
	C16 amine oxide (30% a.i.)	4.0
20	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	3.2

25

AT11M

	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
30	Propiconazole (50% a.i.)	10.0
	Prochloraz (99% a.i.)	2.02
	C16 amine oxide (30% a.i.)	4.0
	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
35	Dowanol DPM®	8.0
	Propionic acid	3.0

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Water	1.18
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AT13M

5	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
	Prochloraz (99% a.i.)	1.01
	Thiabendazole (99% a.i.)	1.01
10	C16 amine oxide (30% a.i.)	4.0
	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
15	Water	1.18

AT21M

	Benzalkonium chloride (80% a.i.)	62.5% w/w
20	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	10.0
	Prochloraz (99% a.i.)	2.02
	Imazalil (99% a.i.)	1.01
	C16 amine oxide (30% a.i.)	4.0
25	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
	Dowanol DPM®	8.0
	Propionic acid	3.0
	Water	0.17

30

AT23M

	Benzalkonium chloride (80% a.i.)	62.5% w/w
	IPBC (98% a.i.)	10.2
35	Propiconazole (50% a.i.)	10.0
	C16 amine oxide (30% a.i.)	4.0

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	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
	Dowanol DPM®	6.0
	Propionic acid	3.0
5	Water	0.1

AT25M

	Benzalkonium chloride (80% a.i.)	62.5% w/w
10	IPBC (98% a.i.)	5.1
	Propiconazole (50% a.i.)	20.0
	C16 amine oxide (30% a.i.)	4.0
	C12 amine oxide (30% a.i.)	4.0
	Defoamer	0.2
15	Dowanol DPM®	0.0
	Propionic acid	3.0
	Water	1.2

The active ingredients in the above formulations are
 20 summarised in table 2:

Form.	Amine Oxide	Azole 1	Azole 2/3	Compound(I)	Add.
1	C12 dimethyl amine oxide	Propiconazole		DDAChloride	IPBC
2	C12 dimethyl amine oxide	Propiconazole		DDAChloride	
3	C12 dimethyl amine oxide	Propiconazole		C12 dimethyl- amine	IPBC
4	C12 dimethyl amine oxide	Propiconazole		C12 dimethyl- amine	
5	C12 dimethyl amine oxide	Propiconazole	Thiabendazole	C12 dimethyl- amine	IPBC
6	C12 dimethyl	Propiconazole	Thiabendazole	C12 dimethyl-	

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	amine oxide			amine	
7	C12 dimethyl amine oxide	Propiconazole		C12 Amine dipropionate	IPBC
8	C12 dimethyl amine oxide	Propiconazole		C12 Amine dipropionate	
9	C12 dimethyl amine oxide	Propiconazole	Imazalil	C12 Amine dipropionate	IPBC
10	C12 dimethyl amine oxide	Propiconazole	Imazalil	C12 Amine dipropionate	
11	C12 dimethyl amine oxide	Azaconazole		DDACarbonate /bicarbonate	IPBC
12	C12 dimethyl amine oxide	Azaconazole		DDACarbonate /bicarbonate	
13	C12 dimethyl amine oxide	Hexaconazole	Imazalil	DDACarbonate /bicarbonate	IPBC
14	C12 dimethyl amine oxide	Hexaconazole		DDACarbonate /bicarbonate	
15	C12 dimethyl amine oxide	Prochloraz		C12 amidopropyl- betaine	IPBC
16	C12 dimethyl amine oxide	Prochloraz		C12 amidopropyl- betaine	
17	C12 dimethyl amine oxide	Propiconazole		C12 dimethyl- amine	
18	C12 dimethyl amine oxide	Propiconazole		Methyl C12 bis(glycol ether) quat. chloride	IPBC
AT9M	C12/C16 mixed dimethyl amine oxide	Propiconazole		Benzalkonium chloride	IPBC
AT9MA	C12/C16 mixed dimethyl amine	Propiconazole		Benzalkonium chloride	IPBC

	oxide				
AT11M	C12/C16 mixed dimethyl amine oxide	Propiconazole	Prochloraz	Benzalkonium chloride	IPBC
AT13M	C12/C16 mixed dimethyl amine oxide	Propiconazole	Prochloraz/ Thiabendazole	Benzalkonium chloride	IPBC
AT21M	C12/C16 mixed dimethyl amine oxide	Propiconazole	Prochloraz/ Imazalil	Benzalkonium chloride	IPBC
AT23M	C12/C16 mixed dimethyl amine oxide	Propiconazole		Benzalkonium chloride	IPBC
AT25M	C12/C16 mixed dimethyl amine oxide	Propiconazole		Benzalkonium chloride	IPBC

Table 2: Summary of formulations according to the invention.

Claims

1. A wood preservative formulation comprising an amine oxide, an azole and a compound of formula (I)

5



wherein

10 R^1 denotes an alkyl group which contains from 6 to 24 carbon atoms, benzyl or substituted benzyl, or $(CH_2-CH_2O)_nH$ where $n = 1-20$;

A is absent or denotes a linker group that may be $C=O$ or $-C=ONH(CH_2)_s-$ where $s = 1-3$;

$p = 2$ or 3 ;

15 and each R^2 , which are the same or different, denotes H, CH_3 , C_2H_5 , $(CH_2-CH_2O)_nH$ where $n = 1-20$, an alkyl group which contains from 6 to 24 carbon atoms, $(CH_2)_mCOOH$, $(CH_2)_mCOO^-$, $(CHX)_mSO_3H$ or $(CHX)_mSO_3^-$ where $m = 1$ to 3 and X denotes H or OH;

20 and wherein if the compound is charged it is accompanied by a counterion X^- .

2. A formulation as defined in claim 1, wherein said amine oxide is:

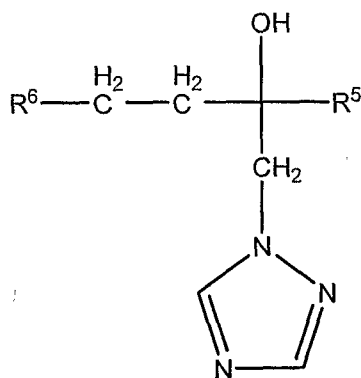
- 25 (i) a trialiphatic substituted amine oxide;
- (ii) an *N*-alkylated cyclic amine oxide;
- (iii) a dialkylpiperazine di-*N*-oxide;
- (iv) an alkyl di(poly(oxyalkylene))amine oxide;
- (v) a dialkylbenzylamine oxide;
- 30 (vi) a fatty amidopropyldimethyl amine oxide;
- (vii) a diamine oxide;
- (viii) a triamine oxide; or
- (ix) any combination of any of the foregoing.

35 3. A formulation as defined in claim 2, wherein said trialiphatic amine oxide has the formula $R^1R^2R^3N \rightarrow O$,

- 53 -

- wherein R^1 , is a linear, branched, cyclic or any combination thereof of saturated or unsaturated C_8 to C_{40} group; and R^2 and R^3 independently are linear, branched, or any combination thereof C_1 to C_{40} saturated or unsaturated groups.
4. A formulation as defined in claim 3, wherein R^1 is a linear, branched or any combination thereof C_8 to C_{22} saturated or unsaturated group; and R^2 and R^3 independently are linear, branched, or any combination thereof C_1 to C_{22} saturated or unsaturated groups.
5. A formulation as defined in claim 4, wherein R^2 and R^3 are both methyl.
6. A formulation as defined in claim 4 or claim 5, wherein R^1 is a linear or branched C_8 to C_{18} alkyl or alkenyl.
7. A formulation as defined in claim 4 or claim 5, wherein R^1 is a linear or branched C_{12} to C_{16} alkyl.
8. A formulation as defined in claim 7, wherein the amine oxide is a mixture of C_{12} and C_{16} dimethyl alkyl amine oxides.
9. A formulation as defined in any one of the above claims, wherein theazole is an imidazole, a 1,2,4-triazole, or mixtures of both.
10. A formulation as defined in claim 9, wherein the imidazole is a benzimidazole.
11. A formulation as defined in claim 9 or claim 10, wherein the imidazole is selected from thiabendazole, imazalil, carbendazim and prochloraz.

12. A formulation as defined in any one of claims 9 to 11, wherein the 1,2,4-triazole is selected from compounds of formula (XI):



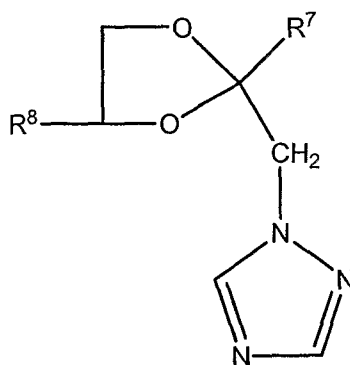
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(XI)

wherein R^5 represents a branched or straight chain C_{1-5} alkyl group (e.g. t-butyl) and R^6 represents a phenyl group optionally substituted by one or more substituents
 10 selected from halogen (e.g. chlorine, fluorine or
 bromine) atoms or C_{1-3} alkyl (e.g. methyl), C_{1-3} alkoxy
 (e.g. methoxy), phenyl or nitro groups;

compounds of formula (XII):

15



(XII)

wherein R^7 is as defined for R^6 above and R^8 represents a hydrogen atom or a branched or straight chain C_{1-5} alkyl group (e.g. n-propyl);

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or selected from the group comprising triadimefon,
 triadimenol, triazbutil, cyproconazole, difenoconazole,
 fluquinconazole, flusilazole, uniconazole, diniconazole,
 5 bitertanol, hexaconazole, flutriafol, epoxyconazole,
 tetraconazole, penconazole, and mixtures thereof

13. A formulation as defined in claim 12, wherein the
 1,2,4-triazole is selected from triadimefon,
 10 triadimenol, triazbutil, propiconazole, cyproconazole,
 difenoconazole, fluquinconazole, tebuconazole,
 flusilazole, uniconazole, diniconazole, bitertanol,
 hexaconazole, azaconazole, flutriafol, epoxyconazole,
 tetraconazole, penconazole and mixtures thereof.

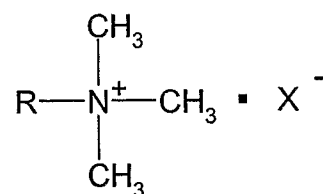
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14. A formulation as defined in claim 12 or 13, wherein
 the 1,2,4-triazole is selected from propiconazole,
 azaconazole, hexaconazole, tebuconazole, cyproconazole,
 triadimefon and mixtures thereof.

20

15. A formulation as defined in any one of the above
 claims, wherein the compound of formula (I) is a
 quaternary ammonium compound.

25 16. A formulation as defined in claim 15, wherein the
 quaternary ammonium compound is selected from compounds
 of formula (XIV):

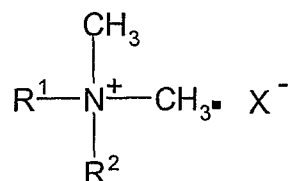


(XIV)

30 wherein R is an alkyl group having from 6 to 22 carbon
 atoms, preferably from 12 to 14 carbon atoms;

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compounds of formula (XV):

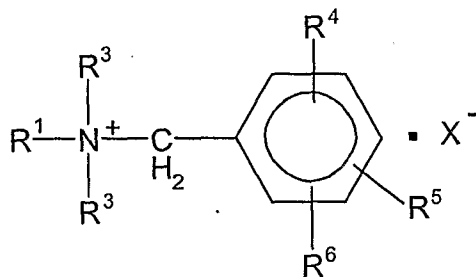


(XV)

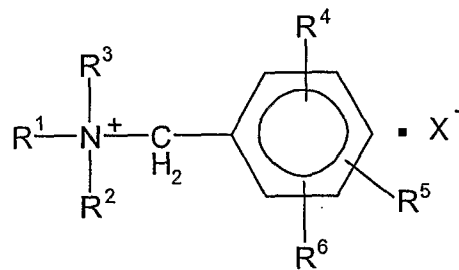
- 5 wherein R^1 and R^2 are alkyl groups which may be the same or different and which contain from 6 to 22 carbon atoms, preferably from 8 to 10 carbon atoms;

compounds of formulae (XVI) or (XVII):

10



(XVI)

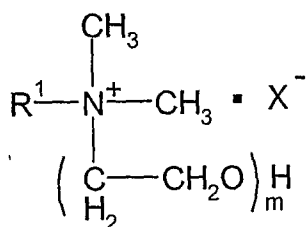


(XVII)

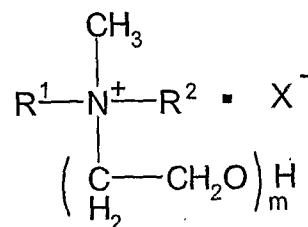
- wherein R^1 and R^2 are alkyl groups which can be the same or different and which contain from 6 to 22 carbon atoms, preferably from 8 to 10 carbon atoms in a dialkyl compound and from 10 to 14 carbon atoms in a monoalkyl compound; R^3 is methyl or ethyl; R^4 , R^5 and R^6 are hydrogen or C_{1-8} alkyl groups;

- 20 or compounds of formulae (XVIII) or (XIX):

- 57 -



(XVIII)



(XIX)

wherein R^1 and R^2 are alkyl groups which may be the same or different and which contain from 6 to 22 carbon atoms, preferably from 8 to 10 carbon atoms in a dialkyl compound and from 10 to 14 carbon atoms in a monoalkyl compound, most preferably 10 carbon atoms. m is a number from 1 to 20 typically from 1 to 8, preferably from 3 to 5;

10 and wherein X^- is an anion chosen to allow ready water solubility of the quaternary ammonium salt.

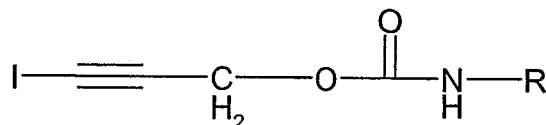
17. A formulation as defined in claim 16, wherein the quaternary ammonium salt is cocotrimethyl ammonium chloride in which the alkyl group R consists of a mixture of predominantly C_{12} and C_{14} .

18. A formulation as defined in claim 16, wherein the quaternary ammonium salt is selected from didecyl dimethyl ammonium chloride, didecyldimethylammonium carbonate, didecyldimethylammonium bicarbonate, dioctyl dimethyl ammonium chloride and octyl decyl dimethyl ammonium chloride either individually or as a mixture containing two or three of these.

19. A formulation as defined in claim 16, wherein the quaternary ammonium salt is selected from coco benzyl dimethyl ammonium chloride and dicoco benzyl methyl ammonium chloride in which the alkyl groups are predominantly C_{12} and C_{14} .

- 58 -

20. A formulation as defined in claim 16, wherein the quarternary ammonium salt is benzalkonium chloride or benzalkonium hydroxide.
- 5 21. A formulation as defined in any one of claims 1 to 14, wherein the compound of formula (I) is a betaine.
22. A formulation as defined in claim 21, wherein the
10 betaine is selected from the group consisting of coco amido propyl dimethyl betaine; cetyl betaine((carboxylatomethyl) hexadecyldimethylammonium); C12 amine dipropionate; and coco amido propyl dimethyl sultaine (cocoamidopropyl-N, N-dimethyl-N-2-
15 hydroxypropyl sulfobetaine.
23. A formulation as defined in any one of claims 1 to 14, wherein the compound of formula (I) is a C12-C14 dimethylalkylamine or salt thereof.
- 20 24. A formulation as defined in any one of the previous claims, further comprising a halopropynyl compound.
- 25 25. A formulation as defined in claim 24, wherein the halopropynyl compound is an iodopropynyl compound of formula (XX):



(XX)

- wherein R is selected from methyl, ethyl, propyl,
30 n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, octadecyl, cyclohexyl, phenyl, benzyl, tolyl, cumyl, chlorobutyl, chlorophenyl, and ethoxyphenyl.

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26. A formulation as defined in claim 25, wherein the iodopropynyl compound is 3-iodo-2-propynyl butyl carbamate.

5

27. A formulation as defined in any preceding claim, wherein the formulation is in a liquid form.

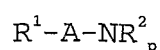
28. A formulation as defined in claim 27, wherein the
10 formulation is an emulsion.

29. A method of protecting a substrate of wood or other cellulosic material which comprises applying to the substrate a formulation as claimed in any one of the
15 preceeding claims or applying the individual components to the substrate such that the substrate effectively receives a formulation as defined in any of the preceding claims.

20 30. A method as claimed in claim 29, wherein the substrate is affected by or at risk of being affected by mould and staining or defacing organisms and in particular sapstain organisms.

25 31. A substrate made of wood or other cellulosic material treated with a formulation as claimed in any one of claims 1 to 28.

30 32. A substrate of wood or other cellulosic material comprising an amine oxide , an azole and a compound of formula (I)



(I)

35 wherein

- 60 -

R^1 denotes an alkyl group which contains from 6 to 24 carbon atoms, benzyl or substituted benzyl, or $(CH_2-CH_2O)_nH$ where $n = 1-20$;

A is absent or denotes a linker group that may be
5 $C=O$ or $-C=ONH(CH_2)_s-$ where $s = 1-3$;

$P = 2$ or 3 ;

and each R^2 , which are the same or different,
denotes H, CH_3 , C_2H_5 , $(CH_2-CH_2O)_nH$ where $n = 1-20$, an alkyl
group which contains from 6 to 24 carbon atoms,
10 $(CH_2)_mCOOH$, $(CH_2)_mCOO^-$, $(CHX)_mSO_3H$ or $(CHX)_mSO_3^-$ where $m = 1$
to 3 and X denotes H or OH,;
and wherein if the compound is charged it is accompanied
by a counterion X^- .

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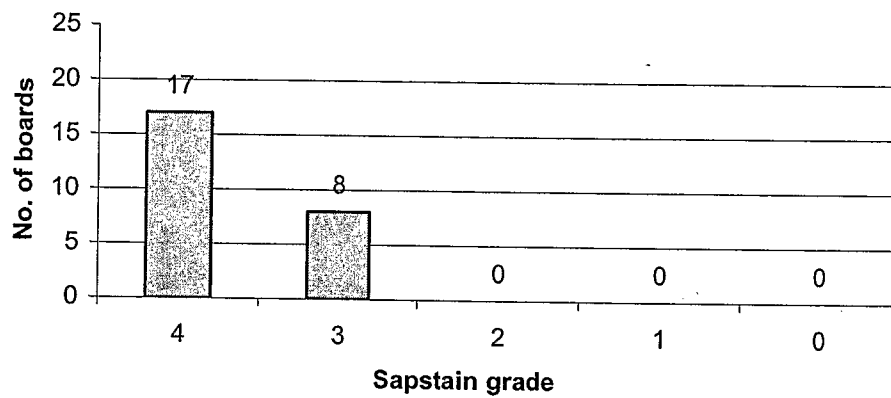
Untreated timber 3 weeks close stacked

Figure 1

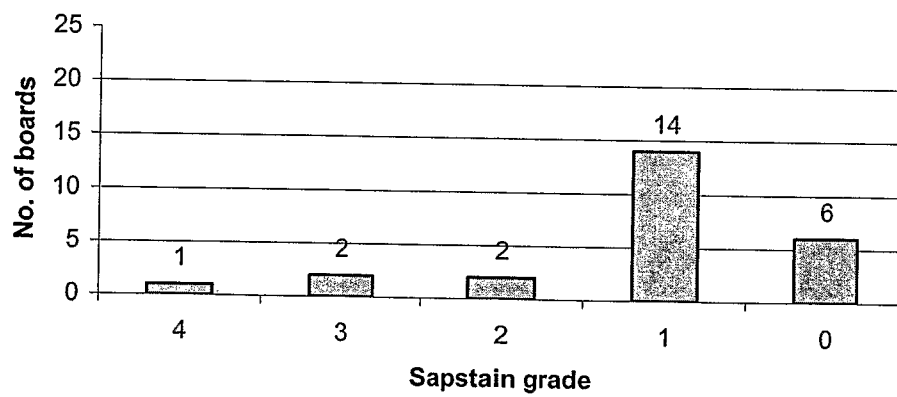
1.35% AT6 3 weeks close stacked

Figure 2

2 / 12

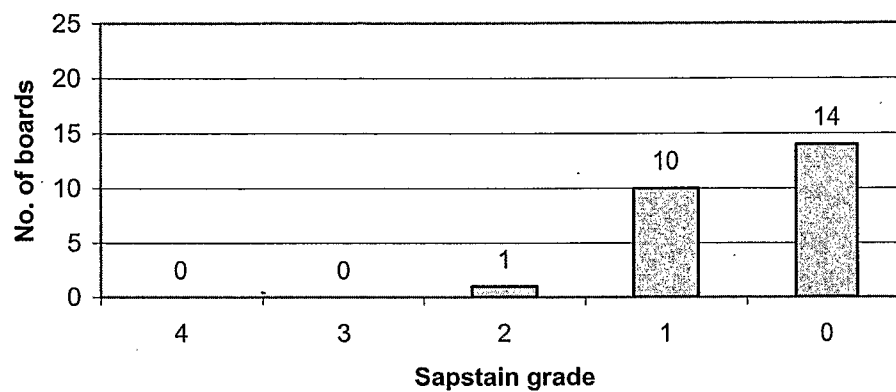
1.15% AT7M 3 weeks close stacked

Figure 3

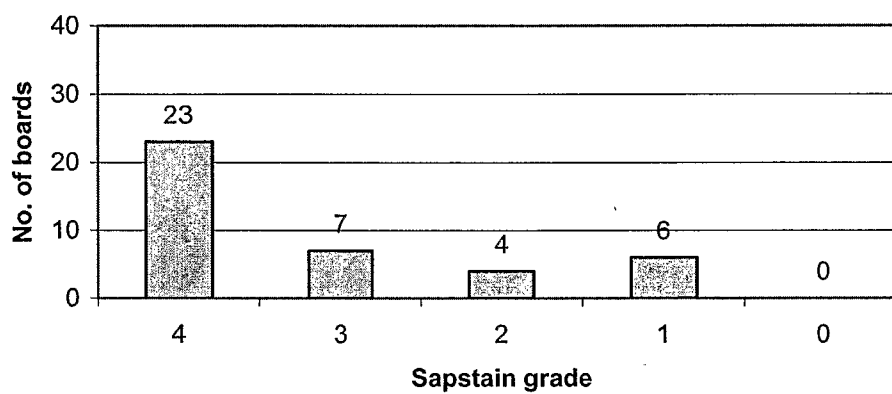
Untreated Pine Close Stacked

Figure 4

3 / 12

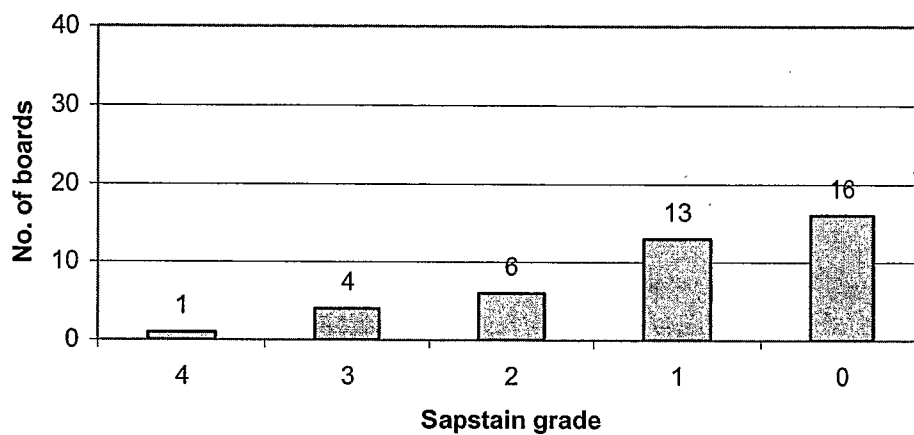
1.02% AT6A Closed Stacked

Figure 5

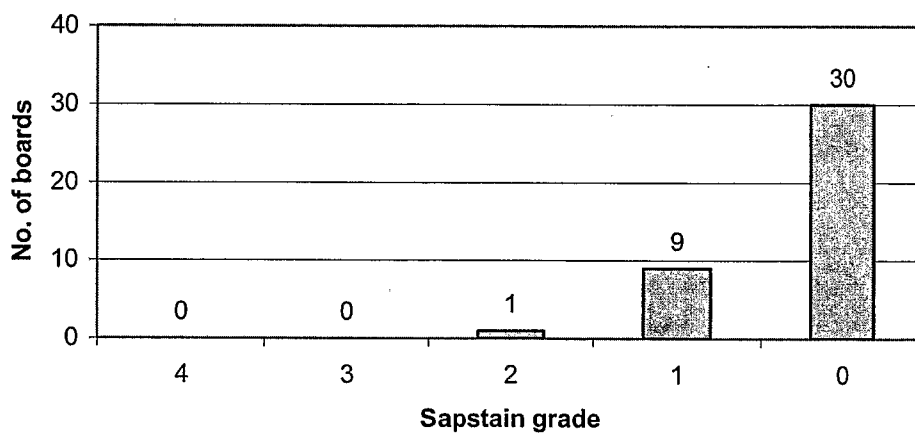
0.88% AT7M Close Stacked

Figure 6

4 / 12

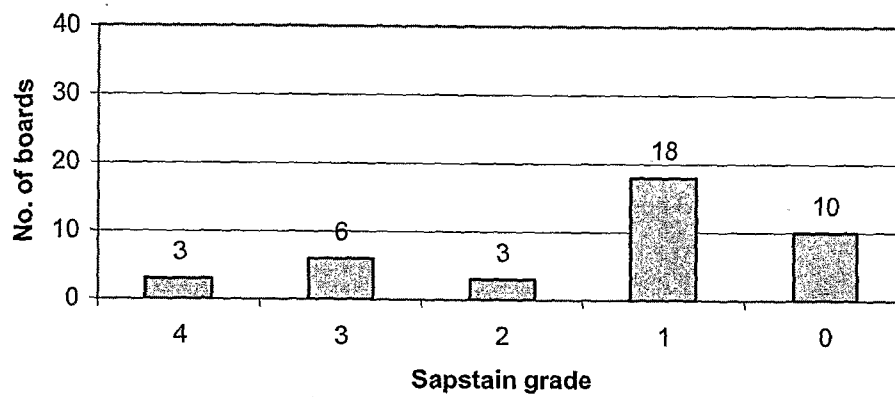
0.84% AT26 Close Stacked

Figure 7

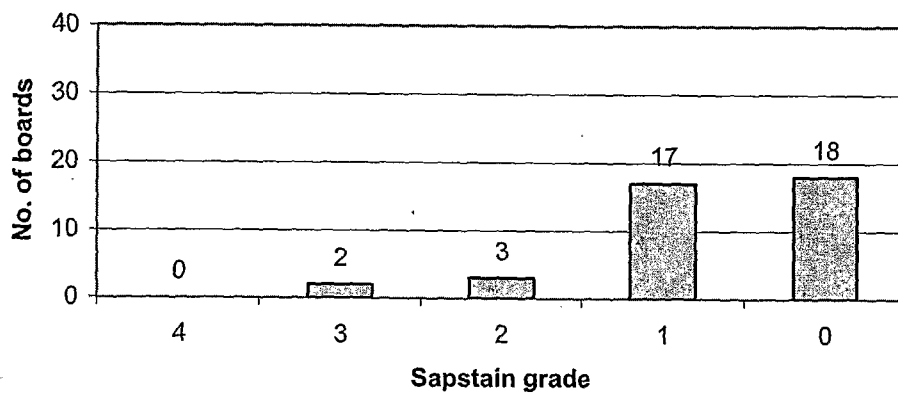
0.80% AT27M Close Stacked

Figure 8

5 / 12

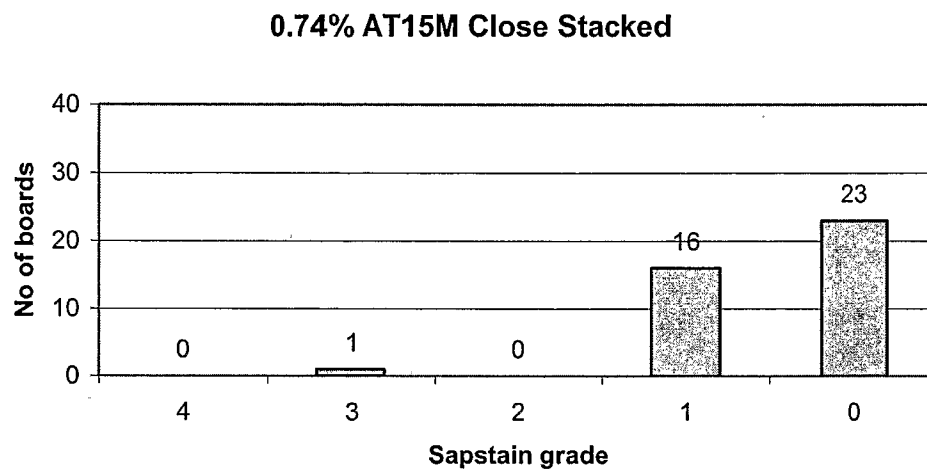


Figure 9

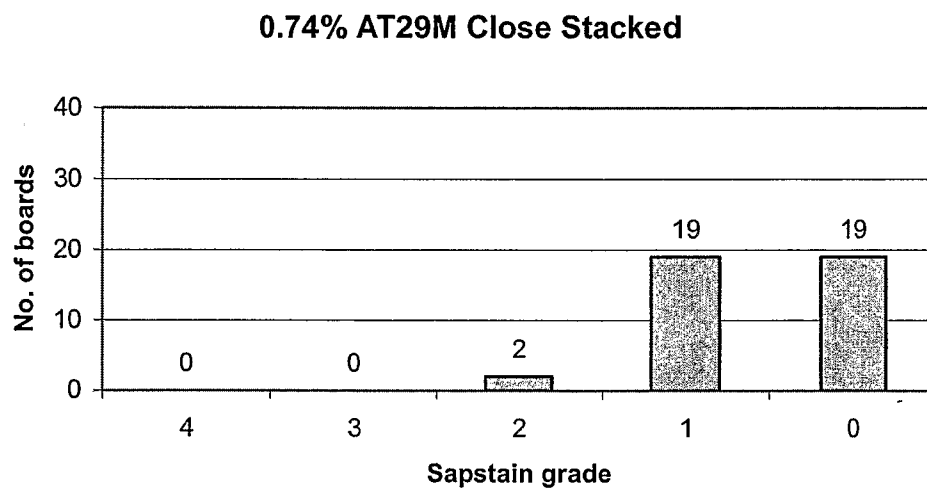


Figure 10

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Untreated close stacked

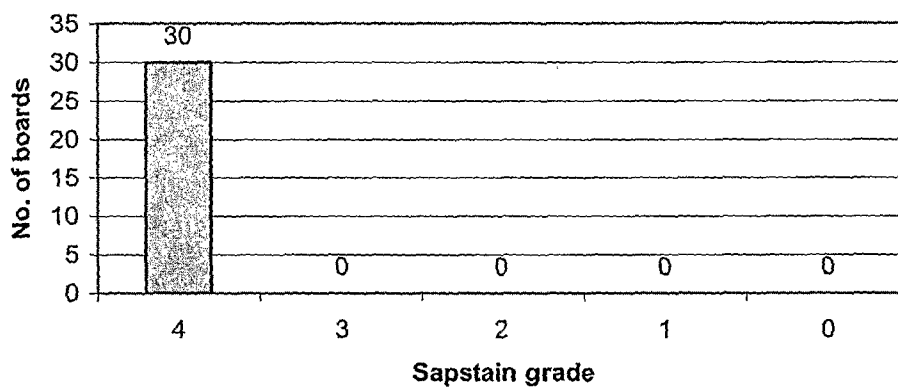


Figure 11

0.69% AT6 close stacked

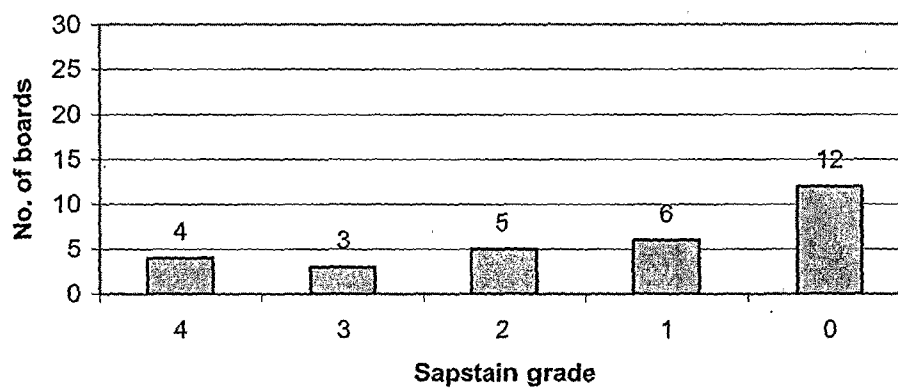


Figure 12

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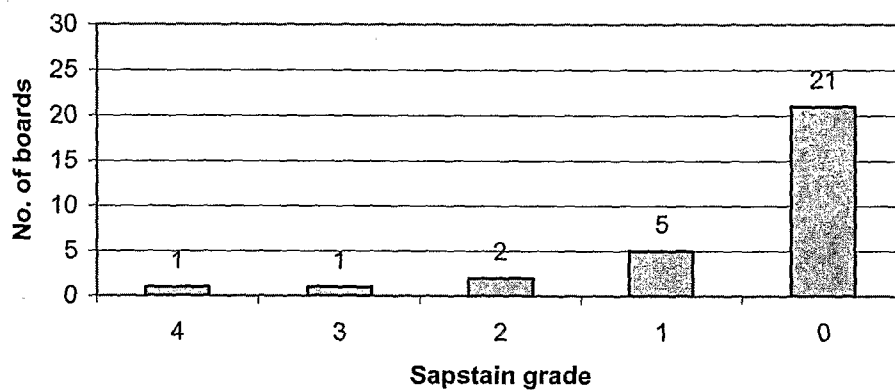
1.03% AT6 close stacked

Figure 13

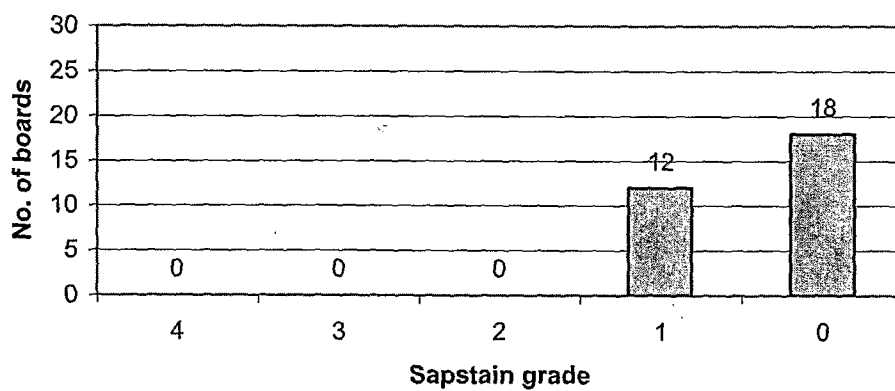
0.62% AT9 close stacked

Figure 14

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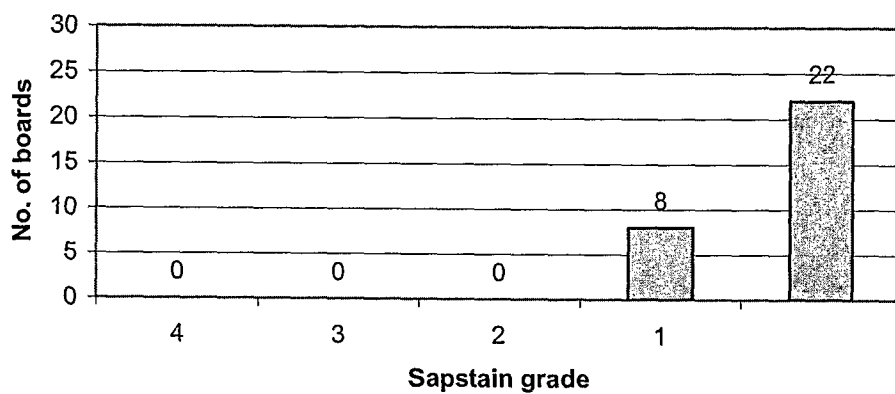
0.93% AT9 close stacked

Figure 15

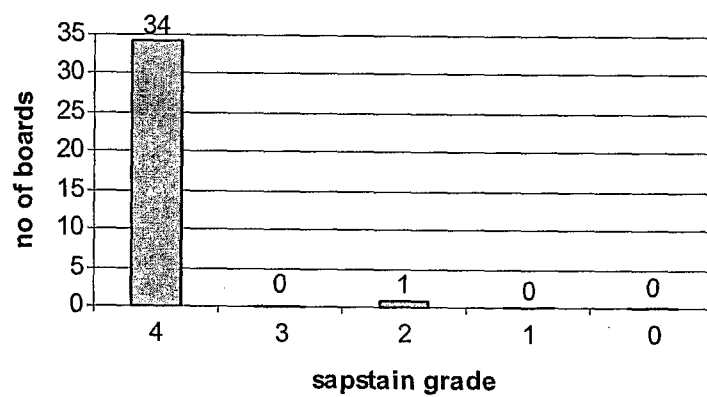
Untreated Pine Close Stacked

Figure 16

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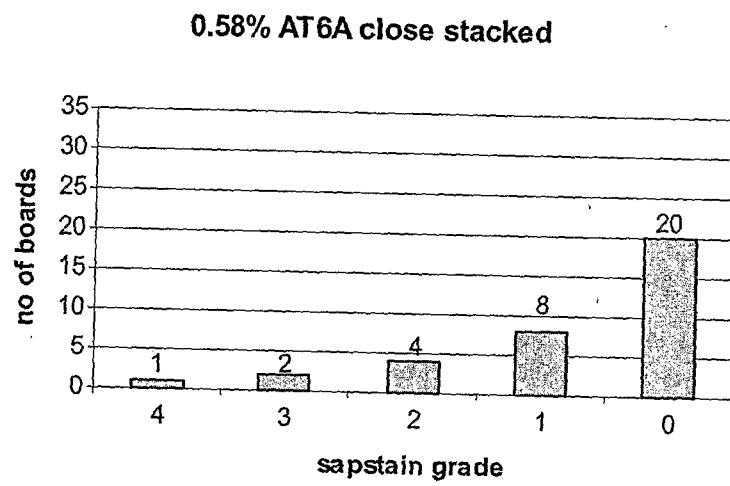


Figure 17

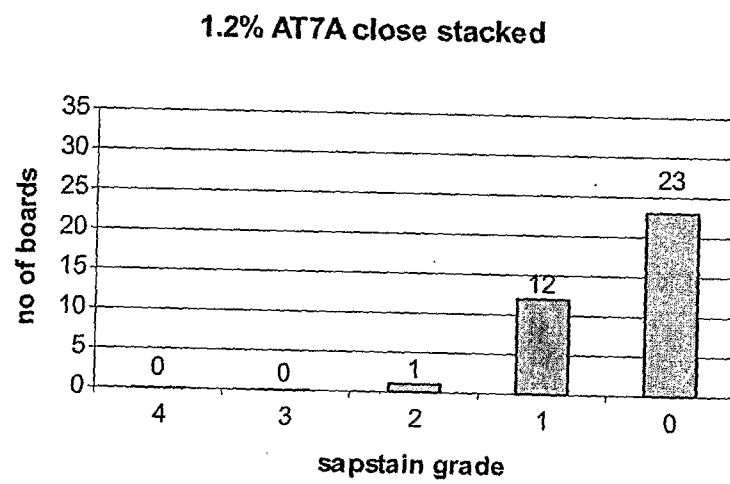


Figure 18

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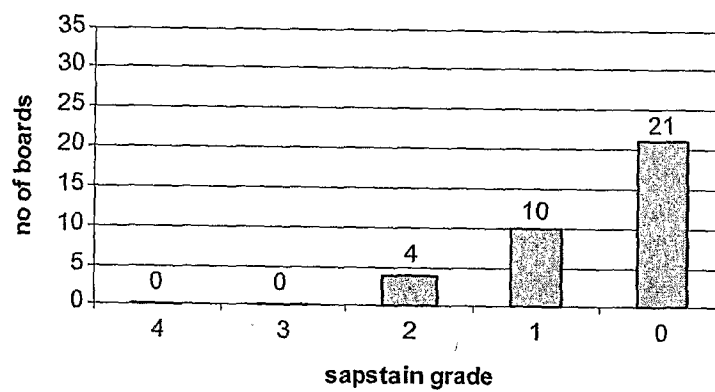
1.2% ATF1 close stacked

Figure 19

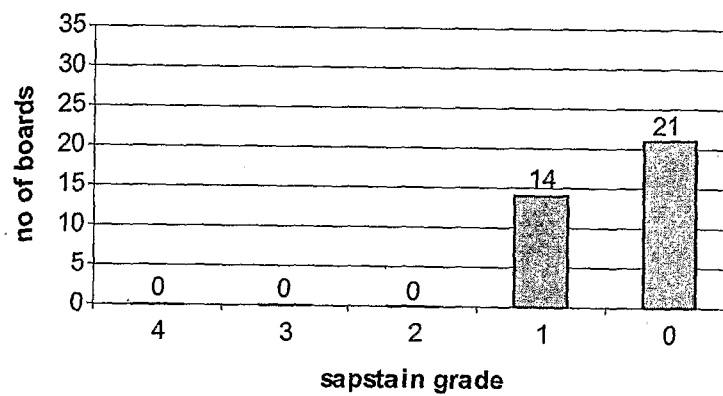
1.2% ATF2 close stacked

Figure 20

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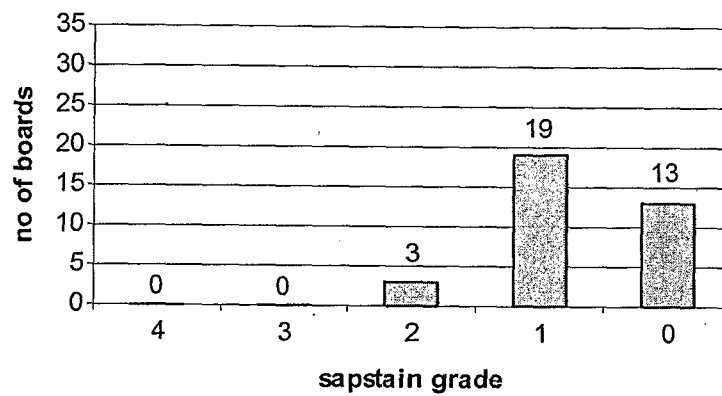
1.2% ATF3 close stacked

Figure 21

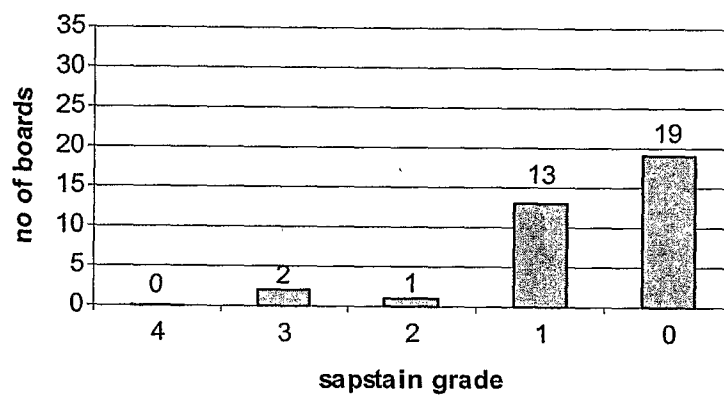
1.2% ATF4 close stacked

Figure 22

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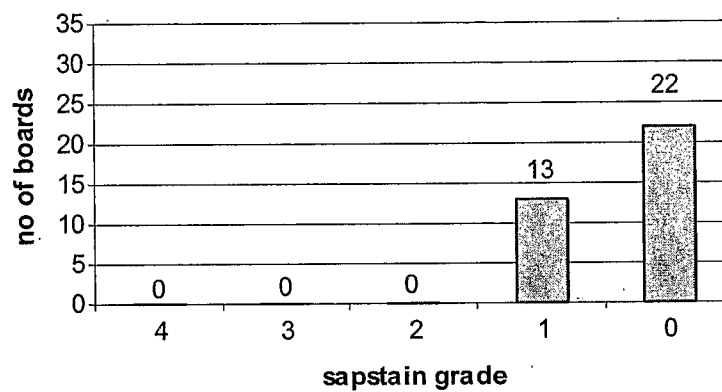
1.2% ATF5 close stacked

Figure 23

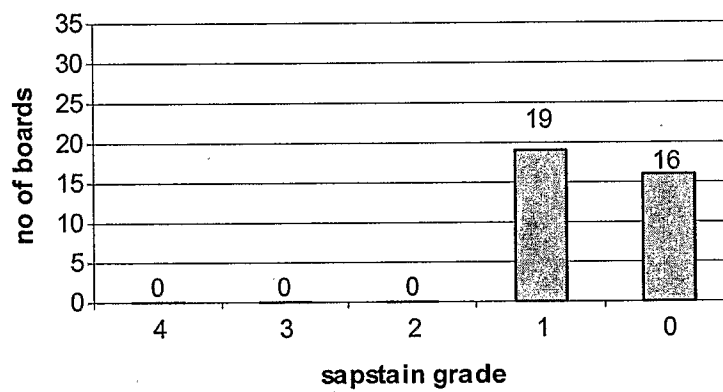
1.2% ATF6 close stacked

Figure 24