Title: BIOCIDAL COMPOSITIONS, THEIR PREPARATION AND USES THEREOF

Abstract: A biocidal composition useful in wood for antifungal purposes. It has at least one oxine metal and at least one aliphatic sulphonic acid. Where the at least one aliphatic sulphonic acid is methane sulphonic acid ('MSA') and where the at least one oxine metal is oxine copper, one or more of the following applies: (i) a weight to weight ratio of MSA to oxine copper is below 10 (i.e. in the ratio x:1, x is below 10), (ii) water is present, (iii) there is no organic co-solvent, and/or (iv) the oxine copper is at least almost exclusively solubilised by the MSA.
BIOCIDAL COMPOSITIONS, THEIR PREPARATION AND USES THEREOF

FIELD OF THE INVENTION

The present invention relates to fungicidal or fungal inhibitory compositions and the preparation and uses thereof.

Particularly, but not solely, the present invention relates to compositions suitable for the fungal protection of wood, in solid or composite form, or substrates containing wood fibre, where at least one active is present and that at least one active includes oxine copper (sometimes referred to as copper-8-quinolinolate or Cu-8) and/or other oxine metal.

Furthermore, the present invention concerns compositions which have favourable attributes, including cost-efficacy, stability and/or corrosivity compared to previously recorded formulations containing oxine copper.

BACKGROUND

With compositions to confer an antifungal effect on a wood or the like substrates it is necessary for the composition to be economic in such use and effective in such use. Economy may be related to direct costs of manufacture, delivery costs related to containerisation and transport of the antifungal composition to the treatment site, and specific plant capital and maintenance costs associated with manufacture and use of the antifungal product, determined by factors such as corrosiveness, or health, safety and environmental properties. Effectiveness can be diminished or negated by at least any lack of chemical stability, any inability to maintain or be usable in some semblance of physical homogeneity, any inability to provide any substantial degree of penetration from a surface to which it is applied prior to fixation in the substrate, any inability to
be applied effectively to a surface or any inability to remain attached to the substrate to which it is applied.

US Patent 4,602,011 of West and Nagle of the Chapman Chemical Company discloses certain antimicrobial agents (including oxine copper) where the metal chelate is solubilised by an alkyl benzene sulphonic acid of which DDBSA is the most preferred. US Patent 4,766,113, also of West and Nagle of the Chapman Chemical Company discloses compositions containing certain antimicrobial agents including oxine copper, where the metal chelate is solubilised in an alkyl benzene sulphonic acid of which DDBSA is again that most preferred.

NZ Patent 225428 to Chemicca relates also to DDBSA formulations of oxine copper combined with other actives. As well as DDBSA, the formulations contain at least one other solvent and one other surfactant. According to the example given in the patent, the formulations, when diluted to wood treatment concentrations, exist as a true solution of the oxine copper together with suspended particles of the co-active.

Wood treatment facilities that either dip or spray logs, lumber and the like may experience difficulties using products containing suspended particles. Problems include long term stability due to particle agglomeration, settling of particles in non-agitated domains of treatment plant, and blocking of nozzles of spray application equipment. Hence it is desired to manufacture compositions not presenting such difficulties and the industry is more favourably inclined towards use of solutions rather than suspensions.

In US Patent 4,766,113, West and Nagel disclose in the examples (as Example 9) solubilisation of 5 parts by weight of oxine copper with 64 parts by weight methane sulphonic acid (MSA) and 31 parts by weight methanol. This disclosure, whilst reporting solubilisation of oxine copper at a weight ratio of oxine copper:MSA, of 1:12.8, is nonetheless in the presence of cosolvent methanol and may be described as a non aqueous formulation.
US Patent 4,766,113 reports adversely in respect of the MSA containing formulation of Example 9, which under conditions of their experimentation, exhibited 62% fungal growth after 42 days. By comparison a composition comprising 5 parts by weight oxine copper, 64 parts by weight DDBSA and 31 parts by weight methanol formulation of Example 5, exhibited only 17% infection in the same trial.

The example in US Patent 4,766,113 is of no particular interest or relevance to our invention except to note the authors’ statement that oxine copper solubilised in several acids, including MSA, did not obtain the desired results of their invention (whereas solubilisation in DDBSA did). It will become apparent how our invention differs from the MSA formulation described in US Patent 4,766,113, in which:

- The ratio of MSA to oxine-copper in the formulation is 12.8:1
- The MSA formulation contains 31% methanol as the sole co-solvent.
- The formulation in concentrate form is non aqueous.
- The efficacy testwork in the US patent involved dipping boards at oxine copper concentrations of 125mg/L. Such low concentrations are not realistic for an industry where only minimal fungal infection may be tolerated and protection for two to six months may be required. Commercial practice in countries such as NZ and Chile typically requires oxine copper concentrations of 1000-2000 mg/L.
- A composition containing high MSA (64%w/w), methanol (31% w/w) and 5% w/w copper-oxine composition (prior to dilution) would not be cost advantageous compared to the DDBSA formulations disclosed.
A composition containing 31% methanol would be classed a flammable product and be subject to hazardous goods transport regulations and site restrictions for storage and usage.

No other references to the use of MSA for solubilisation of oxine copper or other oxine metals have been found in the literature.

Therefore any researcher considering US Patents 4,602,011 and 4,766,113 would be deterred from using MSA with oxine copper by the apparent evidence that a high MSA to oxine copper ratio of over 12:1 is required, thus denoting a comparatively high cost formulation. Furthermore, trial data suggests that such a composition would not rate well against DDBSA formulations with regards to efficacy.

Patent WO 9953760 to Mattersmiths Holdings relates to use of phosphorous acid or phosphite ions in acidic environment as a means of solubilising oxine copper and other fungicidally active ingredients. The biocides so formed may incorporate secondary actives also in true solution. Therefore the compositions may be expected to overcome the problems aforementioned with respect to handling particulate matter in spray application equipment.

The Mattersmiths patent proposes that the phosphite ion has biocidal properties. Various phosphite compositions have been found to be effective in protecting grape vines, citrus and fruit trees and tropical plants against certain pathological diseases (see for example US Patents 4,075,324 to Thizy; 5,070,083 to Bartlett). The principal mode of action of assimilated phosphite is to enhance the plant's phytoimmune system and thereby retard growth of Phycomycetes fungi (Pegg, K.G. and deBoer, R. F., *Proceedings of the Phosphonic Acid Work Shop*, Australian Plant Pathology, Vol 19(4) 1990.

However no pathological mode of action of phosphite has been noted for Ascomycetes fungi (which includes most of the important lumber mould and sapstain infections such as alternaria, candida, trichoderma, penicillium, geotrichium and ophiostoma species). On the contrary it has been noted (US
Patent 5,736,164 to Taylor) that phosphite may enhance the growth of Ascomycetes fungi by reducing the competition from Phycomycetes fungi. This process is termed pathological acerbation.

Therefore we would conclude that if there is any efficacy advantage of using phosphorous acid in compositions for wood treatment, it is unrelated to the reasons described for biocidal efficacy of phosphite ions in the protection of living plants.

A disadvantage of phosphorous acid/copper ion compositions such as described in the Matterssmiths patent, is that in concentrate form they are thermodynamically unstable. Upon standing, copper ions become reduced to copper metal with accompanying oxidation of the phosphite to phosphate species. The actual rate that this reaction occurs with oxine copper solutions has not been reported and the kinetics may be dependent on exogenous factors such as impurities in the composition, or material composition of the storage container. Our experience with laboratory produced samples containing phosphorous acid is that copper deposition is evident within a few weeks of storage.

Phosphorous acid based oxine copper compositions find limited application in the lumber treatment industry because such products are highly corrosive to mild steel. Corrosion of plant and equipment can be mitigated by coating mild steel components or substitution of stainless steel. However this can be expensive, particularly with regards to protection of moving parts such as rollers and chains. As a consequence it may be seen desirable to utilise lowly corrosive oxine copper products and DDBSA formulations compare favourably in this respect.

The present invention has as an aim the provision of oxine copper in an antimicrobial composition solubilised by aqueous formulation of methane sulphonic acid ("MSA") which is sometimes known as methyl sulphonic acid CAS No. 75-75-2).
This invention arises from the surprising discovery that aqueous MSA solutions can afford a means of producing cost competitive and effective antifungal compositions containing oxine copper and optionally other actives, suitable for application to wood or wood fibre related articles.

The low cost of the present invention’s formulations arises in part from much lower concentrations of MSA in aqueous solution required to solubilise oxine copper, compared to levels used in the aforementioned, methanolic MSA example in US Patent 4,766,113, which would be uneconomic from a materials cost perspective and also due to high handling costs of dealing with a flammable product.

In addition, the MSA formulations of the present invention have containerisation and transport cost savings accruing from the ability to produce highly concentrated oxine copper contents of more than 16% w/w, which on a weight basis is at least twice as concentrated as commercial oxine copper products based on DDBSA and phosphorous acid.

Also specific gravities of MSA formulations of this invention are about 10% lower than phosphorous acid formulations of equivalent oxine copper content, which would allow cost savings in transporting oxine copper product in shipping containers, where weight rather than volume packing limitations may apply.

Finally, cost savings may accrue at treatment plants where MSA formulations are (surprisingly) less corrosive than phosphorous acid formulations and more easily handled compared to the viscous and foamy DDBSA products.

Contrary to the poor result of a methanolic MSA formulation of oxine copper in US Patent 4,766,113, the MSA formulations of the present invention are surprisingly effective. Even in the absence of the US Patent data, there would be no reason to predict MSA formulations of oxine copper would be effective, because MSA does not possess similar hydrophobic character to the dodecyl hydrocarbon chain of DDBSA, which the authors of US Patent 4,766,113
believe, is a vehicle to permit penetration of the active into the fungal cell and therefore is the key to DDBSA’s efficacy. Nor does the sulphonate anion of MSA possess any similar biocidal activity ascribed to the phosphite ion, which the author of Patent WO 9953760, believes is the key to the efficacy of phosphorous acid based oxine copper formulations.

We believe that the authors of US 4,766,113 and WO9953760 have both missed identifying the key determinant of efficacy of oxine copper products. In example 6 of this patent we show similar efficacies of oxine copper products formulated with DDBSA, phosphorous acid, phosphoric acid and MSA and mixtures of these acids, suggesting that the nature of the anion is not of great importance. However the example also shows that it is shows that it is possible to enhance or diminish efficacy of the MSA formulation by increasing or decreasing the acidity of the formulation. Similarly increasing the pH of the phosphorous acid formulation (with sodium phosphite) caused a marked decrease in efficacy even though the formulation contained additional “biocidal” phosphite ions.

It is well known in the fermentation and other industries that fungal growth may be inhibited by pH’s less than 2.5-4. The pH’s of working concentrations of the DDBSA, phosphorous acid and MSA formulation of oxine copper range from 1.5 – 2.3 and therefore when freshly applied to wood surfaces, would provide an unfavourable environment for fungal growth. In time, the wood surface re-establishes a higher pH by chemical reaction and water dilution. We hypothesise that the efficacy enhancement by increased acidity formulations of oxine copper is related primarily to the provision of a low pH environment at the wood surface, hostile to fungal growth, over a longer time period.

Unlike phosphorous acid, MSA does not have strong reducing properties and a further efficacy advantage of the MSA/ oxine copper products of this invention is that they are stable for long periods (indefinitely) and not prone to deposition of copper.
SUMMARY OF THE INVENTION

The present invention has as an object the provision of a composition that provides at least an alternative to other oxine copper based antifungal compositions and/or preferably any one or more of the advantages previously stated.

The present invention has at least one object the provision of biocidal compositions (including those useful for treating wood or wood related substrates) which are in the form of solutions and do not give rise to unstable copper complexes, do not cause precipitation of reduced copper species, and/or which may, if desired, include coactives.

Whilst applicable to oxine metal concentrates, the present invention at least in some embodiments has demonstrated that oxine copper concentrates formulated with MSA are not prone to form unstable copper complexes and/or cause precipitation of reduced copper species as with other formulations based on DDBSA or phosphorous acid.

In one aspect the invention consists in a biocidal composition consisting of, including or having at least one oxine metal and at least one aliphatic sulphonic acid but with the proviso that, where the at least one aliphatic sulphonic acid is methane sulphonic acid ("MSA") and where the at least one oxine metal is oxine copper, one or more of the following applies:

(i) a weight to weight ratio of MSA to oxine copper is below 10 (i.e. in the ratio x:1, x is below 10),

(ii) water is present

(iii) there is no organic co-solvent, and/or

(iv) the oxine copper is at least almost exclusively solubilised by the MSA.

In another aspect the present invention consists in a biocidal composition comprising, including or having
oxine copper, and

MSA,

wherein the weight to weight ratio of MSA to oxine copper is below 10 (i.e. in the ratio x:1, x is below 10).

As used herein “biocidal composition” includes but is not restricted to wood treatment compositions nor is it restricted to antifungal compositions.

In another aspect the present invention consists in a biocidal composition comprising, including or having together as a solution at least

oxine copper, and

at least one aliphatic sulphonylic acid.

We consider MSA as belonging to the group of aliphatic sulphonylic acids. This distinguishes it from other commercially produced sulphonylic acids, such as DDBSA, benzene sulphonylic acid and p-toluene sulphonylic acid, all of which have aromatic character. Of the aliphatic sulphonylic acids, MSA is the only member produced in bulk quantities and suitably low cost as it has a range of industrial uses. Other sulphonylic acids, such as ethane sulphonylic acid, di-ethyl sulphonylic acid, n-propyl sulphonylic acid, isopropyl sulphonylic acid, etc could be used but currently cost considerations would rule out usefulness of such materials.

In another aspect the present invention consists in a biocidal composition comprising, including or having

oxine metal (e.g. oxine copper) in solution in

MSA,

wherein the weight to weight ratio of MSA to the oxine metal is below 10.

As used herein “oxine metal” can include one or more oxine complexes of metal. The term “oxine metal” and/or “at least one oxine metal” can include
mixtures of oxine metal whether one is greatly in excess of the other or not and irrespective of whether or not the oxines are the same and/or the metal species are the same.

In addition to Cu-8-O, other metal complexes of oxine are known to be effective antimicrobials. Of these, mercury is generally regarded as being more effective than copper, and the following is a listing taken from literature references of the relative effectiveness of several metal quinolinolates in descending order of activity: mercury, copper, cadmium, nickel, lead, cobalt, zinc, iron and calcium. Aluminium and tin are also useful.

In another aspect the present invention consists in a **biocidal composition** comprising, including or having

- oxine metal (e.g. oxine copper) in solution in
- at least one aliphatic sulphonlic acid.

In another aspect the present invention consists in a **biocidal composition** having

- at least one oxine metal (e.g. oxine copper), as a biocidal active agent,
- MSA, and
- water,

[and, optionally, at least one other biocidal active agent].

optionally the weight to weight ratio of MSA to the oxine metal is below 10:1

In another aspect the present invention consists in a **biocidal composition** having

- at least one oxine metal (e.g. oxine copper), as a biocidal active agent,
- at least one aliphatic sulphonlic acid, and
water,

[and, optionally, at least one other biocidal active agent],

Preferably the oxine metal is oxine copper.

In any of the aforementioned biocidal compositions optionally or 
mandatorily water is present.

In any of the aforementioned biocidal compositions preferably the oxine 
copper is at least almost exclusively solubilised in the MSA.

In any of the aforementioned embodiments of the present invention 
preferably there is no organic co-solvent. However there can be an organic co-
 solvent e.g. alcohol(s), glycol(s), etc. Should any methanol be present 
(preferably there is none) preferably the w/w proportion thereof is below 31% 
w/w (more preferably below 10% w/w).

In yet a further aspect the present invention consists in a liquid biocidal 
composition comprising or including

an effective amount of oxine copper and/or other oxine metal(s) as a first 
biocidal active,

an effective amount of at least one coactive biocidal material, and

MSA in which at least the oxine copper and/or oxine metal(s) (preferably 
acid stable) is solubilised,

[and, optionally, water and/or other component materials].

In yet a further aspect the present invention consists in a liquid biocidal 
composition comprising or including

an effective amount of oxine copper and/or other oxine metal(s) as a first 
biocidal active,

an effective amount of at least one coactive biocidal material, and
at least one aliphatic sulphonie acid in which at least the oxine copper and/or oxine metal(s) (preferably acid stable) is solubilised,

[and, optionally, water and/or other component materials].

Preferably the composition is further characterised in that the coactive biocidal material(s) is (are) further selected from at least the benzimidazoles, morpholine compounds, isothiazolinones, triazoles, quaternary ammonium salts and metal complexes.

Preferably the biocidal compositions of the present invention are a true solution.

As shown in Example 7 hereafter, MSA formulations have relatively low fluid uptakes into wood. Low fluid uptakes can be advantageous if shorter time periods for the treated wood to become drip free are required. However, if desired, small amounts of surface active agents may be added to the composition to increase fluid uptakes by the wood.

The present invention does not exclude the possibility of incorporating corrosion inhibitors, dyestuffs, insecticides, bactericides or any surface modification agents which may advantageously confer additional attributes to the formulation.

The present invention does not exclude the possibility of co-addition of other fungicidal products, corrosion inhibitors, dyestuffs, insecticides, bactericides or any desired substrate surface modification agents at the treatment point of application.

The present invention does not exclude a number of co-actives (e.g. fungicidally active compounds) being utilised.

By way of example substituted benzimidazoles, isothiazolinones, azoles, pyrroles, secondary and tertiary amines, quaternary ammonium salts, morpholines, guazatine, orthophenyl-phenol, organo-metal complexes, chlor0thalonil and methylene bis-thiocyanate form part of the range of
fungicidally active compounds that can be included as representative fungicidally active compounds.

In yet a further aspect the present invention consists in a biocidal composition comprising or including

1 to 25% w/w of at least one oxine metal [e.g. oxine copper] as at least a first biocidal active, and

1 to 60% w/w of MSA in which at least the oxine metal(s) is solubilised,

Optionally and preferably at least some water is present.

Preferably the presence of the at least one oxine metal or at least oxine copper is from 5 to 20%.

More preferably the at least one oxine metal and/or oxine copper is present from 10 to 20%w/w.

Irrespective of the weight percentage of the at least one oxine metal and/or oxine copper present preferably the MSA to oxine copper w/w ratio is less than 10. More preferably the ratio is between 1.1 and 2.5.

In a further aspect the present invention consists in a biocidal composition suitable for use, but not necessarily for use, with a wood or other such substrate, said composition comprising or including as a solution in the context of the overall composition up to 25% w/w oxine copper and up to 60% w/w of MSA,

wherein the w/w ratio of MSA/oxine copper is less than 10 (and preferably between 1.1 and 2.5).

Most preferably therefore the oxine copper levels are below 20% w/w but above 5%.

In yet a further aspect the present invention consists in a biocidal composition comprising or including
1 to 25% w/w of at least one oxine metal [e.g. oxine copper] as at least a first biocidal active, and

1 to 60% w/w of at least one aliphatic sulphonic acid in which at least the oxine metal(s) is (are) solubilised.

Optionally and preferably at least some water is present.

Preferably the presence of the at least one oxine metal or at least oxine copper is from 5 to 20%.

More preferably the at least one oxine metal and/or oxine copper is present from 10 to 20% w/w.

In a further aspect the present invention consists in a **biocidal composition** suitable for use, but not necessarily for use, with a wood or other such substrate, said composition comprising or including as a solution (in the context of the overall composition) up to 25% weight for weight oxine copper and up to 60% w/w of at least one aliphatic sulphonic acid.

In yet a further aspect the present invention consists in a **method of preparing a biocidal composition** comprising or having

at least one oxine metal as a first biocidal active,

[optionally at least one coactive biocidal composition],

MSA in which at least the oxine metal(s) is (are) solubilised, and

water,

said method comprising or including the steps mixing (in any order) the biocidal active(s), the coactive(s) [if any], MSA and water so as to solubilise the biocidal active(s) (preferably without any requirement to provide external heat).

In general, dissolution of the active(s) will be carried out at temperatures higher (e.g. 5–20°C) than ambient because of the exothermic heat of dilution reaction of the aliphatic sulphonic acid and water. However in some circumstances, such as
in the preparation of high active content compositions, it may be advantageous to apply external heat to assist dissolution rates.

In yet a further aspect the present invention consists in a method of preparing a biocidal composition comprising or having

5 at least one oxine metal as a first biocidal active,

optionally at least one coactive biocidal composition,

at least one aliphatic sulphonic acid in which at least the oxine metal(s) is (are) solubilised, and

water,

10 said method comprising or including the steps mixing (in any order) the biocidal active(s), the coactive(s) [if any], at least one aliphatic sulphonic acid and water so as to solubilise the biocidal active(s) at reaction temperatures.

Whilst reference in respect to some of the biocidal compositions previously and/or methods of preparing a biocidal composition has referred to a mandatory or optional water presence, other solvents including alcohols, glycols, etc could fully or partially replace water in the formulation. Where however there is a drive to cost/efficacy of the formulation most preferably this is achieved by the following:

- the use of copper oxine alone as the only oxine metal

20 - the use of MSA alone as the sole aliphatic sulphonic acid
- use of water as the sole solvent or liquid component apart from MSA
- use of acid/active ratios less than 10:1 and preferably in the range 2.5:1 to 1.1:1
- use of acid/active ratios generally one quarter to one half the corresponding acid/active ratios used for DDBSA and phosphorous acid formulations
production of concentrates containing high active concentrates e.g. 20% w/v oxine copper as opposed to more expensive to transport formulations involving DDBSA which are limited to about 4-8% w/v oxine copper.

- the lower density of the MSA product when compared with phosphorous acid products which will allow approximately 10% additional product to be stowed in a shipping container for the same active content thereby again leading to transport cost savings.

In a further aspect, the invention consists in a **method of treating a matrix or substrate** to minimise, prevent or reduce fungal growth, fungal discolouration and/or fungal damage, said method comprising or including the step of coating and/or impregnating the matrix or substrate with a composition of the present invention.

In still a further aspect the invention is a **matrix or substrate** where treated with a composition of the present invention or by a method of the present invention.

As used herein “and/or” means “and” and “or”. As used herein “(s)” after a noun means both the singular and plural forms of the noun.

**DESCRIPTION OF THE INVENTION**

The present invention provides cost competitive formulations containing MSA, which are at least as efficacious as such DDBSA formulations and/or which have greater efficacy than corresponding DDBSA formulations, and this will be surprising to researchers in this field.

The present invention also recognises that MSA affords a convenient and low cost means of incorporating acid stable biocides (such as substituted benzimidazoles, isothiazolinones, azoles, pyrroles, secondary and tertiary amines, quaternary ammonium salts, morpholines, guazatine, orthophenylphenol, organo-metal complexes, chlor0thalonil and methylene bis-thiocyanate)
as secondary actives in solubilised oxine copper compositions. In this regard reference should be made to other patents in this field exemplifying such acid stable biocides concerning dual active oxine copper containing products formulated with DDBSA or phosphorus acid.

The MSA based formulations according to this invention are true solutions in all dilutions in water of both oxine copper and the secondary actives. Therefore the formulated products do not have the physical problems of handling suspensions as with the DDBSA based products.

An additional feature of the application of suspension products such as the DDBSA formulations, to the surface of lumber is that the active ingredient can confer only surface protection of the wood. During storage, the surface of the wood often becomes too dry to support fungal activity, which progressively moves deeper into the wood according to the moisture front. Therefore efficacy advantages accrue to the MSA products of this invention, which contain solubilised actives and have consequently penetrating ability into the wood matrix.

It may also be noted that DDBSA has anionic surfactancy and treatment plants using DDBSA based products generally require use of defoamer products to control foam build-up. However foam control is generally not required for the MSA based products of this invention, which preferably contain no surfactants or low-foaming surfactants.

Where however there is a drive to cost/efficacy of the formulation most preferably this is achieved by the following:

- The use of copper oxine alone as the only oxine metal
- The use of MSA alone as the sole aliphatic sulphonic acid
- Use of water as the sole solvent or liquid component apart from MSA
- Use of acid/active ratios less than 10:1 and preferably in the range 2.5:1 to 1.1:1
- use of acid/active ratios generally one quarter to one half the corresponding acid/active ratios used for DDBSA and phosphorous acid formulations

- production of concentrates containing high active concentrates e.g. 20% w/w oxine copper as opposed to more expensive to transport formulations involving DDBSA which are limited to about 4-8% w/w oxine copper.

- the lower density of the MSA product when compared with phosphorous acid products which will allow approximately 10% additional product to be stowed in a shipping container for the same active content thereby again leading to transport cost savings.

EXAMPLES

Example 1 Preparation of a stock solution of 7% w/v oxine copper in MSA solution

105g oxine copper was dispersed in 1 litre of water and 192g of 99% MSA was added slowly while stirring. The reaction temperature reached was 28°C and the oxine copper dissolved readily. After dissolution further water was added to a final product volume of 1.5 litres. The sample was analysed titrimetrically for copper showing an equivalent oxine copper content of 70g/l. The solution was stored in a glass container in the laboratory at 20°C after four months and after six months storage and no loss of activity was apparent and no sediment was observable in the stored product.

Example 2 Preparation of a high concentration 22.5% w/v oxine copper solution.

22.5g of oxine copper was added to 25.2g MSA and 68.8g of water. The oxine copper dissolved readily when warmed to 50 - 60°C and the solution of
concentration 19% w/w (22.5% w/w) was stable when cooled to room temperature.

Example 3 Preparation of a dual active product containing oxine copper and carbendazim

A composition was produced containing 22.5g oxine copper, 22.5g carbendazim 50g MSA and 230 g water. The clear stable product formed contained 6.8% w/w oxine copper and 6.8% w/w carbendazim.

Example 4 Preparation of a dual active compound containing oxine copper and morpholine

A composition containing 40g oxine copper, 150g MSA, and 65g morpholine was made in one litre total volume in water. The resulting solution of pH=1.9 was clear, stable and contained no discernible ammoniacal odour associated with morpholine at neutral and alkaline conditions.

Example 5 Comparison of the Lumber Protection Efficacies of Oxine Copper products formulated with DDBSA and MSA.

Table 1 shows results of an accelerated field trial of various oxine copper products containing MSA or DDBSA and some products containing carbendazim as a secondary active.

The methodology of this type of trialling is reported elsewhere (Frazer, F.W. et al. Design of Field Trials for Evaluation of Antisapstain Products International Research Group on Wood Preservation, Annual Meeting, Brisbane, Australia, May 2003, IRG/WP 03-20263).
The trialling involves dipping freshly milled boards in the various treatment solutions, leaving the treated boards open to the 25°C atmosphere for three days to lose 5-10% moisture, packaging the treatments in plastic bags and storage at 25°C for suitable periods (e.g. 4-10 weeks) to allow fungal development. Results are expressed as the mean percentage infection of all boards in the treatment as well as the percentage of the inspected board surfaces deemed to have failed, where a "fail" is deemed to have greater than 5% infection.

The products compared as listed in Table 1 are:

- **CTLR** - A formulation containing 70g/L oxine copper in MSA prepared as per Example 1. (Tested at 1%, 1.8% and 2.7% dilutions in water).
- **HER** - A formulation containing 75g/L oxine copper and 75g/L carbendazim prepared as per Example 3. (Tested at 0.6% and 1.2% dilutions).
- **CTLM** - A formulation containing 40g/L oxine copper and 65g/L morpholine prepared as per example 4. (Tested at 2.7% dilution).
- **CTL** - A commercial formulation of 40g/L oxine copper in DDBSA produced by Osmose NZ. (Tested at 4% dilution).
- **HE** - A commercial formulation of 75g/L oxine copper and 75g/L carbendazim in a DDBSA/solvent/surfactant matrix produced by Osmose NZ. (Tested at 0.6% and 1.2% dilutions).

**Table 1 Comparison of DDBSA and MSA formulations of Oxine Copper Products**

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>DILUTION (%) IN WATER</th>
<th>%FAILED SURFACES</th>
<th>%MEAN INFECTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>HER</td>
<td>1.2</td>
<td>4</td>
<td>2.6</td>
</tr>
<tr>
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<td></td>
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<td>--------</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
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<td>10</td>
<td>3.9</td>
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<td>14</td>
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<td>2.7</td>
<td>79</td>
<td>18</td>
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<tr>
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<td></td>
<td>100</td>
<td>&gt;30</td>
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</table>

The above results show that MSA formulations have equal or better efficacy compared to DDBSA formulations containing oxine copper.

5 Example 6 Efficacy Comparison of DDBSA, MSA, phosphorous acid, and phosphoric acids and Various combinations for Lumber Protection

A trial was carried out, as per the methodology of Example 6, to compare the relative efficacies of DDBSA, MSA, phosphorous acid and phosphoric acid for oxine copper formulation. In addition three 50:50 mixtures of MSA/phosphorous acid, MSA/phosphoric acid and phosphorous acid/phosphoric acid were included to determine if any efficacy synergies between the acids exist. Finally pH perturbations of phosphorous acid and MSA treatments were made (with sodium phosphite, borax and added MSA) to determine any efficacy differences.
Phosphoric acid preparations of oxine copper are relatively unstable and must be freshly prepared for such trialling. A composition prepared for this trial contained 75 g oxine copper, and 420g (855) phosphoric acid made up to one litre in water. The MSA and DDBSA formulations used were as in Example 5. The phosphorous acid formulation was prepared as per example 15 of the Matterssmiths patent.

All products were compared at a common oxine copper content of the diluted treatment solution of 1.6g/l. The results are shown in Table 2.

<table>
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<tr>
<th>TREATMENT</th>
<th>% FAILED SURFACES</th>
<th>% MEAN INFECTION</th>
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<tr>
<td>MSA + 15G/L MSA</td>
<td>22</td>
<td>7</td>
</tr>
<tr>
<td>MSA/PHOSPHORIC ACID</td>
<td>39</td>
<td>9</td>
</tr>
<tr>
<td>MSA/PHOSPHOROUS ACID</td>
<td>41</td>
<td>15</td>
</tr>
<tr>
<td>PHOSPHOROUS ACID</td>
<td>48</td>
<td>15</td>
</tr>
<tr>
<td>PHOSPHORIC ACID</td>
<td>50</td>
<td>18</td>
</tr>
<tr>
<td>MSA</td>
<td>54</td>
<td>15</td>
</tr>
<tr>
<td>DDBSA (CUTROL)</td>
<td>56</td>
<td>15</td>
</tr>
<tr>
<td>PHOSPHORIC/PHOSPHOROUS ACID</td>
<td>57</td>
<td>20</td>
</tr>
<tr>
<td>PHOSPHOROUS +20/G/L SODIUM PHOSPHITE</td>
<td>81</td>
<td>26</td>
</tr>
<tr>
<td>MSA + 20G/L BORAX</td>
<td>100</td>
<td>42</td>
</tr>
</tbody>
</table>
The results show no statistical differences between MSA, DDBSA, phosphorous acid and phosphoric acid in this trial. Also there were no apparent synergies from the trialled mixtures of MSA, phosphorous and phosphoric acids. The additional MSA added of 15g/L working solution significantly improved the performance of the MSA formulated material indicated that total acidity may be a controlling efficacy factor. The addition of the alkaline sodium phosphite and borax products to the treatments significantly impaired the performance of the products.

Example 7 Comparison of treatment Solution Uptakes of Oxine Copper Formulations

It is known that different treatments may be up taken by the wood in the dipping process. In particular higher uptakes are associated with products containing surfactants and therefore to compare efficacies at the same active concentrations it is necessary to tailor different working solution concentrations according to differences in uptakes. This is generally not practicable except by follow up trialling but it is useful to know treatment uptakes when making comparisons.

Therefore in conjunction with the trial in Example 6 treatment boards were weighed before dipping and after dipping and drainage for the MSA, DDBSA, phosphorous acid and phosphoric acid treatments.

The resulting aggregate weight gains expressed as a percentage of the undipped boards were:

MSA = 0.88%

Phosphorous acid = 1.035
Phosphoric acid = 1.10%
DDBSA (Cutrol) = 1.11%

The results show that the DDBSA formulation has a 25% greater solution uptake compared to MSA under the trial conditions. Even though all treatment solutions of Example 6 contained a common level of 1.6g/L oxine copper, the DDBSA treatment resulted in 25% more oxine copper transferred to the wood, compared to the MSA treatment. Knowledge of treatment solution uptakes is essential for determining absolute cost-efficiencies.

Example 8 Comparison of the Corrosivity of the Products

Comparison of the relative corrosivities of oxine copper products formulated with MSA, phosphorous acid and DDBSA has been made. Standard coupon corrosion tests are not well adapted to testing oxine copper products because of the electrochemical deposition of copper on the surface of the coupons. An in-house test has been developed for testing corrosivity.

The test involves stirring 500ml of 1g/L oxine copper concentrations prepared from DDBSA, MSA or phosphorous acid matrices as per Examples 5 and 6 and diluted with water. To the test solutions 1g of laboratory reagent cast iron filings are added and aliquots are taken after 1, 2, and 4 minutes and immediately filtered. The filtrates are analysed for iron content, reflecting the quantity of iron solubilised either by direct reaction of the acid or by electrochemical replacement by copper.

The samples chosen for testing comprised oxine copper/carbendazim compositions prepared as per Example 3 with MSA and Example 16 of the Matterssmiths patent. Hylite Extra, a commercial formulation from Osmose NZ was used as a DDBSA type formulation for comparison.

Results are shown in Table 3
TABLE 3 Soluble Iron Contents (ppm) From Corrosivity testing of Oxine Copper products

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Phosphorous Acid</th>
<th>MSA</th>
<th>Hylite Extra</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>31</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
<td>28</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>78</td>
<td>50</td>
<td>11</td>
</tr>
</tbody>
</table>

The results show that the MSA product has an intermediate corrosivity between the highly corrosive phosphorous acid and the relatively non-corrosive DDBSA formulation of oxine copper.

It may appear surprising that the MSA formulation is less corrosive than the phosphorous product, especially as MSA is a stronger acid (pK_a = -1.92) compared to phosphorous acid (pK1 = 1.8; pK2 = 6.15). However there is no basis for utilising equilibrium or other thermodynamic data to predict the kinetics of corrosion reactions, which must be empirically determined.
CLAIMS:

1. A biocidal composition consisting of, including or having at least one oxine metal and at least one aliphatic sulphonie acid but with the proviso that, where the at least one aliphatic sulphonie acid is methane sulphonie acid ("MSA") and where the at least one oxine metal is oxine copper, one or more of the following applies:

   (i) a weight to weight ratio of MSA to oxine copper is below 10 (i.e. in the ratio x:1, x is below 10), and/or

   (ii) water is present.

2. A biocidal composition of claim 4 where one or both of the following applies:

   (i) there is no methanol present, and/or

   (ii) the at least one oxine metal is oxine copper, water and MSA is present and the oxine copper is at least almost exclusively solubilised by the MSA solution.

3. A biocidal composition of claim 1 or 2 wherein the oxine metal is oxine copper, and the at least one aliphatic sulphonie acid is or includes MSA, and wherein the weight to weight ratio of MSA to oxine copper is below 10 (i.e. in the ratio x:1, x is below 10).

4. A biocidal composition of claim 1, 2 or 3 as a solution.

5. A biocidal composition of claim 1 wherein the at least one oxine metal is in solution in MSA, and the weight to weight ratio of MSA to the oxine metal is below 10.

6. A biocidal composition of claim 1 wherein there is at least one oxine metal, as a biocidal active agent, MSA, and
water,

[and, optionally, at least one other biocidal active agent].

7. A biocidal composition of claim 1 wherein there is

at least one oxine metal, as a biocidal active agent,

at least one aliphatic sulphonic acid, and

water,

[and, optionally, at least one other biocidal active agent].

8. A composition of any one of claims 4 to 7 wherein oxine copper is present.

9. A composition of any one of claims 1, 2, 3, 4, 7 and 8 wherein the at least one aliphatic sulphonic acid is selected from the group MSA, ethane sulphonic acid, di-ethyl sulphonic acid, n-propyl sulphonic acid and isopropyl sulphonic acid.

10. A composition of claim 1 wherein oxine copper is at least almost exclusively solubilised in MSA.

11. A composition of any one of the preceding claims wherein no organic co-solvent is present.

12. A composition of any one of claims 1 to 10 wherein an organic co-solvent is present.

13. A composition of claim 12 wherein the organic co-solvent is at least one alcohol or glycol.

14. A composition of claim 12 or 13 wherein, should any methanol be present, the w/w proportion thereof is below 31% w/w

15. A composition of claim 12, 13 or 14 that is less than 10% w/w methanol.

16. A composition of any one of the preceding claims wherein no methanol is present.
17. **A liquid biocidal composition** comprising or including

an effective amount of oxine copper and/or other oxine metal(s) as a first biocidal active,

an effective amount of at least one coactive biocidal material, and

[and, optionally, water and/or other component materials].

18. **A liquid biocidal composition** comprising or including

an effective amount of oxine copper and/or other oxine metal(s) as a first biocidal active,

an effective amount of at least one coactive biocidal material, and

at least one aliphatic sulphonlic acid in which at least the oxine copper and/or oxine metal(s) is solubilised,

[and, optionally, water and/or other component materials].

19. A composition of claim 16 or 17 wherein the oxine metal(s) is acid stable.

20. A composition of claim 16, 17 or 18 wherein the coactive biocidal material(s) is (are) selected from at least the substituted benzimidazoles, isothiazolinones, azoles, pyrroles, secondary and tertiary amines, quaternary ammonium salts, morpholines, guazatine, orthophenyl-phenol, organo-metal complexes, chlor0thalonil and methylene bis-thiocyanate.

21. A composition of any one of the preceding claims wherein at least one surface active agent is present.

22. A composition of any one of the preceding claims wherein any one or more of corrosion inhibitors, dyestuffs, insecticides, bactericides or any surface modification agents is present.
23. A composition of any one of the preceding claims wherein any one or more of other fungicidal products, corrosion inhibitors, dyestuffs, insecticides, bactericides or any desired substrate surface modification agents have or are to be added at the treatment point of application.

24. A biocidal composition comprising or including

1 to 25% w/w of at least one oxine metal [e.g. oxine copper] as at least a first biocidal active, and

1 to 60% w/w of MSA in which at least the oxine metal(s) is solubilised,

25. A composition of claim 24 wherein at least some water is present.

26. A composition of claim 24 or 25 wherein the presence of the at least one oxine metal and/or at least oxine copper is from 5 to 20%.

27. A composition of claim 24, 25 or 26 wherein the at least one oxine metal and/or oxine copper is present from 10 to 20% w/w.

28. A composition of any one of claims 24 to 27 wherein, irrespective of the weight percentage of the at least one oxine metal and/or oxine copper present, the MSA to oxine copper w/w ratio is less than 10.

29. A composition of claim 28 wherein the ratio is between 1.1 and 2.5.

30. A biocidal composition suitable for use, but not necessarily for use, with a wood or other such substrate, said composition comprising or including as a solution in the context of the overall composition up to 25% w/w oxine copper and up to 60% w/w of MSA,

wherein the w/w ratio of MSA/oxine copper is less than 10.

31. A composition of claim 30 wherein said ratio is between 1.1 and 2.5.

32. A composition of claim 30 or 31 where the oxine copper level is below 20% w/w but above 5%.

33. A biocidal composition comprising or including
1 to 25% w/w of at least one oxine metal [e.g. oxine copper] as at least a first biocidal active, and

1 to 60% w/w of at least one aliphatic sulphonie acid in which at least the oxine metal(s) is (are) solubilised.

34. A composition of claim 33 wherein at least some water is present.

35. A composition of claim 33 or 34 wherein the presence of the at least one oxine metal or at least oxine copper is from 5 to 20%.

36. A composition of claim 35 where the at least one oxine metal and/or oxine copper is present from 10 to 20% w/w.

37. A biocidal composition suitable for use, but not necessarily for use, with a wood or other such substrate, said composition comprising or including as a solution (in the context of the overall composition) up to 25% weight for weight oxine copper and up to 60% w/w of at least one aliphatic sulphonie acid.

38. A method of preparing a biocidal composition comprising or having at least one oxine metal as a first biocidal active,

[optionally at least one coactive biocidal composition],

MSA in which at least the oxine metal(s) is (are) solubilised, and water,

said method comprising or including the steps mixing (in any order) the biocidal active(s), the coactive(s) [if any], MSA and water so as to solubilise the biocidal active(s).

39. A method of claim 38 wherein the dissolution of the active(s) is carried out at temperatures higher than ambient because of the exothermic heat of dilution reaction of the aliphatic sulphonie acid and water.

40. A method of claim 39 wherein said temperatures are 5 to 20°C above ambient.
41. A method of claim 39 or 40 wherein external heat is used.

42. **A method of preparing a biocidal composition** comprising or having at least one oxine metal as a first biocidal active, optionally at least one coactive biocidal composition, at least one aliphatic sulphonic acid in which at least the oxine metal(s) is (are) solubilised, and water,

said method comprising or including the steps mixing (in any order) the biocidal active(s), the coactive(s) [if any], at least one aliphatic sulphonic acid and water so as to solubilise the biocidal active(s) at reaction temperatures.

43. The product of the method of claim 38, 39, 40, 41 or 42.

44. **A method of treating a matrix or substrate** to minimise, prevent or reduce fungal growth, fungal discolouration and/or fungal damage, said method comprising or including the step of coating and/or impregnating the matrix or substrate with a composition of any one of claims 1 to 36 and 42.

45. **A matrix or substrate** where treated with a composition of any one of claims 1 to 37 and 43.
# INTERNATIONAL SEARCH REPORT

**International application No.**

**PCT/NZ2004/000303**

## A. CLASSIFICATION OF SUBJECT MATTER

**Int. Cl.**: B27K 3/36, 3/38, 3/50; A01N 43/42

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT, USPTO & JAPIO keywords: oxine, hydroxyquinoline, sulfonic, fungicide and like terms

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>1, 2, 4, 6-10, 12-15, 37-45</td>
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<td>X</td>
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<td>A</td>
<td>US 4608372 A (Muller et al.) 26 August 1986 Column 4 &amp; Examples 1-7</td>
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**X** Further documents are listed in the continuation of Box C  
**X** See patent family annex

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### Date of the actual completion of the international search

7 January 2005

### Date of mailing of the international search report

13 JAN 2005

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