



## **Hazard Assessment for H3.1 and H3.2 Timber Preservatives**

**Report to Abodo Wood Ltd**

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# Hazard Assessment for H3.1 and H3.2 Timber Preservatives

## 1. Introduction

This document provides a summary of the relative hazards of the timber preservatives currently used in New Zealand to treat timber intended for use in the class H3.1 and H3.2 hazard zones. Some proposed additions to the list of approved preservatives have also been included.

The preservatives have been considered in the following broad categories:

- Copper/Chrome/Arsenic (CCA)
- Copper-Based Waterborne Preservatives (Copper Quat and Copper Azoles)
- Other Waterborne Preservatives (Boron and the azole/permethrin mix)
- LOSP Preservatives (Copper Naphthenate and the azole/permethrin mix)

Each of these categories is assessed in the following four sections of the report, with information provided on the following:

- preservative compositions, including timber retention specifications
- toxicity summaries for each preservative component
- the HSNO hazard classifications for the preservatives mixtures or their components
- a discussion of the applicability of the HSNO classifications to different stages of use
- surface residues and leaching from treated timber
- waste disposal
- a final overall hazard summary.

The document has been prepared for Abodo Wood Ltd, and is intended as a starting point for producing summary hazard information suitable for distribution to the company's clients. The summary information will be based on the toxicity summaries given in each section of the report, plus the hazard summary tables given at the end of each section.

## 2 Copper/Chrome/Arsenic (CCA)

CCA wood preservatives are mixtures of soluble salts of copper (Cu), chromium (Cr) and arsenic (As). They have been used in New Zealand for many years for treating timber for use across the full range of possible Hazard Classes (ie. H1 to H6).

### 2.1 Preservative Composition

A wide range of chemical solutions have been approved under the HSNO legislation for use as CCA preservatives<sup>1</sup>, with the total concentrations of metal salts varying from 35 to 674 grams per litre of water (which is equivalent to 3.5 to 67.4% by weight). The relative proportions of the different metals within these solutions are approximately 23 – 25% copper, 38 - 45% chromium, and 30 – 37% arsenic, in accordance with NZS 3640<sup>2</sup>.

The different solutions are used for treating timber to varying degrees of preservative retention in accordance with the different Hazard Classes specified in NZS 3640<sup>2</sup>. CCA timber treated for use in H1.1 situations only requires a minimum metal concentration of 0.04% by weight of arsenic (equivalent to about 0.12% Cu + Cr + As) while timber treated for H6 situations requires a minimum of 0.40% by weight of copper (equivalent to about 1.6% Cu + Cr + As). For H3.1 and H3.2 situations, the minimum metal specification is 0.37% of Cu + Cr + As.

### 2.2 Toxicity Summaries

The following notes provide a brief summary of the toxicities of the preservative chemicals. However, it should be noted that most of the indicated effects are concentration-dependant and will be less significant when the chemicals are in a diluted form. These variations with concentration will be considered in later sub-sections.

#### Copper

Copper is an essential element which forms a normal part of most diets, mainly through food and water<sup>3</sup>. At normal intake levels it is generally considered to be non-toxic to humans, but high copper intakes (eg. through accidental poisoning) can cause vomiting. In workplace exposures some copper salts have been found to cause skin, eye and lung irritation.

The main concern with copper is its very high acute toxicity to fish and other aquatic organisms. The main cause of this toxicity is through rapid binding to gill membranes, which interferes with the processes controlling water absorption. It is also highly toxic to algae, which is why it is commonly used as an algicide.

#### Chromium

It is important to distinguish here between the two common oxidation states for chromium because they have markedly different health and environmental effects. In the CCA treatment chemicals, the chromium is present in a hexavalent (+6) form, but it is reduced to the trivalent (+3) state during the treatment process<sup>4</sup>. In the environment, most chromium is also present in the +3 state.

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<sup>1</sup> Summary of Approvals of Substances Transferred under the Hazardous Substances (Timber Preservatives, Antisapstains, and Antifouling Paints) Transfer Notice 2004 (As Amended), ERMA New Zealand, Wellington, 12 October 2007.

<sup>2</sup> NZS 3640: 2003; Incorporating Amendments 1, 2, 3 and 4. Chemical Preservation of Round and Sawm Timber. Standards New Zealand, Wellington, July 2007.

<sup>3</sup> Re-registration Eligibility Decision (RED) for Coppers. US Environmental Protection Agency, Report No. EPA 738-R-09-304, Washington, May 2009.

<sup>4</sup> Hedley, N, 2003. Copper Chrome Arsenate Wood Preservatives: Their Use and Their Future Use in New Zealand. Chemistry in New Zealand, March 2003.

Trivalent chromium is an essential element in humans and forms a minor part of most diets, mainly through food intake<sup>5</sup>. These low-level exposures do not cause any adverse health effects. By comparison, hexavalent chromium has very high acute toxicity, with accidental exposures to moderately small amounts (eg. less than 1 gram) leading to severe organ damage and even death. Both forms of chromium can cause skin irritation and allergic contact dermatitis, although the hexavalent form is the more potent of the two.

Hexavalent chromium is classified as a known human carcinogen, based on reports of excess lung cancers in workers exposed by inhalation. However, there is no evidence of cancer effects in communities exposed to hexavalent chromium through drinking water.

Both forms of chromium are toxic to fish and other aquatic species, though less so than copper. Once again, the hexavalent form is generally much more toxic than the trivalent form.

### Arsenic

Arsenic occurs naturally in the environment, but has not been shown to be an essential element in humans<sup>5</sup>. It is the most toxic of the three CCA chemicals and has therefore been the primary focus of most CCA risk assessments.

Arsenic is acutely toxic to humans with even very low exposures by ingestion (eg. a few milligrams) causing adverse effects such as vomiting, diarrhoea, abdominal pain, internal haemorrhaging, changes in liver and kidney function, low blood pressure, pulmonary oedema (fluid on the lungs) and breathing difficulties. Exposures to arsenic dust can also be irritating to the nose, throat and lungs.

Inorganic arsenic is classified as a known human carcinogen on the basis of a range of observed effects, including lung cancer by inhalation, and skin, lung and bladder cancers by ingestion. These cancers can develop as a result of prolonged exposures to small amounts of arsenic over long periods of time.

Arsenic salts are toxic to fish and other aquatic species, though less so than copper.

### **2.3 HSNO Hazard Classifications**

The HSNO hazard classifications for a 22% CCA treatment solution are shown in Table 2.1. The 22% solution was chosen as being in the middle of the range of the available formulations. However, there are only minor variations in HSNO classifications for the different solution strengths. For example, the only change in classifications for a 4% CCA solution is the removal of the 8.1A and 8.2C corrosion ratings, while the only change for a 68.7% CCA solution is an increase in the vertebrate toxicity rating from 9.3B to 9.3A.

**Table 2.1: HSNO Classifications for 22% CCA Solution**

<b>HSNO Hazard Class</b>	<b>CCA Classification</b>	<b>Range of Possible Classifications (Highest to lowest)<sup>6</sup></b>
Acute toxicity (6.1, oral, skin or inhalation)	6.1B	6.1A to 6.1E
Skin irritation or corrosion (6.3, 8.2)	8.2C	8.2A to 8.2C (skin corrosion) or 6.3A to 6.3B (skin irritation)
Eye irritation or corrosion (6.4, 8.3)	8.3A	8.3A (eye corrosion) or 6.4A (eye irritation)

<sup>5</sup> Read, D, 2003. Report on Copper, Chromium and Arsenic (CCA) Treated Timber. ERMA New Zealand, Wellington.

<sup>6</sup> Substances can also be assessed as non-hazardous within each class.

Respiratory sensitisation (6.5)	6.5A	6.5A
Skin sensitisation (6.5)	6.5B	6.5B
Mutagenicity (6.6)	6.6A	6.6A to 6.6B
Carcinogenicity (6.7)	6.7A	6.7A to 6.7B
Reproductive/developmental effects (6.8)	6.8A	6.8A to 6.8C
Target organ systemic effects (6.9)	6.9A	6.9A to 6.9B
Metal corrosion (8.1)	8.1A	8.1A
Toxic to aquatic organisms (9.1)	9.1A	9.1A to 9.1D
Toxic to soil organisms (9.2)	9.2C	9.2A to 9.2D
Toxic to terrestrial vertebrates (9.3)	9.3B	9.3A to 9.3C
Toxic to terrestrial invertebrates (9.4)	9.4C	9.4A to 9.4C

## 2.4 Applicability of the HSNO Classifications to Different Stages of Use

The above HSNO classifications show that the concentrated CCA treatment solutions are highly hazardous to humans across most human toxicity classes, and they are highly toxic to aquatic organisms and moderately toxic for other ecosystem effects. These solutions must be handled with extreme care within timber treatment plants, using procedures such as those indicated in the Best Practice Guideline for Timber Preservatives<sup>7</sup>.

Prior to use, the concentrated CCA solutions are diluted with water to produce less concentrated 'working solutions'. However, this dilution will have little or no effect on the degree of hazard. For example, a 10-fold dilution of the 22% CCA solution shown in Table 2.1 will only reduce the acute oral toxicity rating from 6.1B to 6.1C, which is still significant. Also, there will be no change in the ratings for chronic effects such as cancer and target organ toxicity (classes 6.6 to 6.9) because the CCA concentrations will still be above the threshold limits for these effects<sup>8</sup>. Hence, the working solutions and all wet treated timber must be regarded as having similar levels of hazard as the initial concentrates.

Once the treatment process is complete and the timber has been allowed to dry, the degree of hazard will be lower because (a) the quantities of metals retained in the timber are relatively low (eg. 0.37% for H3.1 and H3.2 timber) and (b) most of the chromium will be reduced to the less toxic trivalent (Cr+3) state. The HSNO classifications are not normally applied to processed materials such as treated timber. However, if they were, H3.1 and H3.2 timber would most likely be classified as having only moderate to low acute toxicity (eg. class 6.1D), while the classifications for mutagenicity, carcinogenicity and reproductive/developmental effects would be unchanged. The classification for target organ effects would no longer apply (ie. non-hazardous).

## 2.5 Surface Residues and Leaching from Treated Timber

Some newly-treated CCA timber can have a green surface deposit of copper arsenate, which is highly toxic. The Best Practice Guide<sup>7</sup> includes a specific warning against breathing any dust from these deposits. Protective gloves should also be used when handling any CCA treated timber.

Most of the treatment chemicals in CCA treated timber are considered to be 'fixed' within the wood, but some outwards diffusion is also known to occur. Testing of older timber has shown the

<sup>7</sup> Best Practice Guideline for the Safe Handling and Use of Timber Preservatives and Antisapstain Chemicals. NZ Timber Preservation Council, Wellington, 2005.

<sup>8</sup> The threshold concentrations are 0.1% for mutagenicity, carcinogenicity and reproductive or developmental effects, and 1.0% for target organ effects.

presence of surface residues of small amounts of arsenic, which may pose a risk in some uses, such as children’s playground equipment. A risk assessment published by ERMA in 2003<sup>5</sup> showed that the potential arsenic exposures from these residues should be within acceptable limits. However, it was recommended that exposures should be minimised where possible by, for example, promoting the use of alternative materials for playground equipment, and applying surface coatings as sealants to existing CCA structures.

Small amounts of arsenic can also be released from the timber by leaching with water. Numerous studies have shown the presence of moderate levels of arsenic contamination in the soil beneath timber decks and around timber playground equipment<sup>9</sup>. In-ground leaching from CCA treated posts has also been reported<sup>10</sup>. In most of these studies, the resulting arsenic concentrations have been assessed as within acceptable limits. However, they do help to reinforce the need for a precautionary approach towards the use of CCA treated timber in potentially sensitive locations.

The leaching of copper from CCA treated timber is also a concern, but mainly in the marine and aquatic environments. Copper has been detected in water and sediments close to treated timber structures, such as bridge piles, and in sediment dwelling species such as crabs<sup>11</sup>. This indicates some potential for ecotoxic effects, especially from timber treated to high retention levels (eg. H5 and H6). However, the risk is less significant for H3.1 and H3.2 timber which is only intended for above ground applications.

## 2.6 Waste Disposal

The Ministry for the Environment advises that CCA treated timber should not be disposed at cleanfill sites, because of the potential for leaching of the treatment chemicals<sup>12</sup>. The wastes may be acceptable at municipal landfills, but only if the landfill is fitted with leachate collection and subsequent treatment and disposal.

It is well established that the burning of CCA treated timber can lead to emissions of arsenic vapour, and for this reason no CCA treated timber should be disposed by burning or incineration, including burning in domestic fires. If any such timber is burned, the ashes can contain significant amounts of leachable metals, and should be disposed to landfill.

## 2.7 Hazard Summary

The following hazard summaries are based on the information given above.

**Table 2.2: Hazard Summary for CCA Treated Timber (H3.1, H3.2)**

Use Situation	Relative Hazard and Precautions
Timber treatment process	high to very high, use extreme care
Working with treated timber	moderate, avoid breathing dust and use gloves
Living around finished timber structures	low – moderate, use alternative material where possible, or seal existing surfaces with paint
Leaching from treated timber	low, avoid use around vegetable gardens, play areas
Waste disposal	dispose to landfill only

<sup>9</sup> Eg. see Cookson, L J, 2005. Arsenic Content of Soil and Wood Chip Fines in Three Kindergartens, ENSIS Technical Report No. 151.

<sup>10</sup> Vogeler I, et al, 2005. Environmental Risk Assessment of CCA Leaching from Treated Vineyard Posts. Report to Marlborough District Council, HortResearch Client Report No. 17659.

<sup>11</sup> Treated Wood in Aquatic Environments: Technical Review and Use Recommendations. Stratus Consulting Ltd, Boulder, Colorado, December 2006.

<sup>12</sup> A Guide to the Management of Cleanfills, Ministry for the Environment, Wellington, 2002.

### 3. Copper-Based Waterborne Preservatives

The section covers two types of preservatives; the alkaline copper quaternary mixtures (ACQ or Copper Quat) and Copper Azole, including those involving micronized copper as an alternative form of the copper compounds.

#### 3.1 Preservative Compositions

The H3.1 and H3.2 retention specifications<sup>2</sup> for these preservatives are as follows:

Copper Quat: 0.35% copper + didecyldimethyl ammonium chloride, carbonate or bicarbonate (DDAC)

Copper Azole: 0.2288% copper + tebuconazole

Until recently, these preservatives were all based on the use of relatively insoluble copper salts mixed with co-solvents, such as ammonia or amines. However a change to NZS3640 is currently under consideration to allow the use of the copper salts in a micronized form, in which the material has been milled to produce very fine (sub-micron) particles. This allows the copper salts to penetrate the timber without the use of co-solvents, and also has some in-use benefits in relation to leaching and metal corrosion (see below).

#### 3.2 Toxicity Summaries

##### Copper

The toxicity of copper was summarised in section 2.2 and need not be repeated here. The only additional factor to consider for the micronized copper preservatives is the presence of very fine particles, some of which may be classified as nano-particles<sup>13</sup>. Internationally, there is some concern that nanoparticles may cause specific health problems due to their potential to penetrate the lungs or skin, with subsequent distribution around the body via the blood stream. At present, there is no evidence to show that this is an issue for micronized copper, but it does suggest the need to minimise exposures to the preservative, and especially to any airborne dust. These exposures would mainly be of concern within timber treatment plants.

##### Didecyldimethyl ammonium chloride/carbonate/bicarbonate

DDAC belongs to a group of chemicals known as quaternary ammonium compounds which are used extensively as antiseptics, bactericides, fungicides, sanitisers, deodorants and water softeners. DDAC is known to have only moderate acute toxicity to humans, but can be highly irritating to the eyes and skin<sup>14</sup>. It has not been shown to have any significant chronic toxicity, including mutagenic, teratogenic and developmental effects. The chemical is highly water soluble but has little propensity for accumulation in sediments, bioaccumulation in aquatic organisms, or biomagnification in food chains<sup>15</sup>. It is highly toxic to fish and other aquatic organisms. However this effect is ameliorated to some extent by the tendency of the chemical to absorb strongly to sediments.

##### Tebuconazole

Tebuconazole has moderate to low acute toxicity to humans<sup>16</sup>. It has been classified by the US EPA as a possible human carcinogen, but a recent evaluation by the European Union concluded that the observed liver cancers in mice were not relevant to humans<sup>16</sup>. The chemical is moderately

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<sup>13</sup> There are a number of definitions of nano-particles currently in use. For example, the US EPA defines them as particles less than 100 nanometres (0.1 microns) in size, while some other US agencies include particles up to 300 or 1000 nanometres.

<sup>14</sup> USEPA, 2006. Re-Registration Eligibility Decision for Aliphatic Alkyl Quaternaries (DDAC). US Environmental Protection Agency, Washington. Report No EPA739-R-06-008.

<sup>15</sup> Brooks, K M: Literature Review and Assessment of the Environmental Risks Associated with the Use of ACQ Treated Wood Products in Aquatic Environments. Western Wood Preservers Institute, Vancouver, December 2001

<sup>16</sup> EFSA, 2008. Conclusion on the Peer Review of Tebuconazole. European Food Safety Authority Scientific Report. (2008) 176, 1-109.



persistent in soils, has low to moderate toxicity towards terrestrial vertebrates, and is toxic to fish and crustaceans.

### 3.3 HSNO Hazard Classifications for Copper Quat Preservatives

The HSNO classifications for the two primary components and for an approved Copper Quat concentrate are shown in Table 3.1<sup>17</sup>. The Copper Quat concentrate contains 90.24g/litre copper as copper ammonium carbonate, and 56.4 g/litre DDA chloride. Two other forms of the preservative, Alkaline Copper Quat and Timtech ACQ-D, have similar HSNO classifications.

**Table 3.1: HSNO Classifications for a Copper Quat Mixture**

HSNO Hazard Class	Copper Carbonate	DDAC	Cu/NH <sub>3</sub> /CO <sub>3</sub> + DDAC
Acute toxicity (6.1, oral, skin or inhalation)	6.1C	6.1C	6.1D
Skin irritation or corrosion (6.3, 8.2)	6.3A	8.2B	8.2C
Eye irritation or corrosion (6.4, 8.3)	6.4A	8.3A	8.3A
Respiratory sensitisation (6.5)	no hazard	no hazard	no hazard
Skin sensitisation (6.5)	6.5B	6.5B	6.5B
Mutagenicity (6.6)	no hazard	no hazard	no hazard
Carcinogenicity (6.7)	no hazard	no hazard	no hazard
Reproductive/developmental effects (6.8)	no hazard	no hazard	no hazard
Target organ systemic effects (6.9)	6.9B	no hazard	6.9B
Metal corrosion (8.1)	no hazard	no hazard	8.1A
Toxic to aquatic organisms (9.1)	9.1A	9.1A	9.1A
Toxic to soil organisms (9.2)	no hazard	no hazard	no hazard
Toxic to terrestrial vertebrates (9.3)	9.3B	9.3B	9.3C
Toxic to terrestrial invertebrates (9.4)	no hazard	no hazard	no hazard

#### Copper Quat Mixtures Based on Micronised Copper

To date, the only form of micronised copper approved under the HSNO Act is an Osmose product known as ORD-X370. This was given a hazard classification of 6.1E, 6.6B, 6.9B, and 9.1A. This product is mixed with another substance, Carboquat 250T, to produce the preservative mixtures. Carboquat 250T has a hazard classification of 6.1D, 8.2C, 8.3A, 6.8B, 6.9B, 9.1A and 9.3B, which is similar to that for DDAC but with an additional 6.8B classification, most likely due to the presence of co-solvents.

The two approved preservative solutions, and their hazard classifications are as follows:

ORD-X370 (1.2 – 7.6 g/litre Cu) + Carboquat 250T: 6.3B, 6.9B, 9.1B

ORD-X370 (7.5 – 25.5 g/litre Cu) + Carboquat 250T: 6.3A, 6.4A, 6.8B, 6.9B, 9.1A

The absence of some of the hazard classes (eg. 6.1D for ORD-X370 and 6.1E for Carboquat) and variations in others (eg. 9.1A and 9.1B for the two different mixtures) is due to dilution effects.

Finally, it should be noted that both DDAC and Carboquat 250T have a 3.1C flammability classification, which is due to the use of a flammable solvent. However, the classification does not carry over into the preservative mixtures.

<sup>17</sup> The HSNO classifications have been obtained from the EPA databases ([www.epa.govt.nz](http://www.epa.govt.nz)).

### 3.4 HSNO Hazard Classifications for Copper Azole Preservatives

The HSNO classifications for the two main components of the Copper Azole preservative are shown in Table 3.2. No classification details have been found for the actual preservative (eg. Tanalith E), but it should be very similar to that for copper carbonate. This makes up 12.4% of the preservative solution, while tebuconazole is only present at 0.49%. There may be some additional minor hazards due to the presence of co-solvents.

**Table 3.2: HSNO Classifications for the Copper Azole Components**

HSNO Hazard Class	Copper Carbonate	Tebuconazole
Acute toxicity (6.1, oral, skin or inhalation)	6.1C	6.1D
Skin irritation or corrosion (6.3, 8.2)	6.3A	no hazard
Eye irritation or corrosion (6.4, 8.3)	6.4A	no hazard
Respiratory sensitisation (6.5)	no hazard	no hazard
Skin sensitisation (6.5)	6.5B	no hazard
Mutagenicity (6.6)	no hazard	no hazard
Carcinogenicity (6.7)	no hazard	no hazard
Reproductive/developmental effects (6.8)	no hazard	no hazard
Target organ systemic effects (6.9)	6.9B	6.9B
Metal corrosion (8.1)	no hazard	no hazard
Toxic to aquatic organisms (9.1)	9.1A	9.1A
Toxic to soil organisms (9.2)	no hazard	no hazard
Toxic to terrestrial vertebrates (9.3)	9.3B	9.3C
Toxic to terrestrial invertebrates (9.4)	no hazard	no hazard

### Copper Azole Mixtures Based on Micronised Copper

Once again, the micronized forms of Copper Azoles are based on ORD-X370. In this case the ORD-X370 is mixed with a substance known as TEB EC25, which is a 250 gram/litre emulsifiable concentrate of tebuconazole. The concentrate has additional hazards to that shown above for tebuconazole (6.3A, 6.4A, 6.8A and 9.3C), most likely due to the presence of co-solvents.

Three preservative solutions have been classified under HSNO, on the basis of three different ORD-370/TEB EC25 mixtures. The least hazardous solution has only a single classification of 9.1B, while the most hazardous is classified as 6.4A, 6.8A, 6.9A, 9.1A and 9.3C.

### 3.5 Applicability of the HSNO Classifications to Different Stages of Use

The conventional Copper Quat and Copper Azole preservative solutions provided for use in timber treatment plants have only low acute toxicity, while the solutions based on micronised copper are not acutely toxic. None of the preservative components are carcinogenic, but some of the more concentrated solutions are classified as possibly hazardous with regard to reproductive or developmental effects. In addition, most of the solutions do have some degree of hazard to the skin or eyes. This indicates the need for all of the preservative solutions, and any wet treated timber, to be handled and used with care, including the use of eye protection, gloves, and protective clothing.

The hazards associated with handling and use of dry treated timber will be relatively low. Copper will be the main component present, at concentrations of about 0.2% in H3.1 and H3.2 timber. The DDAC in timber treated with Copper Quat will be present at a concentration of about 0.1%, while the tebuconazole in timber treated with Copper Azole will be substantially lower, at less than 0.01%. At these concentrations the only significant hazard would be a minor risk of skin or eye irritation, which could be adequately addressed through the use of gloves and safety glasses.

Timber treated with Copper Quat is known to be much more corrosive to metal fittings than the corresponding CCA treatments<sup>18</sup>, and this is reflected in the 8.1 hazard classification shown in Table 3.1 for the Copper Quat mixture. Timber treated with Copper Azole is also more corrosive than CCA, but less so than Copper Quat. However, the micronised copper forms of both preservatives are less corrosive than CCA.

### 3.6 Surface Residues and Leaching from Treated Timber

There are no major concerns regarding surface residues on timber treated with these preservatives, mainly due to the absence of any carcinogens such as arsenic and chromium +6. At most, the only potential hazard would be a minor risk of skin irritation, which should be easily addressed through observing appropriate hygiene measures (eg. hand washing after any contact).

Copper leaching from timber treated with Copper Quat or Copper Azole is more pronounced than with CCA, although it can be reduced by kiln drying. Also, the micronized copper preservatives show much lower leaching rates. Copper leaching may be a concern when the timber is being used in or near aquatic or marine environments, but this would mainly be an issue for H4 to H6 timber.

Any potential releases of DDAC from Copper Quat timber would be of little concern because of the moderate to low acute toxicity of this chemical and its relatively rapid degradation in the environment. Tebuconazole is more persistent in the environment but tends to bind to soil, thereby reducing the potential for adverse impacts. The relatively low azole concentrations in treated timber and its moderate to low acute toxicity are also mitigating factors.

### 3.7 Waste Disposal

Wastes from timber treated with Copper Quat or Copper Azole preservatives, including the micronised forms, should be disposed to a landfill fitted with leachate collection, because of the potential for copper leaching. The material may also be disposed by burning in an industrial boiler or wood waste incinerator. The copper will be retained in the ash while the organic components should be effectively destroyed, provided good combustion conditions are maintained.

### 3.8 Hazard Summary

The following hazard summaries are based on the information given above.

**Table 3.3: Hazard Summary for Copper Quat and Copper Azoles (H3.1, H3.2)**

Use Situation	Relative Hazard and Precautions
Timber treatment process	low to moderate, use skin and eye protection
Working with treated timber	low, avoid breathing dust and use gloves
Living around finished timber structures	very low, but apply common-sense hygiene practices
Leaching from treated timber	low (micronised), moderate (other) avoid runoff to waterways
Waste disposal	dispose to landfill or by burning

<sup>18</sup> Freeman, M H and McIntyre, C R, 2008. A Comprehensive Review of Copper-Based Wood Preservatives, with a Particular Focus on New Micronised or Dispersed Copper Systems. Forest Products J, v58(11), p6 - 27.

## 4. Other Waterborne Preservatives

This section covers the two remaining types of class H3 waterborne preservatives; boron compounds and the mixture of tebuconazole, propiconazole and permethrin. Timber treated with either or both of these preservatives is only suitable for use in H3.1 hazard situations.

### 4.1 Preservative Compositions

The retention specifications<sup>2</sup> for these preservatives are as follows:

Boron compounds:	0.8%
Azoles + permethrin:	0.03% of both tebuconazole and propiconazole
	0.1% of each azole in the central ninth of timber ≥30mm thick
	Permethrin should be ≥9% of total azoles, or ≥25% for timber exported to Australia

### 4.2 Toxicity Summaries

#### Boron

Boron has been used for timber treatment in New Zealand since the early 1950s, and is also used extensively in household cleaners, especially soap powders. It occurs naturally in rocks and soils, especially those associated with geothermal and volcanic activity, and as a result, some rivers and streams in the central North Island contain naturally high levels.

Boron is essentially non-toxic to humans, although it can be mildly irritating to the eyes and there is some evidence of possible reproductive/developmental effects from animal studies<sup>19</sup>. It is an essential micronutrient for plants, but can also be phytotoxic at higher concentrations. It has low toxicity in the aquatic environment, with the most significant effect being fish toxicity in the early stages of development. Boron is readily soluble in water and highly mobile in the natural environment, but does not bio-accumulate.

#### Tebuconazole + Propiconazole

A toxicity summary for tebuconazole was given in section 3.2. Propiconazole has moderate to low acute toxicity to humans<sup>20</sup>, but is mildly irritating to the skin and irritating to the eyes. Studies in dogs and rats have shown some potential for adverse effects on the liver. The chemical is moderately persistent in soils but does not leach into water. It has low to moderate toxicity towards terrestrial vertebrates, and is very toxic to fish and other aquatic species.

#### Permethrin

Permethrin is one of the more common members of the class of synthetic pyrethroids, which have been manufactured to replicate the naturally occurring substances. Pyrethroids are widely used as insecticides, including in household insect sprays.

Permethrin has moderate acute toxicity to humans, is irritating to the skin, eyes and lungs, and can cause sensitisation in some individuals. It is also known to be a neurotoxin. In mammals a single dose produces toxic signs such as tremors, hyper-excitability, salivation, and paralysis, although these effects disappear fairly rapidly after exposure. The chemical shows no tendency to accumulate in human or animal tissues, and it is readily degraded in the environment. It is toxic to fish and other aquatic species, but in practice the effects are rarely noticed because the usage rates are usually quite low.

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<sup>19</sup> WHO, 1998. Environmental Health Criteria No. 204, Boron. World Health Organisation, Geneva.

<sup>20</sup> EC, 2003. Review Report for the Active Substance Propiconazole. Health and Consumer Protection Directorate General, European Commission, Report No. SANCO/3049/99.

### 4.3 HSNO Hazard Classifications for Boron Compounds

The classifications for two forms of sodium borate are given in Table 4.1. The powder is essentially 100% sodium borate, while the solution has a strength of 333 grams/litre.

**Table 4.1: HSNO Classifications for Boron Compounds**

HSNO Hazard Class	sodium borate, powder	sodium borate, solution
Acute toxicity (6.1, oral, skin or inhalation)	6.1E	no hazard
Skin irritation or corrosion (6.3, 8.2)	no hazard	no hazard
Eye irritation or corrosion (6.4, 8.3)	6.4A	6.4A
Respiratory sensitisation (6.5)	no hazard	no hazard
Skin sensitisation (6.5)	no hazard	no hazard
Mutagenicity (6.6)	no hazard	no hazard
Carcinogenicity (6.7)	no hazard	no hazard
Reproductive/developmental effects (6.8)	6.8B	6.8B
Target organ systemic effects (6.9)	no hazard	no hazard
Metal corrosion (8.1)	no hazard	no hazard
Toxic to aquatic organisms (9.1)	9.1D	9.1D
Toxic to soil organisms (9.2)	no hazard	no hazard
Toxic to terrestrial vertebrates (9.3)	no hazard	no hazard
Toxic to terrestrial invertebrates (9.4)	no hazard	no hazard

### 4.4 HSNO Hazard Classifications for Azoles and Permethrin

The azole classification shown below is for an emulsifiable concentrate containing 279 gram/litre of each of the azoles, while the permethrin classification is for the pure powder. The permethrin hazards would be considerably lower in the preservative mixture where it is a minor component.

**Table 4.2: HSNO Classifications for the Azoles and Permethrin**

HSNO Hazard Class	Tebuconazole + propiconazole	Permethrin
Acute toxicity (6.1, oral, skin or inhalation)	6.1D	6.1C
Skin irritation or corrosion (6.3, 8.2)	6.3A	6.3B
Eye irritation or corrosion (6.4, 8.3)	6.4A	6.4A
Respiratory sensitisation (6.5)	no hazard	no hazard
Skin sensitisation (6.5)	6.5B	6.5B
Mutagenicity (6.6)	no hazard	no hazard
Carcinogenicity (6.7)	no hazard	no hazard
Reproductive/developmental effects (6.8)	6.8A	no hazard
Target organ systemic effects (6.9)	6.9B	6.9B
Metal corrosion (8.1)	no hazard	no hazard

Toxic to aquatic organisms (9.1)	9.1A	9.1A
Toxic to soil organisms (9.2)	no hazard	no hazard
Toxic to terrestrial vertebrates (9.3)	9.3C	9.3B
Toxic to terrestrial invertebrates (9.4)	no hazard	9.4A

#### 4.5 Applicability of the HSNO Classifications to Different Stages of Use

The preservative solutions used for boron treatment have little or no acute toxicity, while the azole/permethrin combination has low to moderate acute toxicity. Neither type of preservative is carcinogenic, but they are both classified as possibly hazardous with regard to reproductive or developmental effects, and the azole mix has limited potential for adverse effects on the liver or the neurological system. In addition, both of the solutions do have some degree of hazard to the skin or eyes. This indicates the need for all of the preservative solutions, and any wet treated timber, to be handled and used with care, including the use of eye protection, gloves, and protective clothing.

The hazards associated with handling and use of dry treated timber will be mainly limited to a minor risk of skin or eye irritation, which could be adequately addressed through the use of gloves and safety glasses.

Some H3.1 timber is treated with a combination of both boron and the azole/permethrin mix. However, this should have no significant effects on the overall hazard characteristics. In other words, the preservative solutions should still be handled and used with care, while the potential hazards for dry treated timber would be limited to skin or eye irritation.

#### 4.6 Surface Residues and Leaching from Treated Timber

There are no major concerns regarding surface residues on timber treated with these preservatives, mainly due to the absence of any carcinogens such as arsenic and chromium +6. At most, the only potential hazard would be a minor risk of skin irritation, which should be easily addressed through observing appropriate hygiene measures (eg. hand washing after any contact).

Boron can be leached from the treated timber by rainfall, and the main concern here would be for potential adverse effects on any nearby plant matter, such as garden vegetables. Leachates from timber treated with the azole/permethrin mix may be toxic to aquatic species.

Any potential releases of the azoles or permethrin from the treated timber would be of little concern for human health because of the moderate to low acute toxicity of these chemicals. The relatively low preservative concentrations in the treated timber are another mitigating factor.

#### 4.7 Waste Disposal

Wastes from timber treated with boron preservatives should be disposed to a landfill fitted with leachate collection, because of the potential for boron leaching. Leachate collection would not be a pre-requisite for landfills used for the disposal of wastes from timber treated with the azole/permethrin mix.

The burning of boron treated timber can cause irritating fumes, due to the presence of boric acid. In addition, the ash produced is known to be very corrosive to metals. For this reason, boron treated timber should not be disposed by burning in an industrial boiler or wood waste incinerator.

Waste from timber treated with the azole/permethrin mix may be disposed by burning in an industrial boiler or wood waste incinerator, provided good combustion conditions are maintained to ensure that the organic components are effectively destroyed.

#### 4.8 Hazard Summary

The following hazard summaries are based on the information given above.

**Table 4.3: Hazard Summary for Boron Compounds (H3.1)**

<b>Use Situation</b>	<b>Relative Hazard and Precautions</b>
Timber treatment process	low, use skin and eye protection
Working with treated timber	low, but wear gloves
Living around finished timber structures	very low, but apply common-sense hygiene practices
Leaching from treated timber	moderate, avoid runoff to nearby plants
Waste disposal	dispose to landfill

**Table 4.4: Hazard Summary for Azoles plus Permethrin (H3.1)**

<b>Use Situation</b>	<b>Relative Hazard and Precautions</b>
Timber treatment process	low to moderate, use skin and eye protection
Working with treated timber	low, but wear gloves
Living around finished timber structures	very low, but apply common-sense hygiene practices
Leaching from treated timber	low, avoid runoff to waterways
Waste disposal	dispose to landfill or by burning

## 5. LOSP Preservatives

Light organic solvent preservatives (LOSP) involve the use of an organic solvent which acts as the carrier for the preservative, rather than water, to ensure effective penetration into the wood. LOSP formulations are mainly used for the treatment of pre-cut timber components, or Engineered Wood Products, such as laminated veneer lumber, where dimensional stability is essential for the finished product; ie. no need for additional drying and machining after treatment. The preservatives are applied using vacuum or pressure treatment plants, and a holding period of several days is recommended after treatment, to allow the residual solvent to flash off.

LOSP-treated timber is usually only suitable for timber intended for above-ground applications and at least partially protected from the weather. In New Zealand, only one LOSP preservative, copper naphthenate, is approved for use in both H3.1 and H3.2 situations. Two other preservatives, an azole/permethrin mix and tributyl tin compounds are only approved for use in H3.1 situations. The tin preservatives have not been included in this review as they are no longer in widespread use.

### 5.1 Preservative Compositions

The retention specifications<sup>2</sup> for these preservatives are as follows:

Copper naphthenate:	0.05% for H3.1 and 0.10% for H3.2
Azoles + permethrin:	0.03% of both tebuconazole and propiconazole
	0.1% of each azole in the central ninth of timber $\geq 30$ mm thick
	Permethrin should be $\geq 9\%$ of total azoles, or $\geq 25\%$ for timber exported to Australia

The solvent to be used is specified as White Spirits, but a change to NZS 3640 is currently under consideration to also allow the use of methylene chloride.

### 5.2 Toxicity Summaries

#### Copper Naphthenate

Copper naphthenate salts have only low to moderate acute toxicity in humans, but can be mildly irritating to the skin and eyes<sup>21</sup>. Other potential health effects are largely related to the copper component, although dietary studies in rats have shown decreased body weights in response to copper naphthenate exposures. The copper also accounts for significant aquatic toxicity.

#### Tebuconazole, Propiconazole and Permethrin

Toxicity summaries for these were given in section 4.2.

#### White Spirits

The key hazardous property of White Spirits is its flammability. In use, there is a risk of lung damage (pneumonitis) if droplets of the substance are aspirated into the lungs when swallowed, and the substance can be mildly irritating to the skin<sup>22</sup>.

#### Methylene Chloride

Methylene chloride is a non-flammable solvent which is used in many different types of work activities, such as paint stripping, polyurethane foam manufacturing, metal cleaning, and degreasing<sup>23</sup>. Workers exposed to methylene chloride are at increased risk of developing cancer, adverse effects on the heart, central nervous system and liver, and skin or eye irritation. Exposure may occur through inhalation, by absorption through the skin, or through contact with the skin.

<sup>21</sup> US EPA, 2007. Re-registration Eligibility Decision for Copper and Zinc Naphthenate Salts. US Environmental Protection Agency, Washington, Report No. EPA 739-R-07-003.

<sup>22</sup> WHO, 1996. Environmental Health Criteria No 187; White Spirits (Stoddard Solvent). World Health Organisation, Geneva.

<sup>23</sup> WHO, 1996. Environmental Health Criteria No 164; Methylene Chloride. World Health Organisation, Geneva.



### 5.3 HSNO Hazard Classifications

The hazard classifications for copper naphthenate, White Spirits and methylene chloride are shown in Table 5.1. These classifications apply to the individual components, but the classifications for the copper naphthenate preservative solutions will be very similar. In addition, the White Spirits and all formulations based on this solvent carry a 3.1C or 3.1D flammability classification.

**Table 5.1: HSNO Classifications for a Copper Naphthenate, White Spirits and Methylene Chloride**

HSNO Hazard Class	Copper Naphthenate	White Spirits	Methylene Chloride
Acute toxicity (6.1, oral, skin or inhalation)	6.1D	6.1E	6.1D
Skin irritation or corrosion (6.3, 8.2)	6.3B	6.3B	6.3A
Eye irritation or corrosion (6.4, 8.3)	6.4A	no hazard	6.4A
Respiratory sensitisation (6.5)	no hazard	no hazard	no hazard
Skin sensitisation (6.5)	no hazard	no hazard	no hazard
Mutagenicity (6.6)	no hazard	no hazard	no hazard
Carcinogenicity (6.7)	no hazard	no hazard	6.7B
Reproductive/developmental effects (6.8)	no hazard	no hazard	no hazard
Target organ systemic effects (6.9)	6.9B	no hazard	6.9B
Metal corrosion (8.1)	no hazard	no hazard	no hazard
Toxic to aquatic organisms (9.1)	9.1A	9.1B	no hazard
Toxic to soil organisms (9.2)	9.2C	no hazard	no hazard
Toxic to terrestrial vertebrates (9.3)	9.3C	no hazard	9.3C
Toxic to terrestrial invertebrates (9.4)	no hazard	no hazard	no hazard

The classifications for the water-based azole/permethrin mixes were given previously in Table 4.2. The classifications for the LOSP formulations will be very similar to these, but with the addition of any hazards specific to the solvents (eg. 3.1C for White Spirits and 6.7B for methylene chloride).

### 5.4 Applicability of the HSNO Classifications to Different Stages of Use

The potential workplace hazards from the active ingredients in the LOSP formulations will be much the same as those discussed previously for the waterborne copper preservatives (section 3) and the azole/permethrin mixes (section 4). However, the presence of the organic solvent introduces some additional hazards. In particular, it is important that the preservative solutions be used with adequate ventilation, to avoid the build-up of unsafe concentrations of solvent fumes. Appropriate protection is also required for the eyes and skin, including the use of solvent resistant gloves. And of course, all facilities using White Spirits must have appropriate fire protection systems.

The hazards from the handling and use of dry LOSP-treated timber should be limited to minor risks of skin and eye irritation. However, that is contingent on adequate time being allowed for the solvents to evaporate from the treated timber. If significant amounts of residual solvent remain, the timber should be handled with adequate ventilation and using gloves.

### 5.5 Surface Residues and Leaching from Treated Timber

There are no major concerns regarding surface residues on timber treated with these preservatives. Leachates from timber treated with copper naphthenate or the azole/permethrin

mix may be toxic to aquatic species but, other than that, any potential releases would be of little concern because of the moderate to low acute toxicity of these chemicals. The relatively low preservative concentrations in the treated timber are another mitigating factor.

### 5.6 Waste Disposal

Wastes from timber treated with copper naphthenate should be disposed to a landfill fitted with leachate collection, because of the potential for copper leaching. Leachate collection would not be a pre-requisite for landfills used for the disposal of wastes from timber treated with the azole/permethrin mix.

Wastes from timber treated with either of these preservatives may also be disposed by burning in an industrial boiler or wood waste incinerator. The copper will be retained in the ash while the organic preservatives should be effectively destroyed, provided good combustion conditions are maintained.

### 5.7 Hazard Summary

The following hazard summaries are based on the information given above.

**Table 5.2: Hazard Summary for Copper Naphthenate (LOSP, H3.1 & 3.2)**

Use Situation	Relative Hazard and Precautions
Timber treatment process	low to moderate, use skin and eye protection, adequate ventilation and fire protection systems
Working with treated timber	low, but wear gloves and allow adequate time and ventilation for solvent flash off
Living around finished timber structures	very low, but apply common-sense hygiene practices and allow for ventilation of any residual solvent
Leaching from treated timber	moderate, avoid runoff to waterways
Waste disposal	dispose to landfill or by burning

**Table 5.3: Hazard Summary for Azoles plus Permethrin (LOSP, H3.1)**

Use Situation	Relative Hazard and Precautions
Timber treatment process	low to moderate, use skin and eye protection, adequate ventilation and fire protection systems
Working with treated timber	low, but wear gloves and allow adequate time and ventilation for solvent flash off
Living around finished timber structures	very low, but apply common-sense hygiene practices and allow for ventilation of any residual solvent
Leaching from treated timber	low, avoid runoff to waterways
Waste disposal	dispose to landfill or by burning