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Combining fire retardant and preservative systems for timber products in exposed applications – state of the art review

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Combining fire retardant and preservative systems for timber products in exposed applications – state of the art review

Prepared for the

**Forest and Wood Products
Research and Development Corporation**

by

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**Publication: Combining fire retardant and preservative
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Executive summary

Objective

The purpose of this review is to identify fire retardants that may be combined with a preservative to protect timber from both fire and biodegradation when used in external applications.

Key findings

The major findings of the review are:

- To the best of our knowledge, there are currently no commercially available combined fire retardant/preservative systems for exterior timbers that comply with both fire and durability standards.
- The only fire retardants currently approved for exterior use are those based on heat-cured polymeric systems. Timber treated with these systems is not considered to be preservative treated, although it has been shown that this timber is more durable than if it were untreated.
- The most thorough studies on combined preservative and fire retardant treated timber were carried out at the USDA Forest Products Laboratory in Wisconsin. It was found that timber treated with amino resins (urea or melamine, dicyandiamide, phosphoric acid and formaldehyde) and quaternary ammonium salts such as didecyldimethylammonium chloride performed well in fire tests, even after accelerated weathering. These systems are covered by a patent.
- Some inorganic fire retardants that claim to be suitable for timber in exterior applications can be found within the patent literature. However, these are generally applied via a double treatment.
- There are a significant number of organic fire retardants that would appear to be compatible with solvent- or oil-borne preservatives. Very few systems of this type appear to have been examined in timber.
- Some organic fire retardants containing halogens or phosphorus are currently under scrutiny on account of environmental and health issues associated with their use. Specifically the compounds of concern include penta and octa-bromo-diphenyl oxide (or ether) in terms of halogenated compounds and in terms of phosphorus based compounds, these include red phosphorus and the phos-chek family of compounds. As a result of these concerns, we have excluded these compounds from our list of candidate fire retardants
- Organic fire retardants can be used in isolation, although significant benefits can be achieved by combining with an additive that provides synergism.
- The permanence of the candidate fire retardants in timber exposed to outdoor, above ground weathering trials remains to be established.
- Costs for the candidate fire retardants will need to be obtained from the appropriate suppliers.

Conclusions

There is no prior art to suggest that the approach proposed for this project, as outlined in the original proposal, does not have merit. The first stage of the project will provide an indication as to the likelihood of a combined fire retardant and preservative satisfying the technical requirements of the relevant performance standards.

Table of contents

Executive summary	i
1. Introduction.....	1
1.1 Background.....	1
1.2 Objective of Review	1
2. Wood preservatives currently in use in Australia and New Zealand	3
2.1 Existing preservatives	3
2.2 Preservative use in Australia	6
2.3 The New Zealand situation.....	7
2.4 The application of industrial wood preservatives.....	9
3. Thermal degradation of wood.....	10
4. Overview of fire retardants	13
4.1 Fire retardant mechanisms.....	13
4.2 Types of fire retardants	14
4.3 Chemical classes of fire retardants	14
4.3.1 Halogen-containing fire retardants.....	14
4.3.2 Phosphorus-containing fire retardants.....	15
4.3.3 Nitrogen-containing fire retardants	16
4.3.4 Inorganic-based fire retardants.....	16
5. Fire retardants currently used for wood.....	17
5.1 Fire retardants for wood.....	17
5.1.1 Fire retardant coatings for wood	19
5.1.2 Fire retardants for impregnation into wood	20
5.2 Fire-retardant-treated wood for exterior applications	21
5.2.1 The issue of leach resistance.....	21
5.2.2 Non-Com Exterior [®] (NCX) and FRX [®]	22
5.2.3 Exterior Fire-X [®] (EFX)	23
5.2.4 Dricon [®]	23
5.2.5 Moelven fireproof products	24
5.2.6 Suitability for use in Australasia.....	24
6. Candidates for a combined fire retardant / preservative treatment for wood.....	25
7. Previous studies of combined fire retardant / preservative systems	30
8. Conclusions	33
Appendix A – Methods of testing for fire retardant efficiency... 34	
Appendix B – Fire retardant manufacturers.....	35

1. INTRODUCTION

1.1 Background

Wood is one of the most versatile building materials available. It is a renewable material that can be harvested and converted into useable components at relatively low cost. Wood is easily workable, does not pollute the environment to any significant extent and has a number of aesthetically pleasing attributes which, when coupled with its outstanding physical and mechanical properties, provides a cost effective material for a wide range of end uses. The use of wood can, however, be restricted by safety regulations concerned with its ignitability and flame spreading characteristics. The careful selection and application of an appropriate flame retardant system can overcome these concerns and enable wood-based products to satisfy regulatory requirements and thus be used in a wide range of applications.

During the recent extensive consultation process undertaken by the FWPRDC with its levy payers and stakeholders to develop a new five year Research and Development Plan, one of the areas of importance that was identified was the need for timber products for exposed applications in bushfire prone areas. Specifically, the need for a cost effective dual fire retardant and preservative treatment for timber that is to be used outdoors was highlighted. The aim of this project is to develop a ‘proof of concept’ for a dual fire retardant/preservative treatment technology for softwood and/or hardwood species that are of low natural durability, to satisfy AS 3959 – 1999 *Construction of buildings in bushfire-prone areas*, and at the same time comply with the primary preservation standard, AS 1604.1 – 2000, *Specification for preservative treatment Part 1: sawn and round timber*.

1.2 Objective of review

In order to develop a technology in the most time efficient manner, the approach adopted in this project is to focus on combining an existing preservative system with a known fire retardant(s). Several commercial fire retardant systems that appear suitable in terms of their chemical and physical properties have been identified. The purpose of the review is to ensure that all potential fire retardants that fulfill, or at least partially fulfill, the pre-requisite criteria (see Section 6) are identified and incorporated into the first stage of the project. This will involve an experimental program, the objective being to establish a short list of possible combinations of fire retardants and preservatives that are most promising in terms of their performance (fire and durability), resistance to weathering and ease of application.

The review commences with a description of the preservatives currently in use in Australia and New Zealand, and some comments about the uses of preservative treated timber in Australasia (Section 2). Trends in preservative usage are important, since the choice of preservative to which a compatible fire retardant is sought is a critical variable in the matrix of possible combinations of preservatives and fire retardants. A brief review of the thermal degradation of wood (Section 3) serves as a general introduction to fire retardants and the mechanisms by which they function (Section 4). Existing fire retardant treatments for timber in interior and exterior applications are reviewed

(Section 5) and their limitations discussed. Commercial fire retardants that may be suitable for the project are then presented (Section 6), prefaced by a discussion of the important chemical and physical properties that are considered as criteria for selection of an exterior fire retardant. A summary of previous studies of combined fire retardant and preservative systems completes the main body of the review (Section 7).

2. WOOD PRESERVATIVES CURRENTLY IN USE IN AUSTRALIA AND NEW ZEALAND

2.1 Existing preservatives

Wood preservatives that are applied to timber via industrial processes, *e.g.* vacuum and/or pressure impregnation, and dipping or spraying, are considered as agricultural chemicals and their introduction and use is regulated by the Australian Pesticides & Veterinary Medicines Association (APVMA).¹ It is the role of the APVMA to ensure that chemicals offered for sale are safe when used in accordance with directions, do not impact negatively on the environment and are efficacious for their intended use.

Table 1 Hazard class selection guide from AS 1604.1

Hazard Class	Exposure	Specific service conditions	Biological hazard	Typical end-uses
H1	Inside, above ground	Completely protected from the weather and well ventilated. Protected from termites	Lyctids	Susceptible framing, flooring, furniture, interior joinery
H2	Inside, above ground	Protected from leaching, nil wetting	Borers and termites	Framing, flooring, and similar, used in dry situations
H2F	Inside, above ground	Protected from leaching, nil wetting	Termites	Framing only
H3	Outside, above ground	Subject to periodic wetting and leaching	Moderate decay, borers and termites	Weatherboards, fascias, pergolas (above ground), window joinery, framing and decking
H4	Outside, in ground	Subject to severe wetting and leaching	Severe decay, borers and termites	Fence posts, greenhouses, pergolas (in ground) and landscaping timbers
H5	Outside, in ground contact with or in fresh water	Subject to extreme wetting and leaching and/or where the critical use requires a higher degree of protection	Very severe decay, borers and termites	Retaining walls, piling, house stumps, building poles, cooling tower fill
H6	Marine waters	Subjected to prolonged immersion in sea water	Marine wood borers and decay	Boat hulls, marine piles, jetty cross-bracing, landing steps and similar

¹ <http://www.apvma.gov.au/>

Various government agencies and bodies assist the APVMA in this activity. The Australasian Wood Preservation Committee (AWPC) has produced a protocol that lays out standard methodologies that should be used in generating data to support the demonstration of performance of a preservative, which are related to the hazard class for which the product is intended.² Experts in the appropriate field generally assist the APVMA with matters relating to efficacy and fitness for purpose of the product. In the case of wood preservatives, the technical specifications that a preservative must meet are laid out in an Australian Standard, AS 1604.1 – 2000 *Specification for preservative treatment Part 1: sawn and round timber*. The standard describes the preservative, the loading at which it should be applied and the penetration requirements, depending upon the intended end-use for the treated timber. End-use is classified according to the severity of exposure to which the timber will be subjected. The classifications of end-use used in the standard, or hazard class system as it is known, are shown in Table 1.

Industry representatives have suggested that timber used in hazard class 3 applications is in the first instance the most likely to come under scrutiny in areas that are designated as being of high bushfire hazard. This would include commodities such as fencing, decking, cladding, fascia and window/door frames. Therefore, the initial focus of the project will be on identifying fire retardants that are compatible with hazard class 3 preservatives. The preservatives currently listed in hazard class 3 of AS 1604.1 – 2000 are summarised in Table 2 and a brief description of each preservative is given below.

Chromated copper arsenate (CCA) comprises a mixture of pentavalent arsenic, hexavalent chromium and divalent copper in an appropriate ratio.³ What is referred to as ‘Type C’ CCA is that which is included in AS 1604.1 – 2000. The actual compounds used in the formulation of CCA oxide are typically arsenic acid (H₃AsO₄), chromium trioxide (CrO₃) and cupric oxide (CuO). Following the decision to selectively phase out CCA in North America⁴ and Europe,⁵ the APVMA announced a review of the use of arsenic in pesticide applications, specifically wood preservation.⁶ The APVMA released its preliminary findings in December 2003 and a final report is still to be delivered.⁷

Two non-arsenic, non-chromium preservatives are listed in AS 1604.1 – 2000. Ammoniacal copper quaternary (ACQ) is an alkaline mixture of divalent copper, commonly copper carbonate and an organic quaternary ammonium salt such as didecyldimethylammonium chloride.⁸ Copper azole (CuAz)⁹ is similarly a combination of divalent copper and an organic biocide, although in this case the latter is a triazole

² Anon (1997). Protocols for the assessment of wood preservatives. Australasian Wood Preservation Committee, pp. 24.

³ Humphrey, D. G. (2002). *The Chemistry of Chromated Copper Arsenate Wood Preservatives*, Reviews in Inorganic Chemistry, 22, 1-40.

⁴ See various documents located at: <http://www.epa.gov/pesticides/factsheets/chemicals/1file.htm>

⁵ Anon (2003). Commission Directive 2003/02/EC of 6 January 2003, Commission of the European Communities. http://europa.eu.int/eur-lex/pri/en/oj/dat/2003/l_004/l_00420030109en00090011.pdf

⁶ Anon (2003). *Arsenic Timber Treatments (CCA and Arsenic trioxide) Review Scope Document*. March 2003. http://www.apvma.gov.au/chemrev/arsenic_scope.pdf

⁷ Anon (2003). *The Reconsideration of registrations of arsenic timber treatment products (CCA and arsenic trioxide) and their associated labels. Technical Report*. December 2003.

<http://www.apvma.gov.au/chemrev/arsenic.shtml>

⁸ Preston, A. F. (2000). *Wood preservation trends today that will influence the industry tomorrow*. Forest Products Journal, 50, 12-19.

⁹ Fox, R. F. and Williams, R. (1995). *Copper azole as an alternative wood preservative system*. Wood Preservation in the 90's and beyond, Proceedings no. 7308, Forest Products Society, pp. 198-211.

fungicide, tebuconazole.¹⁰ The organic biocides are essential to provide the broad spectrum of activity required by a wood preservative, in particular to prevent decay by copper tolerant fungi. Both of these copper-based preservatives are formulated in aqueous ethanolamine.

Creosote is one of the oldest wood preservatives in existence and is still used to some extent today, although mainly in hazard class 6 applications. It is a by-product of coal-tar distillation, and is a complicated mixture of literally hundreds of individual compounds. Creosote frequently has an unpleasant odour and can cause skin irritations. Although there are currently no restrictions on its use in Australia, globally its use is declining.

Table 2 Preservatives currently listed in hazard class 3 of AS 1604.1 – 2000

Preservative	Composition ^a (% w/w)	Carrier	Retention (% m/m) ^b
Chromated copper arsenate (CCA)	As 30-37 Cr 38-45 Cu 23-25 (Equivalent to Type C formulation)	Water	0.380
Ammoniacal copper quaternary (ACQ)	Cu 57-66 DDAC 34-43	Water	0.350 sw 0.390 hw
Copper Azole (CuAz)	Cu 95.82-96.38 Tebuconazole 3.62-4.18	Water	0.270
Creosote	Type 1 or Type 2 (as defined by boiling point fractions)	Oil	8.00
Organo-tin compounds, bis(tributyltin)oxide (TBTO) and tributyltin naphthenate (TBTN)	TBTO, must comply with BS 4630 TBTN, must comply with BWPDA Manual 1991	Light organic solvent	0.080 (0.160) ^c
Copper naphthenate (CuN)	Must comply with AWPA P8/77 1977	Light organic solvent	0.100
Pentachlorophenol (PCP)	Must comply with BS 3175 and BS 5707	Light organic solvent	0.700
Synthetic pyrethroids	Permethrin Deltamethrin Cypermethrin	Light organic solvent	0.020

^a Relative proportions of each component. For the metal-based preservatives, the relative proportions are based on elemental concentration.

^b sw = softwood, hw = hardwood.

^c Proposed new retention shown in parentheses.

¹⁰ Buschhaus, H.-U. (1995). *Tebuconazole - Efficacy, toxicity, physical properties*. The 26th Annual Meeting of the International Research Group on Wood Preservation. Helsingør, Denmark, 95-30093.

Light organic solvent preservatives (LOSP) are comprised of a combination of a fungicide and an insecticide. The organo-tin compounds, bis(tributyltin)oxide (TBTO) and tributyltin naphthenate (TBTN), are at present the fungicides of choice for LOSP's. They are usually applied in combination with permethrin. An amendment to AS 1604.1 – 2000 is currently available for public comment. The proposed revision of the standard includes an increase in the hazard class 3 retention of TBTO and TBTN, from 0.08 to 0.16 % m/m elemental tin. The increased retention has arisen through some failures of LOSP treated timber in recent years, particularly in situations where the timber was exposed in horizontal end-uses that favoured water entrapment. With the phasing out of organo-tin compounds from anti-fouling applications, these compounds are expected to have a limited lifetime in the Australasian preservatives market.

Copper naphthenate (CuN) and pentachlorophenol (PCP) are currently not used to any significant extent by industry. At present all of the hazard class 3 preservatives are metal-based, however, it is anticipated that non-metallic preservatives will be incorporated into AS 1604.1 at some point in the future.

For wood treated with a preservative and fire retardant to fall under the auspicious of AS 1604.1, and in so doing be classified as 'preservative treated wood',¹¹ the efficacy of the combination of preservative and fire retardant would need to be demonstrated using the standard methods described in the protocol, so as to ensure that inclusion of the fire retardant has not reduced the performance of the preservative.

2.2 Preservative use in Australia

It is estimated that *ca.* 516,000 m³ of timber are treated to Hazard Class 3 retentions with the preservatives listed in Table 2.¹² Of the 516,000 m³ of timber treated, approximately 70 % are treated with CCA. It is anticipated that the proportion of CCA treated timber will decline over the coming years, regardless of the final outcome of the current APVMA Review. The focus of the current project will be on finding fire retardants to combine with preservatives other than CCA.

Previously, CCA formulations were available that included additives to combat 'afterglow', a phenomenon where CCA treated timber continues to smoulder after the fire front has passed. Tanalith AG[®], which was available from Koppers Australia Pty Ltd, was a CCA formulation developed by CSIRO that contained zinc phosphate.¹³ In 1985 approximately 80 tonnes of this formulation were being sold; however, its consumption decreased substantially in subsequent years. There were reports of vineyard trellis posts treated with Tanalith AG[®] failing through excessive decay in

¹¹ It should be noted that fire retardant treated wood that is produced commercially for exterior applications in North America is not specified as 'preservative treated wood'. Although the fire retardant treatment indirectly makes the wood somewhat durable, the product is sold with the understanding that it cannot be used in an application that requires preservative treated wood.

¹² Carruthers, P. (2003). *The Treated Timber Market and Wood Preservative Industry*, Termite Protection Workshop, Melbourne, 25th November, 2003.

¹³ McCarthy, D. F., Seaman, W. G., DaCosta, E. W. B. and Bezemer, L. D. (1972). *Development and evaluation of a leach resistant fire retardant preservative for pine fence posts*. Journal Institute Wood Science, **6**, 24-31.

South Australia, and exhibiting poor fire performance.¹⁴ This formulation is no longer sold. Interestingly, there were also reports that suggested creosote treated fence posts were better able to withstand fire than CCA treated posts. More recently, similar anecdotal evidence arose in relation to creosote treated poles in WA.¹⁵

2.3 The New Zealand situation

Wood preservatives used in New Zealand are regulated by the Environmental Risk Management Authority (ERMA),¹⁶ that performs a similar role to the APVMA in Australia. New Zealand has its own standard, the primary preservation standard being NZS 3640, *Chemical Preservation of Round and Sawn Timber*.¹⁷ This standard has recently undergone significant amendment, with hazard classes 1 and 3 each being split into two categories, catering for different commodities that in practice can be subjected to substantially different exposure conditions. The recently updated hazard classification scheme is summarised in Table 3.

The major differences between the two standards, NZS 3640 and AS 1604.1, are the preservatives that are included for each hazard class. In NZS 3640, 3-iodo-2-propynylbutyl-carbamate (IPBC), in combination with permethrin, is included for use in H1.2. The LOSP organo-tin compounds (TBTO and TBTN) are only approved for use in H3.1. In addition, a new preservative has recently been included in H3.1. A non-metallic LOSP is now available in New Zealand. The preservative consists of a 1:1 mixture of two triazoles, tebuconazole and propiconazole, that is applied at a retention of 0.06 % m/m. Other differences include the use of CuAz in H5 applications and the absence of creosote from NZS 3640.

Following the selective phasing out of CCA in North America and Europe, ERMA in New Zealand commissioned an independent review of the public and occupational health risk associated with using CCA treated timber in domestic and public settings. The review found that there was no conclusive evidence to suggest that arsenic in CCA treated timber posed a significant health risk to children.¹⁸ As a consequence, the use of CCA treated timber in New Zealand has not been restricted to date.

The requirements for demonstration of preservative efficacy in New Zealand are broadly consistent with those in Australia, such that a combined fire retardant / preservative treatment suitable for use in Australia could in principle also be registered for use in New Zealand, assuming that the preservative component was listed in NZS 3640:2003.

¹⁴ Schmalzl, K.S. (1986). *Fire retardant chemicals for wood preservation in Australia*. CSIRO Forestry & Forest Products internal communication.

¹⁵ Cobham, P. (2003). Personal communication.

¹⁶ <http://www.ermanz.govt.nz/>

¹⁷ <http://www.standards.co.nz/index.asp>

¹⁸ Read, D. (2003). *Report on Copper, Chromium and Arsenic (CCA) Treated Timber*. April 2003. <http://www.ermanz.govt.nz/news-events/focus/cca.asp>

Table 3 Hazard class selection guide from NZS 3640

Hazard Class	Exposure	Service conditions	Biological hazard	Typical uses
H1.1	Protected from weather, above ground	Protected from weather, always dry	Borers	Interior finishing timber
H1.2	Protected from weather, above ground, but with a possibility of exposure to moisture	Protected from weather, but with a risk of moisture content conducive to decay	Borers, decay	Wall framing
H2	Protected from the weather, above ground	Protected from the weather, dry, exposed to ground atmosphere where well ventilated but not in contact with ground	Borers and termites	Framing timber in Australia
H3.1	Exposed to the weather, above ground	Periodic wetting, not in contact with the ground	Decay fungi and borers	Cladding, fascia, joinery
H3.2	Above ground, exposed to weather, or protected from the weather but with risk of moisture entrapment	Periodic wetting, not in contact with the ground, more critical end uses (than H3.1)	Decay fungi and borers	Structural, decking
H4	Exposed to the weather, in ground or in fresh water	Ground contact, or conditions of severe or continuous wetting	Decay fungi and borers	Fence posts, landscaping timbers
H5	Exposed to the weather, in ground or in fresh water	Ground contact, or conditions of severe or continuous wetting, where uses are critical and where higher level of protection than H4 is required	Decay fungi and borers	House piles and poles, crib walling
H6	Sea water or estuarine ground	Immersion in sea water or estuarine ground	Marine wood borers and decay	Marine timber and piles

2.4 The application of industrial wood preservatives

Most methods of applying preservatives to timber fall into one of two general categories.¹⁹ The first category is a batch process that involves placing the timber to be treated in a suitable vessel and applying vacuum and/or pressure to maximise the penetration of preservative, which is introduced as a liquid at some stage of the process.²⁰ There are a number of variations of this process, based on the sequence of events of filling/emptying of the vessel with the preservative formulation and the sequence of applying vacuum and/or pressure. Aside from the process variables, the species of wood, the proportion of heartwood/sapwood, grain orientation, physical dimensions, pre-conditioning regime and moisture content can all impact on the distribution of the preservative through the cross-section of the timber being treated. This method of application would be suitable for the treatment of timber with a fire retardant/preservative combination. If, as a result of impregnation, the fire retardant is distributed through the interior of the wood, it would remain even after destruction of the surface has taken place.

An alternative method of applying preservatives to the surface or outer regions (envelope) of timber is via dipping or spray. This method is more applicable to continuous, in-line processing. All of the non-process variables that effect the penetration of preservatives applied via vacuum-pressure impregnation similarly will influence in some way the distribution of preservative when it is applied via dip or spray. There are also other variables, such as the physical properties of the preservative formulation that influence the end result. For example, the viscosity of the formulation has a more substantial effect on the preservative uptake in dip treatments than it does in vacuum-pressure treatments.

There are some diffusible preservatives that can be applied via dipping or spray and, providing the moisture content is sufficient, the preservatives will diffuse through the cross-section over a period of time. The industry in Australia has used aqueous boron-based preservatives to treat eucalypts susceptible to the *lyctus* borer via dip treatments for many years.²¹ Packs of unseasoned eucalypts are immersed in a bath of the preservative for a short period of time, then wrapped and left standing to allow diffusion to occur. A similar process was used in New Zealand pre-1995 to treat unseasoned *P. radiata* framing for protection against the *anobium* borer.

There are some other prototype methods for applying preservatives to timber, *e.g.* the vapour boron process²² and timber in-line treatment (TILT).²³ However, these have not been recognised commercially and adopted by industry. For a combined fire retardant/preservative to have widespread acceptance amongst the treatment industry, the combined system would need to be able to be applied using conventional treatment technologies, most probably vacuum-pressure impregnation.

¹⁹ Purslow, D.F. (1974). *Methods of applying wood preservatives*. Building Research Establishment Report. Her Majesty's Stationary Office, London, pp. 26.

²⁰ Wilkinson, J.F. (1979). *Industrial timber preserving processes*. Industrial Timber Preservation. The Rentokil Library. Associated Business Press, London. Chapter 8, pp. 211-246.

²¹ Cookson, L.J. (1996). *Survey on treatment methods for the protection of hardwood sapwood from Lyctus borer*. CSIRO Forestry & Forest Products Report, pp. 1-78.

²² Vinden, P., Burton, R.J. and Bergervoet, A.J. (1991). *Vapour phase treatment of wood with trimethylborate*. The Chemistry of Wood Preservation, ed. R. Thompson, The Royal Society of Chemistry, Cambridge, pp. 265-274.

²³ Hedley, M. (2000). *Timber in-line treatment (TILT) process*. Abstracts from FIEA Timber Preservation Workshop – Fine Tuning Your Operation for Performance and Profit, Rotorua, November 2000.

3. THERMAL DEGRADATION OF WOOD

Wood is made up of three major polymeric components, cellulose, hemicellulose and lignin,^{24,25,26,27} with small amounts of organic extractives and inorganic trace elements.²⁸ The polymeric components make up the cell wall and are responsible for most of the physical and chemical properties exhibited by wood. Cellulose is a long-chained, linear sugar molecule or polysaccharide composed of glucose monomers. Glucose is a hexose or six-carbon ring sugar, and as a cellulose polymer it accounts for about 40-45% of the dry weight of wood.²⁹ The high molecular weight of cellulose is primarily responsible for wood strength. Hemicellulose molecules are lower molecular weight polysaccharides that contain short side chains. They contain mainly combinations of various five-carbon sugars (xylose and arabinose) and six-carbon sugars (glucose, mannose and galactose) and make up between 20 to 35% of the dry weight of wood.²⁹ Lignin is a random three-dimensional network polymer that makes up between 15 to 35% of the dry weight of wood. It is a hydrophobic, phenolic material comprised of hydroxyl- and methoxy-substituted phenylpropane units that hold the wood (cellulose and hemicellulose) together and is also responsible for imparting rigidity to wood.^{30,31}

The burning of wood, like that of any material, is not a singular process. It can be defined as a set of chemical and/or physical processes that break bonds within the wood structure and release and/or produce volatile products. The burning process may be broken down into a number of steps. The initial step involves heating or pyrolysis of the wood, which generates char (solid residue), tar (liquid residue) and gases (or volatiles). The amount of volatile matter released and the proportion of each volatile species present depends upon the burning conditions and the type of wood used. This is followed by the reaction of the volatiles with oxygen (combustion) in the presence of a suitable ignition source to form carbon monoxide and carbon dioxide. The heat generated by these exothermic reactions acts to sustain the pyrolysis of the solid wood/char, thus releasing more volatiles. This cycle continues until such time as the

²⁴ Bourgois, J. and Guyonnet, R. (1988). *Characterization and analysis of torrefied wood*. Wood Science and Technology, **22**, 143-155.

²⁵ Fang, J. B. (1966). *Wood Fire Behaviour and Fire Retardant Treatment: A Review of the Literature*. Ignition Properties of Cellulose Materials: A Survey of the Literature. Canadian Wood Council, Ottawa, Canada.

²⁶ Meier, D. and Faix, O. (1999). *State of the Art of Applied Fast Pyrolysis of Lignocellulosic Materials - A Review*. Bioresource Technology, **68**, 71-77.

²⁷ Rowell, R.M. (1984). *Penetration and Reactivity of Cell Wall Components*. The Chemistry of Solid Wood, Advances in Chemistry Series, ed. R. Rowell, American Chemical Society, Washington, DC, Volume 207, pp. 175-210.

²⁸ Alén, R. (2000). *Structure and Chemical Composition of Wood*. Forest Products Chemistry, Papermaking Science and Technology Book 3. ed. P. Stenius, Fapet Oy, Finland. Chapter 1, pp. 12-57.

²⁹ Parham, R. A. and Gray, R. L. (1984). *Formation and Structure of Wood*. The Chemistry of Solid Wood, Advances in Chemistry Series, ed. R. Rowell, American Chemical Society, Washington, DC, Volume 207, pp. 3-56.

³⁰ Miller, R.B. (1999). *Structure of Wood*. Wood Handbook – Wood as an Engineering Material. USDA Forest Service, Forest Products Laboratory, Madison WI. FPL-GTR-113.

³¹ Winandy, J.E. and Rowell, R.M. (1984). *The Chemistry of Wood Strength*. The Chemistry of Solid Wood, Advances in Chemistry Series, ed. R. Rowell, American Chemical Society, Washington, DC, Volume 207, pp. 211-255.

wood is entirely converted to char and all available volatiles have been released. This burning cycle is represented schematically below in Figure 1.³²

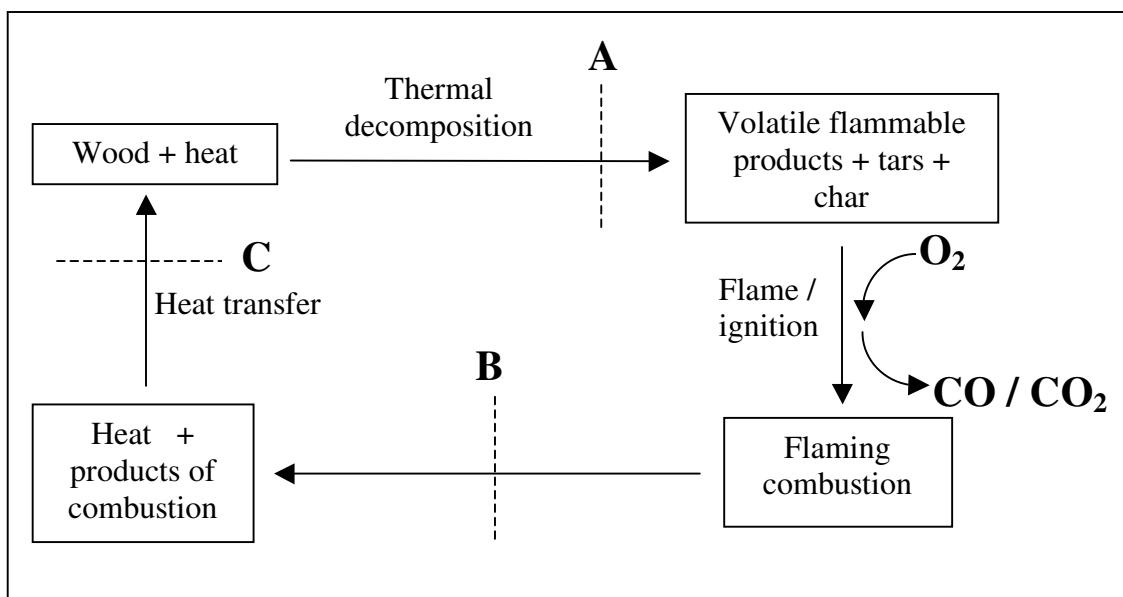


Figure 1 The burning cycle of wood

Each of the polymeric wood components degrades in a slightly different manner. Cellulose decomposes in the temperature range between 260 °C and 350 °C and it is mainly responsible for the formation of flammable, volatile compounds.³³ The molecular weight of cellulose decreases as the material degrades with increasing temperature.^{27,33,34} Hemicellulose is less thermally stable than cellulose and degrades in the range 200 °C to 260 °C, evolving more non-combustible gases and less tar than cellulose.³⁴ Lignin is the most thermally stable component of wood, and it generally pyrolyses at a slower rate than cellulose or hemicellulose. The degradation period, however, begins earlier at around 160 °C and lignin continues to degrade until around 400 °C.³⁴ Lignin contributes more to char formation than cellulose or hemicellulose. Increased char formation reduces the emission of flammable gases and helps insulate wood from further thermal degradation.²⁷

At the macroscopic level, the combustion of wood follows a series of events with increasing temperature that are reasonably well validated.^{35,36} These are summarised in Table 4.^{25,33,34,37}

³² Grassie, N. and Scott, G. (1985). *Polymer Degradation and Stabilisation*. Cambridge University Press, New York, pp. 172-217.

³³ Shafizadeh, F. (1984). *The Chemistry of Pyrolysis and Combustion*. The Chemistry of Solid Wood, *Advances in Chemistry Series*, ed. R. Rowell, American Chemical Society, Washington, DC, Volume 207, pp. 489-529.

³⁴ LeVan, S. L. and Winandy, J. E. (1990). *Effects of Fire Retardant Treatments on Wood Strength: A Review*. *Wood and Fiber Science*, **22**(1), 113-131.

³⁵ White, R.H. and DiTenberger, M.A. (2002). *Wood products: thermal degradation and fire*. *Encyclopedia of Materials: Science and Technology*. Elsevier Science Ltd., pp. 9712-9716.

³⁶ Babrauskas, V. (2001). *Ignition of wood. A review of the state of the art*. *Interflam 2001*, Interscience Communications Ltd., London, pp. 71-88.

Table 4 The combustion of wood

Temperature (°C)	Reactions
100-200	The wood steadily loses weight and evolves non-combustible gases, such as carbon dioxide, traces of formic and acetic acids and water vapour, through slow pyrolysis.
160	Lignin begins to decompose resulting in the formation of char
200-260	Exothermic reactions begin and are characterised by the release of an increased quantity of decomposition gases and high boiling point tar. There is also the appearance of local ignition areas of hydrocarbons with low boiling points.
275-280	Uncontrolled release of large amounts of heat occurs and an increased production of liquid and gaseous products including methanol, ethanoic acid and its homologues.
> 280	Beyond 280 °C the release of gases increases and this is accompanied by the rapid formation of charcoal. The reactions are highly exothermic when peak temperatures are in the range 280 – 320 °C.
> 300	At this point if there is sufficient oxygen, the mixture of gases formed will ignite. Combustion proceeds in the gas phase at a small distance from the surface rather than on the wood surface itself. From this moment, wood can burn, even after the removal of the heat stimulus. The ignition of wood occurs between 300 – 400 °C, depending on the origin of the wood, and will continue to burn until all wood components end their volatile emissions at around 450 °C.
> 450	The remaining wood residue is char, which undergoes further degradation by being oxidised to carbon dioxide, carbon monoxide and water.

³⁷ Kozłowski R. and Władya-Przybylak, M. (2001). *Natural polymers, wood and lignocellulosic materials*. Fire Retardant Materials. ed. A. R. Horrocks and D. Price, Woodhead Publishing Limited, Cambridge, England, pp. 293-317.

4. OVERVIEW OF FIRE RETARDANTS

4.1 Fire retardant mechanisms

Fire retardants act to inhibit or even suppress the combustion process through a number of mechanisms and sub-mechanisms. Depending on their nature, fire retardants can act chemically and/or physically in the solid, liquid or gas phase to retard combustion processes.³⁸ They interfere with a particular stage of combustion cycle, as shown in Figure 1, by modification of the thermal degradation process (A), quenching the flame (B) or reducing the supply of heat from the flame back to the decomposing polymer (C).³²

4.1.1 Physical action

There are a number of physical processes including:

Cooling: Endothermic processes triggered by additives cool the substrate to a temperature below that required for sustaining the combustion process, *e.g.* magnesium hydroxide.

Formation of a protective layer (or coating): The condensed combustible layer can be shielded from the gaseous phase with a solid or gaseous protective layer. The condensed phase is thus cooled, smaller quantities of pyrolysis gases are evolved, the oxygen necessary for the combustion process is excluded and heat transfer is impeded, *e.g.* phosphorous and boron compounds.

Dilution: The incorporation of inert substances (*e.g.* fillers) and additives that evolve inert gases on decomposition dilute the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not exceeded, *e.g.* aluminium hydroxide leaving water.

4.1.2 Chemical action

The most significant chemical reactions interfering with the combustion process take place in the solid and gas phases:

Reaction in the gas phase: The free radical mechanism of the combustion process that takes place in the gas phase is interrupted by the fire retardant. The exothermic processes are thus stopped, the system cools down, and the supply of flammable gases is reduced and eventually completely suppressed, *e.g.* halogenated fire retardants.

Reaction in the solid phase: The fire retardant can cause a layer of carbon to form on the polymer surface. This can occur, for example, through the dehydrating action of the fire retardant generating double bonds in the polymer. These form the carbonaceous layer by cyclising and cross-linking, *e.g.* phosphorus compounds.

³⁸ Troitzsch, J.H. (1998). *Overview of Flame Retardants*. Available at http://www.bsef-site.com/science/over_fr.pdf.

4.2 Types of fire retardants

A distinction is made between *reactive* and *additive* fire retardants. Combinations of fire retardants may produce a *synergistic* effect, which is of considerable practical importance, as it can allow the loading of one or more of the retardants to be reduced without compromising performance. These types are defined below and specific examples are provided in Table 6.^{37,39}

Reactive fire retardants are chemically bound to the material, *i.e.* attached via a covalent bond. This prevents the fire retardant from leaching out of the material or volatilising, thus retaining their flame retardance.

Additive fire retardants are incorporated into the material by addition, and are not covalently linked to the substrate. Weaker, secondary bonding interactions such as hydrogen bonding or dipole-dipole interactions may contribute to the retention of the additive in the substrate, in much the same way as some preservatives are retained in the wood matrix.

Combinations of additive or reactive fire retardants can produce an additive, synergistic or antagonistic effect. While the additive effect is the sum of the individual actions, the effects of synergism and antagonism are higher and lower, respectively, than this sum. When used alone, synergists show no or only negligible effectiveness. The synergistic effect occurs when they are used together with specific fire retardants. The fire retardant/synergist systems have achieved great importance in practical use because they are usually less expensive than fire retardants used alone.

4.3 Chemical classes of fire retardants

4.3.1 Halogen-containing fire retardants

Halogen-containing fire retardants function by trapping free radical species formed during combustion of materials, thereby limiting the flame propagation.⁴⁰ The relative effectiveness of the various halogens as flame inhibitors appears to be directly proportional to their atomic weights.⁴¹ The effectiveness of halogen-containing fire retardants follows the order $F < Cl < Br < I$. Of the four halogens, chlorine and bromine are the most extensively used; iodine compounds are not used extensively because of their high cost and because of the high sensitivity of the carbon – iodine bond to thermal and photochemical degradation. Bromine compounds, especially aliphatics also suffer from poor light stability and high cost. Chlorine compounds while lowest in cost and highest in light stability, (apart from fluorine which is excluded because of its high cost), are not as effective on a weight basis as the corresponding bromine compounds. Carbon-fluorine bonds are thermodynamically stable up to relatively high temperatures, whereas carbon-iodine bonds dissociate at relatively low temperatures. Bromine is most effective since its bonding to carbon enables it to interfere at a more favourable point in

³⁹ Troitzsch, J.H. (2004). *Plastics Flammability Handbook*. ed. J.H. Troitzsch, Hanser Gardner Publications, Inc., Munich.

⁴⁰ Alaei, M., Arias, P., Sjodin, A. and Bergman, A. (2003). *An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release*. *Environmental International*, **29**, 683-689.

⁴¹ Larson, E.R. (1974). *Fire and Flammability / Flame Retardant Chemistry*, **1**, 4.

the combustion process. It is assumed, moreover, that the effective agent, HBr, is liberated over a narrow temperature range so that it is available at a high concentration in the flame zone. The disadvantage of bromine may often be the relative instability of the carbon – bromine bond as it is subject to thermolysis during processing and photolysis during commercial usage.⁴² Chlorine-containing fire retardants release HCl over a wider temperature range. Thus, the latter is considered to be present at relatively lower concentrations and therefore less effective.

Both aliphatic and aromatic brominated compounds are used in large quantities as commercial fire retardants. The more effective aliphatic halogen compounds are easier to break down and, hence, are less temperature resistant than aromatic fire retardants. Their suitability depends on the material and the method of incorporation. There is, however, increasing concern over the use of certain brominated fire retardants, as these compounds have been shown to persist in the environment, bioaccumulate and may impact on human health.⁴³ Risk assessments for penta- and octabromodiphenyl ether (penta-BDE, octa-BDE) have been carried out and these compounds will not be used in Europe from August 2004.⁴⁴ Decabromodiphenyl ether (deca-BDE) has also been assessed. However, no restriction on its use is planned at this stage. Tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD) are currently undergoing risk assessments. These compounds and polybrominated diphenyl ethers (PBDE) such as penta-BDE and octa-BDE have been detected in the environment and there is evidence to suggest that levels are increasing.⁴⁵ PBDE have also been found in humans. However, it is acknowledged that a risk assessment is difficult given the limited knowledge on bioavailability, toxicity and environmental behaviour,⁴⁶ and there is considerable debate over the toxicity of these compounds.

4.3.2 Phosphorus-containing fire retardants

While halogen containing fire retardants act in the gas phase, phosphorus-containing fire retardants mainly influence the reactions taking place in the condensed phase. They are particularly effective in materials with high oxygen content, such as cellulose. The fire retardant is converted by thermal decomposition to phosphoric acid, which in the condensed phase extracts water from the pyrolysing substrate causing it to char and, in the case of wood, enhancing its already substantial charring properties. Phosphorus-based fire retardants act on a burning situation in more than one way: they coat the condensed combustible layer, thereby cooling the condensed phase and excluding the access of oxygen and thus ignition. In addition, they form or help form a carbon char on the surface, thereby protecting the remaining condensed combustible layer from escaping into the flame and combining with oxygen to propagate the flame. The reaction steps are: (i) thermal decomposition resulting in the formation of phosphoric

⁴² Kuryla, W. C. and Papa, A. J. (1978). *Flame Retardance of Polymeric Materials*. Volume 4, Marcel Decker Inc, New York, pp. 2-102.

⁴³ Rahman, F., Langford, K. H., Scrimshaw, M. D. and Lester, J. N. (2002). *Polybrominated diphenyl ether (PBDE) flame retardants*. *Science of the Total Environment*, **275**, 1-17.

⁴⁴ Steukers, V., Kroon, S. and Drohmann, D. (2004). *Flame retardants: European Union risk assessments update*. *Plastics, Additives & Compounding*, March/April, pp. 26-29.

⁴⁵ Alae, M. and Wenning, R. J. (2002). *The significance of brominated fire retardants in the environment: current understanding, issues and challenges*. *Chemosphere*, **46**, 579-582.

⁴⁶ de Wit, C. A. (2002). *An overview of brominated flame retardants in the environment*. *Chemosphere*, **46**, 583-624.

acid and (ii) the acid esterifies and dehydrates the oxygen-containing polymer, thus causing charring.

Phosphorous compounds have also been observed to act in the gas phase in certain materials as far back as the early 1960's, via a similar mechanism to that previously outlined for halogens.⁴⁷

4.3.3 Nitrogen-containing fire retardants

Nitrogen-based fire retardants have been used primarily as melamine and melamine phosphates. Specifically, developed systems based on melamine and derivatives are used in intumescent systems. In addition, melamine phosphate and ammonium polyphosphate type compounds, which take advantage of the N-P synergism, are more recent, very effective additions to the nitrogen-based retardants.⁴⁸

Melamine-based fire retardants normally employ more than one mechanism and often several mechanisms to flame retard a material. Since several different types of mechanisms can operate, including condensed phase reactions and intumescence, the amounts of gases evolved are lower than mechanisms employing purely gas phase reactions such as halogens.

The mechanism by which melamine fire retardants (and other triazine type derivatives) function, involves vaporisation in a fire situation thus diluting the fuel gases and oxygen near the combustion source. Normally such compounds are mixed with another fire retardant additive that allows the formation of a condensed phase or gas phase reaction to form char or scavenge free radicals.

4.3.4 Inorganic-based fire retardants

Unlike organic compounds, inorganic fire retardants do not evaporate under the influence of heat. Instead, they decompose, giving off non-flammable gases like water, carbon dioxide, sulphur dioxide, hydrogen chloride *etc.*, via endothermic reactions. In the gas phase, these act by diluting the mixture of flammable gases and by shielding the surface of the substrate against oxygen attack. The inorganic fire retardant acts simultaneously on the surface of the solid phase by cooling the substrate via endothermic breakdown process and reducing the formation of pyrolysis products. In addition, as in the case of inorganic boron compounds, a glassy protective layer can form on the substrate, fending off the effects of oxygen and heat.

⁴⁷ Ibiricu, M. and Gaydon, A. G. (1964). *Spectroscopic studies of the effects of inhibitors on counterflow diffusion flames*. Combustion and Flame, **8**, 51-62.

⁴⁸ Levchik, S. V., Balabanovich, G. F., and Costa, L. (1997). *Effect of Melamine and its Salts on Combustion and Thermal Decomposition of Polyamide 6*. Fire and Materials, **21**, 75-83.

5. FIRE RETARDANTS CURRENTLY USED FOR WOOD

Introduction

This section of the literature review draws upon currently available reviews by Kozłowski and Władyka-Przybylak in Horrocks and Price,⁴⁹ LeVan,⁵⁰ Troitzsch³⁸ and White,⁵¹ as well as the current journal literature with updates where appropriate. There was a great deal of work in this area during the 80's and early 90's. However, there seems to have been a slow down over the last 5-10 years. A discussion of fire retardant application to timber, and the common problem of leaching (during usage) of the fire retardant from the timber is presented.

As previously mentioned, fire retardants act by inhibiting or suppressing the combustion process. They interfere with combustion during a particular stage of this process, i.e., during heating, decomposition, ignition or flame spread, and the means of retardation may be either chemical or physical.³⁸

The most widely accepted fire retardant mechanism for wood is referred to as the chemical theory.^{34,52} This theory suggests that the fire retardant acts by lowering the temperature at which pyrolysis of wood occurs so that the degradation of wood is directed toward the production of more char and less production of volatile, combustible vapours. Mono-ammonium phosphate is typical of the type of fire retardant that acts in this manner; it supports the acceleration of char formation as well as suppressing the production of flammable volatile compounds.

5.1 Fire retardants for wood

In general most, if not all of the commercial fire retardant systems for wood mentioned in this review, rely on the elements phosphorus, boron or nitrogen; phosphorus is usually the central element.

Phosphorus containing chemicals are the most widely used fire retardants for wood products. The fire retardant is converted by thermal decomposition to phosphoric acid, which in the condensed phase extracts water from the pyrolysing substrate, causing it to char. Two of the most effective fire retardants used in wood are diammonium phosphate and monoammonium phosphate.⁵³ They do, however, have the potential to increase the

⁴⁹ Kozłowski, R. and Władyka-Przybylak, M. (2001). *Fire Retardant Materials*. ed. A.R. Horrocks and D. Price, Woodhead Publishing Limited, Cambridge England, p. 293-317.

⁵⁰ LeVan, S. (1984). *Chemistry of Fire Retardancy*. The Chemistry of Solid Wood, Advances in Chemistry Series, ed. R. Rowell, American Chemical Society, Washington, DC, Volume 207, pp. 531-574.

⁵¹ White, R. H. and Sweet, M. S. (1992). *Flame retardancy of wood: Present status, recent problems and future fields*. Recent Advances in Flame Retardancy of Polymeric Materials: Proceedings of 3rd Annual BCC Conference on Flame Retardance, ed. Lewin, M., Stamford, CT. Business Communications Company Inc., pp. 250-257.

⁵² Holmes, C. A. (1977). *Effect of Fire-Retardant Treatments on Performance Properties of Wood*. Wood Technology: Chemical Aspects. ed. I. S. Goldstein, ACS Symposium Series 43, American Chemical Society, Washington DC.

⁵³ Grexa, O. and Lubke, H. (2001). *Flammability parameters of wood tested on a cone calorimeter*. *Polymer Degradation and Stability*. **74**, 427-432.

moisture content of wood in humid conditions, promoting fungal decay, and hence are more suited to interior applications where leaching is not an issue.

Fire retardants based on boron compounds give a long-lasting protection due to their deep penetration into wood.³⁷ Mixtures of borax and boric acid also impart preservative properties to wood as well as having a reduced impact on mechanical properties of wood compared to some other flame retardant chemicals.⁵⁴

Nitrogen-based fire retardants vapourise in a fire situation, thus diluting the fuel gases and oxygen near the combustion source. Melamine is the primary nitrogen-based fire retardant used, and seldom works well on its own. It is usually mixed with another fire retardant additive that enables the formation of a condensed phase to form char, *e.g.* phosphorus, or gas phase reaction to scavenge free radicals.

Phosphorus and nitrogen are frequently used together in wood because they behave synergistically.⁵⁰ Nitrogen-Phosphorus (N-P) based fire retardants display properties of both phosphorus and nitrogen type compounds. The phosphorus acts to protect the burning surface by forming a char and the nitrogen is released as a gas and dilutes combustible volatile products released from wood. Melamine phosphate and guanidine phosphate type compounds, which take advantage of the N-P synergism, are more recent additions to the nitrogen-based retardants.⁴⁸

Metal hydrates, which as previously mentioned, act by cooling the fuel source and dilution of the gases, are normally required in large quantities to be effective. The most common metal hydrate used as a fire retardant for wood is alumina tri-hydrate.⁵⁵ Some fire retardants currently used for wood are listed below in Table 5.

Table 5 Common fire retardants for wood

Class	Fire retardant
Phosphorus-based	Phosphoric acid, Ammonium polyphosphate
Boron-based	Boric acid, Boric oxide, sodium tetraborate (both the pentahydrate and anhydrous forms), sodium perborate tetrahydrate
Nitrogen-based	Melamine, melamine-formaldehyde resins, urea, dicyandiamide
Combined phosphorus – nitrogen systems	Ammonium polyphosphate, diammonium phosphate, melamine phosphate, guanidyl phosphate,
Combined sulfur – nitrogen systems	Ammonium sulfate, ammonium sulfamate
Metal hydrates	Aluminium trihydroxide

⁵⁴ LeVan, S.L. and Tran, H.C. (1990). *The role of boron in flame-retardant treatments*. 1st International Conference on Wood Protection with Diffusible Preservatives. Nashville, TE. ed. M. Hamel, Forest Products Research Society, pp. 39-41.

⁵⁵ Mukherjee, A. Melamine Derivatives as Flame-Retardant Additives in Polymers. (2001) *Journal of Plastics Engineering*, LVII, (2), 42.

Fire-retardant treatments for wood can be divided into two general classes, according to how they are applied:^{56,57}

- i. Those applied as surface coatings (non-intumescent or intumescent), and;
- ii. Those impregnated into the wood or incorporated into wood composite products.

5.1.1 Fire retardant coatings for wood

This section draws largely on the work by Kozłowski and Władyka-Przybylak in Horrocks and Price,⁵⁸ which is relatively recent in terms of the reviews on this subject.

One of the most effective methods of protecting wood and lignocellulosics from fire is with fire retardant coatings, particularly intumescent coatings.⁴⁹ When heated, they form a thick, porous carbonaceous layer. This provides ideal insulation of the surface against excessive increases in temperature and oxygen availability, thus intervening at a critical point in the wood burning cycle - see section 3, Figure 1. Intumescent-based fire retardants in general expand by up to 200 times their volume,⁴⁹ thus forming a thermal barrier between the heat and the fuel. They are made up of materials which form large amounts of non-flammable residues when heated. These residues form a foam with good insulating properties. This foam should be sufficiently durable and adhere to the surface of the substrate in order to act as a thermal barrier, and it should be able to withstand some of the other harsh conditions experienced under fire conditions.^{49,59} Coatings are in general easy to apply and are quite economical. They are used mostly to protect materials which are already elements of construction. Their drawbacks, however, include the formation of cracks and susceptibility to abrasion and wear, which result in the loss of fire retardant efficiency.

Intumescent coatings have many advantages, among which are a low mass requirement, as well as a relatively thin coating in order to secure effective fire protection over a given period. They exhibit the unique property of intumescence when exposed to flame and of creating a barrier against flame and oxygen access to the protected surface. For an intumescent coating to work as a fire retardant, it needs to be made up of:

- a carbonising compound,
- a foam forming compound,
- a dehydrating compound,
- modifying agents (to maximise the amount of carbonaceous mass)
- film-forming substances.⁴⁹

A proper selection of film-forming substances is extremely important. Amino-formaldehyde, polyvinyl and acrylic resins are preferred. Currently there is a trend towards using epoxy resins in intumescent systems. However, to satisfy the Building Code of Australia, the fire retardant must be impregnated into the timber. Hence, this project will focus on systems that are impregnated into the timber.

⁵⁶ Grexa, O., Poutch, F., Manikova, D., Martvonova H. and Bartekova, A. (2003). *Intumescence in fire retardancy of lignocellulosic panels*. *Polymer Degradation and Stability*, **82**, 373.

⁵⁷ White, R.H. and Diertenberger, M.A. (1999). *Fire Safety*. Wood Handbook – Wood as an Engineering Material. USDA Forest Service, Forest Products Laboratory, Madison WI. FPL-GTR-113.

⁵⁸ Kozłowski, R. and Władyka-Przybylak, M. (2001). *Fire Retardant Materials*. ed. A.R. Horrocks and D. Price, Woodhead Publishing Limited, Cambridge England, p. 293-317.

⁵⁹ Władyka-Przybylak, M. and Kozłowski, R. (1999). *The thermal characteristics of different intumescent coatings*. *Fire and Materials* **23**, 33-43.

5.1.2 Fire retardants for impregnation into wood

Again, the primary references for this section include Kozłowski and Władyka-Przybylak in Horrocks and Price,⁶⁰ LeVan,⁶¹ Troitzsch³⁸ and White.⁶²

The classification of fire retardants as either additive or reactive, which is often used in the case of synthetics, can also be applied to those used in wood. Additive compounds (as previously defined in section 4.2) are those that interact with the wood (or substrate) matrix in a manner that is largely physical in its nature. Their interaction with the substrate often involves relatively weak bonding interactions, such as hydrogen bonding. Reactive compounds on the other hand can form direct, covalent bonds with the wood constituents (i.e., lignin, hemicellulose and cellulose).^{42,63}

A range of commonly used fire retardants is provided below in Table 6. A number of these, although reducing the combustion potential of wood, can also affect such properties as strength, hygroscopicity, stability, toxicity, adhesive and mechanical properties, and receptivity to paint-coatings^{34,49} in a negative manner. They are used mainly in the form of impregnants for wood in relatively large doses (up to 20% by weight).⁶⁴ One of the most widely used fire retardants is mono-ammonium phosphate; which acts by acceleration of char formation and inhibits the release of flammable volatile compounds.⁶⁵ Evidence of its fire retardant efficacy includes more smoke and a greater CO:CO₂ ratio in the smoke gases, which are both strong indicators of inefficient combustion. Compounds of phosphorus and nitrogen are frequently applied jointly because of the synergy of their interaction, as previously mentioned in section 4.3.3. Inorganic fire retardants, which are often based on their salts, have the disadvantage of relatively easy leaching by water. Some of them can absorb moisture, and allow the penetration of water into the bulk of wood, which promotes decay, and also leads to the destruction of metal joints and building elements via corrosion chemistry. Boron-based compounds can give reasonable performance when present at relatively high loadings, and these compounds have the added advantage of fungicidal and insecticidal properties. Their mechanism in fire retardance is one of a flame and smoke inhibitor. Their primary disadvantage is that they are not resistant to leaching from wood products. Boron and phosphorus compounds, can, however, be used in a synergistic manner; where the phosphate compound may be applied to the interior and the boron compounds to the exterior of wood in order to increase the amount of charred mass on its surface. Further synergy may be obtained by utilisation of nitrogen-based compounds which liberate nitrogen gas, which can dilute combustible volatile products released from wood.^{63,66}

⁶⁰ Kozłowski, R. and Władyka-Przybylak, M. (2001). *Fire Retardant Materials*. ed. A.R. Horrocks and D. Price, Woodhead Publishing Limited, Cambridge England, p. 293-317.

⁶¹ LeVan, S. (1984). *Chemistry of Fire Retardancy*. The Chemistry of Solid Wood, Advances in Chemistry Series, ed. R. Rowell, American Chemical Society, Washington, DC, Volume 207, pp. 531-574.

⁶² White, R. H. and Sweet, M. S. (1992). *Flame retardancy of wood: Present status, recent problems and future fields*. Recent Advances in Flame Retardancy of Polymeric Materials: Proceedings of 3rd Annual BCC Conference on Flame Retardance, ed. Lewin, M., Stamford, CT. Business Communications Company Inc., pp. 250-257.

⁶³ Lewin, M., Atlas, S.M. and Pearce, E.M. (1975). *Flame Retardant Polymeric Materials*. Volume 1, Plenum Press, New York and London.

⁶⁴ Nussbaum, R. (1988). *The effect of low concentration fire retardant impregnations on wood charring rate and char yield*. Journal of Fire Sciences. **6**, 290-307.

⁶⁵ Grexa, O. and Kosik, M. (1992). *Flammability of wood treated with diammonium phosphate and toxicity of its fire effluents*. IURPO Meeting, Nancy, France.

⁶⁶ Lewin, M. (1997). *Flame retarding wood by chemical modification with bromate-bromide solutions*. Journal of Fire Sciences. **15**, 29-51.

Table 6 Examples of additive and reactive fire retardants, which have been used for wood

Additive Fire Retardants	Reactive Fire Retardants
Simple salts such as mono- and diammonium phosphate, ammonium polyphosphate, ammonium fluoroborate and ammonium chloride	Chlorendic anhydride (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic anhydride)
Hydrated alumina, magnesium hydroxide	Tetrabromophthalic anhydride
Amino resins. Compounds used for their manufacture are dicyandiamide, phosphoric acid, formaldehyde, melamine and urea	Derivatives of polyhydric alcohols such as halogeno-phosphorus polyols, chlorinated bisphenols and chlorinated neopentyl glycols
Inorganic compounds such as antimony oxide and halogenated hydrocarbons	SF ₃ Br
Zinc chloride and boron compounds such as boric acid, sodium tetraborate, zinc borate, triammonium borate, ethyl and methyl borates	Various halogenated methanes and ethanes, e.g. CH ₂ BrCl, CF ₂ BrCl, CF ₂ Br ₂ , CF ₂ Br-CF ₂ Br

NOTE: The loadings of these compounds are mentioned in the text (previous paragraph) and the references are Nussbaum (1988), in which doses up to 20% by wt were used; as well in the following paragraph we refer to work by LeVan (1984) in which doses between 15 and 30% by wt were used. Additional references regarding the amounts used are made in the paragraphs mentioned; these include work by Lewin (1997) and Rowel et. al. (1984).

Reactive fire retardants used in wood (see Table 6) tend to be resistant to water leaching and can often form water-insoluble complexes or polymer-specific systems based upon amino resins and monomers that undergo polymerisation inside wood.^{50,63} A number of the reactive fire retardants are based on halogens.⁶⁷ It is well known that halogens such as chlorine and bromine are efficient inhibitors of the formation of free radicals i.e., flame propagating species, however, a relatively large quantity, (15—30% by weight) of the material is often required.⁵⁰

5.2 Fire-retardant-treated wood for exterior applications

5.2.1 The issue of leach resistance

Wood fire retardancy with limited leachability can be achieved by means of a two-stage impregnation (first a fire retardant treatment and then a water-proofing treatment) or by chemical modification of wood. According to the review by Kozłowski and Władya-Przybylak⁵⁵ in Horrocks and Price - "...this is called flame retardancy created '*in statu nascendi*' by chemical reaction with components of lignocellulosics such as cellulose, hemicelluloses and lignin."³⁷ It is based on the chemical reaction between hydroxyl groups of cellulose or lignin with reactive fire retardant. In the case of wood and other lignocellulosic raw materials, lignin and its hydroxyl groups are much more accessible to chemical reagents than crystalline cellulose."

⁶⁷ Petrella, R.V. and Sellers, G.D. (1970). *Flame inhibition by bromine compounds*. Fire Technology. 6, 93-101.

Inorganic salts such as di- and monoammonium phosphate, ammonium sulfate, zinc chloride, sodium tetraborate, borax and boric acid are the most commonly used fire retardants for interior wood products. However, they are water-soluble and are leached out in exterior applications or with repeated washings.^{35,52,68} Some of them can absorb moisture, and the penetration of water into the bulk of the wood promotes not only its decay (e.g. due to fungi) but also leads to mould growth, the corrosion of metal fixings and the reduction of mechanical strength.

Water insoluble organic fire retardants have been developed to meet the need for leach-resistant systems. Such treatments are also an alternative when a low hygroscopic treatment is needed. These water-insoluble systems include:

- i) Resins polymerised after impregnation into wood; and
- ii) Graft polymer fire retardants attached directly to cellulose.

Aside from coatings, there are a number of fire retardant systems that are used commercially to produce fire retardant treated timber for exterior applications. These systems cannot, however, be considered as combined fire retardant and preservative treatments. Although they do impart some durability to the timber, this arises primarily through preventing the ingress of moisture, rather than through the presence of chemical preservatives. These systems are in general based on post-treatment curing of a thermosetting polymer. The timber is impregnated with the appropriate ratio of monomers and polymerisation achieved by heat treatment. Leach resistant systems include mixtures of urea, melamine, dicyandiamide, phosphoric acid and formaldehyde.³⁵

Because these systems do not contain chemical preservatives, they cannot be used in situations where preservative treated wood is specified. These systems, which are polymeric in nature, are not regulated by the appropriate pesticide management authorities. Instead, they typically receive an assessment of fitness for purpose by government or independent assessors, e.g. Underwriters Laboratory Inc.⁶⁹ The branding of the treated timber is dependent upon plants operating under strict quality control procedures and having samples regularly tested to ensure that they comply with the relevant performance and safety standards.

5.2.2 Non-Com Exterior® (NCX) and FRX®

NCX and FRX® are fire-retardant systems for wood-based materials that are designed to be used in exterior or severely damp applications. NCX is marketed in the UK⁷⁰ and FRX® in the USA.^{71,72} They are both products of Arch and its subsidiary businesses. NCX and FRX® are applied as water-based formulations of various monomers⁷³ that are incorporated into wood-based materials via vacuum-pressure impregnation. After treatment, the wood is kiln dried, then heat cured to promote polymerization. The heat and time required for this polymerization reaction is dependent upon the dimensions of the treated product. NCX and FRX® treatments must be carried out in a dedicated plant

⁶⁸ Östman, B., Voss, A., Hughes, A., Hovde, P.J. and Grexa, O. (2001). *Durability of fire retardant treated wood products at humid and exterior conditions: Review of literature*. Fire and Materials, **25**, 95-104.

⁶⁹ <http://www.ul.com/about/>

⁷⁰ <http://www.archtp.com/fire-non-com.php4>

⁷¹ <http://www.frxwood.com/>

⁷² <http://www.chemco.org/corp/>

⁷³ Proprietary information.

that is operated under approved quality control procedures, with products being periodically tested by an independent authority.

When exposed to fire, an insulating layer of char forms on the surface of the NCX or FRX[®] treated timber. The rate of char formation is more rapid than with untreated timber. The charring effect slows the normal process of combustion, reducing the amount of heat that is evolved and decreasing the rate of flame spread.

The NCX and FRX[®] treatments do not reduce the strength or stiffness of the timber (modulus of rupture and modulus of elasticity), nor do they substantially increase the hygroscopicity of the treated product. The rate of corrosion of mild steel, galvanised steel, aluminium, brass and copper fasteners or fittings are no different to that in untreated timber. The treatments can be applied to solid wood as well as engineered wood composites. Suitable timbers include Southern Yellow Pine, European Redwood, Spruce, Douglas Fir, Hemlock and Western Red Cedar.

5.2.3 Exterior Fire-X[®] (EFX)

An American owned company, Hoover Treated Wood Products Inc., produces fire retardant treated timber for external use.⁷⁴ Little information is available in the public domain about the details of the formulation and how it is applied to timber. The composition of the fire retardant system is unknown; however it is likely to be similar to NCX and FRX[®], being a heat cured polymeric system.

Like NCX[®] and FRX[®], the product is not specifically treated with a preservative; instead the fire-retardant imparts some durability to the timber, presumably through exclusion of moisture. EFX cannot be used in ground contact. The specification for the product states that:

*“Exterior Fire-X[®] is a non-leachable fire retardant treatment and may be installed with direct exposure to precipitation, however, it cannot be substituted for preservative treated wood”.*⁷⁵

5.2.4 Dricon[®]

Dricon[®] is another Arch product that, although it does not have the same range of applications as those mentioned above, is of interest because it is a recognised fire retardant that is also registered as a preservative in both the USA and UK. Dricon[®] is primarily an interior fire retardant, although the product literature states that it can be used in what are classified as ‘protected exterior situations’, where the timber is ‘suitably treated or protected from direct wetting’.⁷⁶ It is uncertain as to what constitutes adequate treatment/protection for the product to perform satisfactorily under exterior conditions, or what kind of exterior conditions that the product may be suitable for, *e.g.* cladding protected by roof overhang *etc.*

⁷⁴ <http://www.frtw.com/about/about.html>

⁷⁵ http://www.frtw.com/products/retardants/efx_specs.html

⁷⁶ <http://www.archtp.com/fire-dricon.php4>

Dricon[®] is comprised of boric acid and guanylurea phosphate (30/70%, w/w). Timber is treated with an aqueous formulation by vacuum-pressure impregnation, followed by kiln drying. The biocidal activity of boric acid is well documented,⁷⁷ and at the loadings required for fire retardancy, the quantity of boric acid should be more than that required to control decay fungi. It is reported that the Dricon[®] treatment does not reduce the strength of the timber, nor does it make the timber hygroscopic or corrosive to metal fasteners and fittings. When exposed to fire Dricon[®] treated timber produces very low levels of smoke, and can be glued and painted, providing that the applied coating does not affect the fire retardant properties of the treatment.

5.2.5 Moelven fireproof products

Moelven Industries is a Scandinavian company that supplies building products to a range of different markets. The Wood Division of the Timber Group produces ‘fireproof products’, treated via a ‘special impregnation process’.⁷⁸ Timber treated with this process can be used in specific exterior applications, *e.g.* cladding. Little information is available about the nature of the process, or the specifications to which the product complies.

5.2.6 Suitability for use in Australasia

Even if it were acceptable to use treatments of the type described previously in some exterior applications, *i.e.* where only fire retardant treated wood was required, the consensus amongst some industry representatives in Australia is that they are too expensive when applied to local timbers, *e.g.* *Pinus radiata*. For example, in North America FRX[®] is applied to western red cedar at a loading of approximately 30 kg m⁻³. *P. radiata* treated to the same loading does not however meet the relevant performance standards. It has been estimated that loadings of approximately 80 kg m⁻³ would be required for *P. radiata*, and this would make the product too expensive for it to be competitive with alternative materials. Further enquiries are currently in progress in an effort to obtain more detailed information relating to the performance of Australian species that have been treated with FRX[®]. In addition, treatments like FRX[®] must be applied in a dedicated plant so that demand would need to warrant this investment. A further barrier to adoption is the uncertainty associated with the durability of local timbers treated with treatments of this type.

To the best of our knowledge, there are currently no commercially available combined fire retardant/preservative systems for exterior timbers that comply with both fire and durability standards.

⁷⁷ Drysdale, J. A. (1995). *Boron treatments for the preservation of wood - A review of efficacy data for fungi and termites*. The 25th Annual Meeting of the International Research Group on Wood Preservation. Bali, Indonesia, 94-30037.

⁷⁸ <http://www.moelven.no/index.asp?menuItem=L8>

6. CANDIDATES FOR A COMBINED FIRE RETARDANT / PRESERVATIVE TREATMENT FOR WOOD

A number of criteria were identified to aid selection of the candidate fire retardants for the experimental program. These are summarised in Table 7. For the most important criteria, *i.e.* efficacy and permanence, there is a notable lack of data available in the public domain. It is possible that information does exist, but it may be considered proprietary information by the manufacturers (further discussions are in progress with industry representatives in an attempt to establish what research has previously been undertaken outside of Australia). The criteria that have been used assume that the process would be a single-stage process (multiple stages would likely to be too costly), involving an additive as opposed to a reactive fire retardant (enhanced wood properties versus modified wood product). The focus is on non-water borne systems since there is currently renewed interest in oil-borne preservatives that do not have the same VOC issues as LOSP systems.

Table 7 Criteria for fire retardant selection

Criteria ^a	Description	Comments
Efficacy in wood	Ability of the fire retardant treated product to meet the relevant performance standards. ^b	Can be established via an experimental program.
Permanence in wood in exposed applications	The fire retardant must be resistant to leaching and stable towards ultraviolet exposure.	Some insight can be gained by considering the solubility of the candidate fire retardant. Accelerated weathering trials provide an indication of the relative permanence of compounds in wood. $K_{o/w}$ may be a useful parameter to consider when comparing the permanence of fire retardants. ^c
Solubility	The fire retardant must be able to be co-formulated with the preservative.	For fire retardants that are not soluble in water, they may be applied from light organic solvents, oils or as oil-in-water emulsions (the feasibility of forming formulating emulsions will be explored as part of the project).
Availability	Commercial sources	Fire retardant must be available in commercial quantities.
Cost	The cost and loading are the most important factors in estimating process costs.	Costs are currently being sought. In many instances the cost of sourcing large quantities of chemicals is substantially different to that of small quantities.
Toxicity	Short and long term effects of the fire retardant on health and the environment	

^a Not listed in order of importance.

^b Both fire and preservative standards must be met. It is critical to establish if the fire retardant influences the behaviour of the preservative, and *vice-versa*. Ideally, the combination of both fire retardant and preservative may lead to synergism, rather than antagonism.

^c Partition co-efficients ($K_{o/w}$), *e.g.* octanol/water.

Searching the products available from commercial manufacturers identified a host of potential fire retardants for the present project. Some of these are listed in **Error! Reference source not found.** These compounds have been largely chosen the basis of their physical and chemical properties, rather than their performance as fire retardants in wood, since there is in general very little of this data available. In some instances, *e.g.* phosphate esters, there are many examples that could be considered. Not all of these have been listed.

Table 1 Candidate fire retardants (FR)

Compound name or trade name	FR classification	CAS Registry Number	Physical description	Solubility	Toxicity	Use	Availability	Other Comments
Tribromoneopentyl alcohol (TBNPA, FR-513)	Brominated aliphatic alcohol	36483-57-5	White solid, mp = 65 °C	Water (25 °C) ≈ 0.2 g / 100 g, methanol (25 °C) ≈ 270 g / 100 g	Acute oral (rat) LD ₅₀ = 2823 mg/kg Dermal irritant (rabbit) = mild irritant	Reactive FR for use in polyurethanes, often in combination with phosphorus based FR	Dead Sea Bromine Group	Light stable. Can be contaminated with FR-522 (see below), a potential carcinogen.
Dibromoneopentyl glycol (FR-522)	Brominated aliphatic alcohol	3296-90-0	White solid, mp = 110 °C	Water (25 °C) ≈ 2 g / 100 g, acetone (25 °C) ≈ 83 g / 100 g, isopropanol (25 °C) ≈ 52 g / 100 g	Acute oral (rat) LD ₅₀ > 2000 mg/kg, Dermal irritant (rabbit) = mild irritant. Possible carcinogen	Reactive FR for thermosetting polyester resins	Dead Sea Bromine Group	Light stable
Brominated trimethylphenyl-indan (FR-1808)	Brominated aromatic	155613-93-7	White solid, mp = 240-255 °C	Toluene ≈ 1.8 g / 100 g	Acute oral (rat) LD ₅₀ > 2000 mg/kg, Dermal (rabbit) LD ₅₀ > 2000 mg/kg	Polymers	Dead Sea Bromine Group	High thermal stability
Decabromo-diphenyl ether	Brominated aromatic	1163-19-5	White to off-white solid, mp = 303-307 °C	Water (25 °C) < 0.01 g / 100 g, toluene ≈ 0.76 g / 100 g	Acute oral (rat) LD ₅₀ > 2000 mg/kg	Varied, including textiles	Albemarle	Not restricted as yet but some issues around its use

Tribromophenol allyl ether (PHE-65)	Brominated aromatic	3278-89-5	Off-white powder mp = 74-76 °C	Water (25 °C) < 0.1 g / 100 g Toluene ≈ 6 g / 100 g		Polystyrene	Great Lakes	
Chlorinated paraffins	Chlorinated alkane	Dependent on alkane chain length, <i>e.g.</i> C ₁₂₋₁₄ 85536-22-7, C ₁₀₋₁₄ 85681-73-8	Varies, liquid to waxy solid	Variable	Low acute oral toxicity, not absorbed through skin	Metal working fluids, paints, coatings and textiles	Euro Chlor	Often used with Sb ₂ O ₃
Dechlorane Plus®	Chlorinated cyclooctene	1560-88-9	White solid mp = 350 °C (decomp.) Vap. Press. negligible	Benzene ≈ 2.0 g / 100 g Methyl ethyl ketone ≈ 0.7 g / 100 g	Acute oral (rat) LD ₅₀ > 2500 mg/kg, Inhalation (rat) LC ₅₀ > 2250 mg/m ³ Skin (rabbit) LD ₅₀ > 2500 mg/kg	Nylon	Oxychem	Light stable. Degrades in soil under aerobic conditions
Phosphonates R ₁ PO(OR ₂)(OR ₃) Substituents can be the same or different	Phosphorus based	Variety of R groups, <i>e.g.</i> Dimethyl methyl (R ₁ =R ₂ =R ₃) 756-79-6	Varies, R ₁ =R ₂ =R ₃ =Me Clear liquid bp = 181 °C	-	Acute oral (rat) LD ₅₀ = 8210 mg/kg	Polyurethanes	Numerous, <i>e.g.</i> AKZO	Some issues around chronic toxicity
Halogenated phosphate esters	Combine halogen (usually chlorine) and phosphorus	Variety available, <i>e.g.</i> Tris(2-chloroethyl)phosphate 115-96-8	Liquid	Typically have low solubility in water, high solubility in hydrocarbon solvents	Varied	Metal working fluids, paints, coatings and textiles	AKZO (Fyrol range), Bayer, Clariant, Rhodia	Some halogenated phosphate esters undergoing risk assessment, <i>e.g.</i> Tris-(2-chloro-1-methylethyl)-phosphate.

Tris(tribromoneopentyl)phosphate (FR-370)	Brominated phosphate ester	19186-97-1	White powder, mp = 181 °C	Water (20 °C) ≈ 0.016 mg / l (practically insoluble), hexane & CH ₂ Cl ₂ ≈ 9.75 g / 100 g solvent	Acute oral (rat) LD ₅₀ > 5000 mg/kg Dermal (rabbit) LD ₅₀ > 2000 mg/kg	Polymers, <i>e.g.</i> polypropylene	Dead Sea Bromine Group	High UV stability, does not require Sb ₂ O ₃ synergist
Trialkyl phosphate esters	Many examples, <i>e.g.</i> Reomol [®] TOP, trioctyl phosphate	78422	Liquids, generally low vapour pressure. Reomol [®] TOP clear liquid, bp = 215 °C, 4 mm Hg	High solubility in organic solvents, solubility in water varies. For Reomol [®] TOP < 0.1 % in water at 25 °C	Acute oral (rat) LD ₅₀ > 40,000 mg/kg Dermal (rabbit) LD ₅₀ > 20,000 mg/kg	Various polymers	Various, <i>e.g.</i> Reomol [®] TOP from Great Lakes	Reomol [®] TOP reported to improve fungal resistance of plastics
Triaryl phosphate esters	Many examples, <i>e.g.</i> Reofos [®] 65, Isoproylated triaryl phosphate	68937-41-7	Clear liquid	Completely soluble in organic solvents such as toluene, methanol. Insoluble in water	Acute oral (rat) LD ₅₀ > 5000 mg/kg Dermal (rabbit) LD ₅₀ > 2000 mg/kg	Various polymers, cellulosic resins, PF resins	Great Lakes	Can contain triphenyl phosphate
Reofos [®] RDP	Biphosphate-ester of resorcinol. Other examples available from AKZO	57583-54-7	Clear liquid	High solubility in organic solvents, insoluble in water	Acute oral (rat) LD ₅₀ > 5000 mg/kg Dermal (rabbit) LD ₅₀ > 2000 mg/kg	Various polymers	Great Lakes	Proprietary product. Offers improved flame retardance and lower volatility than conventional triaryl phosphate esters

7. PREVIOUS STUDIES OF COMBINED FIRE RETARDANT / PRESERVATIVE SYSTEMS

Somewhat surprisingly, there are relatively few studies on the fire performance and durability of wood that has been treated with combinations of commercial fire retardants and preservatives. In their review from 1992, White and Sweet state that '*successful exterior use of a combined fire retardant / preservative treatment has yet to be developed*'.⁷⁹ They cite formulation of fire retardant and preservative as being the major barrier to such a development.

LeVan and DeGroot investigated combining preservatives with leach resistant fire retardants to treat wood in a one step process.^{80,81} They looked at a number of systems and found that the most effective combinations consisted of fire retardants such as urea, dicyandiamide, phosphoric acid and formaldehyde (UDPF), melamine, dicyandiamide, phosphoric acid and formaldehyde (MDPF), or dicyandiamide, phosphoric acid and formaldehyde (DPF) with preservatives such as didecyldimethylammonium chloride (DDAC) or a combination of the DDAC with 3-iodo-2-propynyl-butyl carbamate (IPBC). UDPF, MDPF and the combination of DDAC with IPBC are covered by the patent.

There are a considerable number of reports that describe the treatment of timber with some fire retardant system that contains boric acid, then re-treating the timber with another agent to improve its permanence in wood. Wood strips were treated by Ishikawa and Adachi with a barium chloride and boric acid solution.⁸² The wood was then impregnated with a diammonium phosphate and boric acid solution and finally bonded together with a water-resistant adhesive. Ishikawa and Adachi claimed the resulting product had good fire performance and was termite resistant. Double treatments may in practice be too expensive to commercialise.

Thompson treated wood with a one step system using a combination of boron compounds, urea, magnesium chloride, ammonium polyphosphate, ammonium thiosulfate and triethylamine.⁸³ The inorganic salts were encapsulated by a water-based acrylic resin and carried into the wood during treatment. Once the water had evaporated, the inorganic salts were retained in the treated wood and were resistant to leaching or being washed out. The compounds, however, need to be mixed in specific sequences to avoid coagulation.

⁷⁹ White, R. H. and Sweet, M. S. (1992). *Flame retardancy of wood: Present status, recent problems and future fields*. Recent advances in flame retardancy of polymeric materials: Proceedings of 3rd annual BCC conference on flame retardance, Stamford, CT. Business Communications Company Inc., ed. M. Lewin, pp. 250-257.

⁸⁰ LeVan, S. L. and DeGroot, R. C. (1993). *One step process for imparting decay resistance and fire retardancy to wood products*. United States Patent No. 5,185,214.

⁸¹ Sweet, M. S., LeVan, S. L., Tran, H. C., and DeGroot, R. C. (1996). *Fire performance of wood treated with combined fire-retardant and preservative systems*. FPL-RP-545. USDA Forest Products Laboratory, Madison, WI. pp. 10.

⁸² Ishikawa, H. and Adachi, A. (1991). *Modified wood containing fireproofing agent for exterior wood*. Japan Patent No. 3-110103.

⁸³ Thompson, D. C. (1991). *Weather resistant, fire retardant preservative and protective compositions for the treatment of wood and cellulosic products*. United States Patent No. 5,151,127.

Inorganic boron containing compounds impart fungicidal, insecticidal and fire retardant properties to wood products. Since inorganic boron compounds are readily soluble in water, exposure to atmospheric moisture can cause leaching of the boron compounds. Schubert and Manning disclosed that aqueous compositions of boron compounds in and with zinc zirconium salts imparted wood preservative qualities to treated wood as well as protection against fire, fungi and termites.⁸⁴ Schubert disclosed that the zirconium borate compositions were resistant to leaching.

Basson and Conradie impregnated wood with a combination of fire retardant and preservative.⁸⁵ The fire retardant was formulated as an aqueous solution containing urea, phosphoric acid and ethanol and the preservative was formulated as a dry salts mixture of boric acid and borax pentahydrate. The borate salts were dissolved in water before the aqueous fire retardant solution was added. The wood was treated by pressure impregnation. The treated wood was then close-stacked and completely covered to ensure that the wood moisture was retained for a period of time so that the required depth of penetration of the active ingredients into the timber could be achieved by diffusion.

Lopez treated wood with a stable, non-corrosive preservative composition that imparted fire, insect and fungus resistant qualities to wood products.⁸⁶ The treatment composition comprised mixing a fire retardant agent containing a source of boron, such as boric acid or the water soluble salts of boric acid (preferably disodium octaborate tetrahydrate), with a melamine binder resin *i.e.* any amino resin made from melamine and formaldehyde, and a urea casein activator resin that can be any liquid urea formaldehyde resin. After treatment the wood was dried in ambient air and not with heat until the hygroscopic moisture content was at or below 19%.

Juneja developed a leach resistant fire retardant consisting of urea, dicyandiamide, phosphoric acid and formaldehyde (UDPF) in a molar ratio of 1:3:4:8.⁸⁷ Juneja and Shields found that despite the fact that UDPF was heat cured to fix the resin in the wood, leaching was still a problem.⁸⁸ Juneja and Calve examined the effect of curing on the leachability of UDPF and found that even at very high curing temperatures (150 °C), > 70% of the phosphorus and > 50% of the nitrogen impregnated in the wood was lost as a result of leaching.⁸⁹ A major problem was that the phosphoric acid was not bound in the polymer itself, but was only associated with the polymer through ionic bonding.

Advances have been made in the area of deposition of insoluble inorganic compounds. Wood has been treated with a cation containing solution and then an

⁸⁴ Schubert, D. M. and Manning, M. J. (1997). *Compositions and methods for preserving wood products*. United States Patent No. 5,612,094.

⁸⁵ Basson, G.R. and Conradie, W.E. (2001). *Preservative and fire retardant composition and combination and process*. United States Patent No. 6,319,431.

⁸⁶ Lopez, R. A. (2003). *Fire retardant compositions and methods for preserving wood products*. United States Patent No. 6,620,349.

⁸⁷ Juneja, S. C. (1972). *Urea based fire retardant formulations and products*. Canada Patent No. 917334.

⁸⁸ Juneja, S. C. and J.K. Shields (1973). *Increased fungal resistance of wood treated with modified urea-based fire-retardant resins*. *Forest Products Journal*. **23**, 47-49.

⁸⁹ Juneja, S. C. and Calve, L. (1977). *Curing and fixation of amino-resin fire retardants*. *Journal of Fire Retardant Chemistry*. **4**, 235-240.

anion containing solution that forms insoluble products that precipitate in the solid wood. Yasuda and Ota treated wood with a calcium chloride solution and then a sodium hydroxide solution to form insoluble calcium hydroxide.⁹⁰ The wood was then treated with sodium aluminate and sodium sulfate to precipitate the mineral known as ettringite ($\text{Ca}_{12}\text{Al}_{24}(\text{OH})_{24}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$). This precipitate is insoluble and the authors claimed that the treated wood showed good resistance to insects and had good fire performance.

Vinden and Romero developed a process whereby the wood surface was treated by applying a boron-based preservative that reacts with the moisture in the wood to form a boron compound and alcohol.⁹¹ The wood was then subjected to a moisture free and enclosed environment in order for the preservative and the alcohol by-product to be absorbed into the wood structure. The treatment imparted fire resistant properties to the wood as well as protection from termite attack and fungal decay. The treatment was not, however, leach resistant.

In personal communications with M. Lewin, it was suggested that perhaps the most effective way to fire retard wood is by the use of halogens, and in particular he referred to the bromine-bromate process originally developed by the Dead Sea Bromine Corporation. This process involves impregnation of the halogen into the timber as a reactive, thus providing permanent fire retardancy as well as ensuring decay resistance.⁹²

In personal communications with a representative from Osmose, it was suggested that many phosphorus-based fire retardants were not necessarily appropriate for external use because they degraded to phosphoric acid and in this form had an adverse (strong) effect on the timber strength. There are currently some lawsuits in the USA regarding this issue.⁹³

In personal communications with a representative of the Borax Corporation, it was suggested that boron-based compounds were not ideal because of their relatively strong propensity to be leached from the timber. He did suggest that one method of utilising boron may be via an in-situ preparation of zinc borate within the timber pores. However, this process may have some hazardous aspects.⁹⁴

⁹⁰ Yasuda, H. and Ota, Y. (1987). *Improved wood*. Japan Patent No. 62-116103.

⁹¹ Vinden, P. and Romero, F. J. (2002). *Process for treating wood to protect from fungal decay, by applying boron based preservative and subjecting to moisture free environment to produce boron and alcohol by-product on reaction with moisture in wood*. World Patent No. 2002/102560.

⁹² Menachem Lewin, Polytechnic- New York (2004). BCC conference, Stamford CT.

⁹³ Douglas J Herdman – Wood Technologist – Research Division – Osmose – Buffalo (2004). BCC conference, Stamford CT.

⁹⁴ Kelvin K Shen – Fire retardant Industry Technical Manager – Luzenac/Borax – Huntington Beach CA (2004). BCC conference, Stamford CT.

8. CONCLUSIONS

The following conclusions can be drawn from this review:

- There are a significant number of commercially available fire retardants that meet at least some of the designated selection criteria.
- There is a notable absence of data that quantify the required loadings of these fire retardants for timber to meet performance standards for fire control for the types of timber we propose to examine in this work.
- Similarly, there is a lack of data relating to the resistance of these fire retardants to weathering when impregnated into timber. These systems have, however, been chosen for their low solubility in water. Some qualitative observations have been made as to the stability of these fire retardants when exposed to ultraviolet radiation.
- Many of the organic fire retardants should be readily co-formulated with light organic solvent preservatives.
- For water-borne preservatives, oil-in-water emulsions would, in principle, be the most appropriate formulation for organo-soluble fire retardants.
- The standard accelerated weathering regime for fire retardants (ASTM D-2898) is likely to be more severe than that used for preservatives. There do not appear to be any reports of the performance (durability) of preservative treated wood that has been weathered according to this procedure.
- It remains to be established if any of the existing preservative systems can withstand the harsh accelerated weathering regime employed for exterior fire retardants (ASTMD-2898).
- There is no prior art to suggest that the approach proposed for this project, as outlined in the original proposal, does not have merit.
- The commercial viability of the approach adopted in this project will only become apparent with knowledge of fire retardant loadings required in timber to meet performance standards, which, when coupled with the unit cost, will enable the economics of the treatment to be estimated.
- The primary tool for determining if the FR treatment is successful or not will be the cone calorimeter.

APPENDIX A

Methods of testing for fire retardant efficacy

Methods used for the determination of the efficiency of fire retardants for wood include:

Thermal analytical techniques such as TGA, DTA and DSC, which give basic information on the mechanism of pyrolysis and combustion as well as data on the effect of fire retardants and different materials.

Oxygen index testing, where it is possible to determine the minimum concentration of oxygen necessary to sustain combustion of a material.

Direct burning techniques such as cone calorimetry measurements, where it is possible to determine a range of parameters including propensity to ignition, efficiency of combustion, rate of heat release, amount and quality of smoke released on combustion.

The identity (and quantity) of gases released from the burning of the timber can be determined directly from the cone calorimetry method by inclusion of an FTIR spectrometer. Knowledge of the gases released enables the toxicity of the combustion gases and their potential environmental impact to be determined, as well as allowing deductions to be made about the mechanism by which the fire retardant is operating.

In a paper recently presented by White⁹⁵, it was suggested that the cone calorimeter is the fundamental tool for examining flammability / fire retardance of timber because of the quality and amount of data which is able to be collected.

⁹⁵Robert H. White and Mark A. Dietenberger – Forest Products Laboratory – Madison, WI (2004). BCC conference, Stamford CT.

APPENDIX B

Fire retardant manufacturers

Company	Classes of fire retardants ^a	Address
AKZO Nobel Chemicals	P, Br, N	www.fyrol.com www.phosphoruschemicals.com
Albermarle	Br, P	www.albermarle.com
Ameribrom Inc.	Br	Part of Dead Sea Bromine Group
Atochem	Br, N	www.atofina.com/groupe/gb/f_elf_2.cfm
Bayer	P	www.rubber.bayer.com
Budenheim Iberica	AP, P, N	www.budenheim.es
Ceca	Br, P	www.ceca.fr/ceca/gb/f_elf.cfm
Ciba	P, N	www.cibasc.com
Clariant	AP, P	www.additives.clariant.com
Dead Sea Bromine Group	Br	www.dsbgr.com
Ethyl Corporation	Br	www.ethyl.com/EthylHome.htm
Eurobrom	Br	Part of Dead Sea Bromine Group
Euro Chlor	Cl	www.eurochlor.org
Ferro	P	www.ferro.com
Great Lakes Chemicals	Br, P	pa.greatlakes.com
Matsunaga	Br	-
Nippo	Br	-
Oxychem	Cl	www.oxychem.com
Potasse et Produit Chimiques	Br	-
Rhodia	AP, P	Rhodia.com
Riedal de Haen	Br	
Tosoh	Br	-
Warwick Chemicals	Br	-

^a AP = Ammonium phosphate, Br = Brominated FR, Cl = Chlorinated FR, N = Nitrogen-based FR, P = Phosphorus-based FR (but not simple ammonium phosphates)