## PROVIDING TERMITE AND FUNGAL PROTECTION TO WAFERBOARD USING NOVEL TERMITICIDES AND FUNGICIDE

By

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#### Abstract

The compatibility of eight liquid PF resins and one pMDI-resin with three termiticides and two fungicides, provided by Dr. Wolman GmbH, was evaluated by measuring changes in gelation time and viscosity. The results indicate that the termiticides are generally compatible with the phenolic resins and the pMDI-resin. The fungicides were only compatible with two phenolic resins and neither was compatible with the pMDI-resin. Based on these results it was concluded that the three termiticides would be fully compatible with the two liquid phenolic based resins, BB7028, and GP70CR66, and the pMDI-resin and can be incorporated into these resins as a glue-line additive during waferboard manufacture. The fungicides were found not to be compatible in the resins and thus would have to be applied onto the strands separately from the resins. Even then they may cause some interference with the glue curing.

The fungicide, formulated with both KHDO and fenpropimorph, were sprayed onto strands during the manufacture of the waferboard at the same time as the resin but using a separate spray line, enhanced the waferboard durability against both brown and white rot fungi. The mass losses of the test blocks cut from the boards manufactured with different concentrations of fungicide and exposed to four decay fungi, suggested that, 0.44 % KHDO and fenpropimorph (based on the oven dry weight of the strands) provided the same protection from two white rot (*T. versicolor* and *P. ostreatus*) and two brown rot fungi (*G trabeum* and *P. placenta*) attacks as waferboard which incorporated 0.83 % zinc borate. The fungicide was most effective against the brown rot fungi, while a toxic threshold of

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0.29 % KHDO and fenpropimorph was observed. For the two white rot fungi the toxic threshold was determined to be 0.44 % KHDO and fenpropimorph.

At all concentrations the fungicide had no adverse effect on the static bending strength of the waferboard, but caused a slight (17%) loss in internal bond strength. The mechanical strength loss of samples heeded in this way was much lower than the mechanical strength loss of commercial 1% zinc borate treated boards tested tested in the same manner. Based on data generated in this study and commercial information on untreated waferboard, 0.83 % zinc borate caused a 7.13% loss in MOE, a 14.98% loss in MOR and a 21% loss in IB strength.

Based on all of the results of decay testing and mechanical strength evaluation, it may be concluded that the fungicide, at 0.44 % active ingredient, could be sprayed onto furnish simultaneously for the GP70CR66 and GP265C54 PF-resins for manufacturing waferboard to improve its fungal resistance without causing significant reduction in strength.

The three termiticides, LP 15406A, LP 15406B, and LP 15447, were sprayed onto the furnish as an additive by dissolving in the BB7028, and GP70CR66 liquid PF-resins. None of the three termiticides had any significant effect on IB strength. However, static bending strength was affected. LP 15406A did not negatively affect MOE, but did cause a slight reduction in the mean value of the MOR. However, this change was not statistically significant. LP 15406B had no affect on the waferboard MOR, but significantly increased the MOE; a similar trend was also noted for the LP 15447. These results suggest that all

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three termiticides can be considered as suitable additives to liquid resins during the manufacture of termite resistant boards, over the range of concentrations evaluated in this research.

Based on the results for the pMDI-resin waferboard which incorporated the three termiticides, the mechanical strength data indicates that, LP 15406B, with 0.0073 % chlorfenapyr content in waferboard is the most promising termiticide because it had no effect on the mechanical properties of the waferboard. LP 15406A, with 0.0052 % bifenthrin content in waferboard, could be added to pMDI-resin. However, more research is needed since it did cause a 12 % mean reduction in the internal bond strength, although this reduction was found to be not statistically significant. LP 15447, with 0.0052 % 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(1R,S)-(trifluoromethyl)sulfinyl]-1H-pyrazol-3-carbonitrile caused a 37 % reduction in the mean internal bond strength and therefore is not suitable for addition to pMDI in waferboard manufacture.

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## **List of Abbreviations**

ACA	ammoniacal copper arsenate	
ACQ	alkaline copper quat	
CCA	chromated copper arsenate	
DDAC	didecyldimethylammonium chloride	
DOT	disodium octaborate tetrahydrate	
DSC	differential scanning calorimeter	
FST	formosan subterranean termites	
IB	internal bond	
IPBC	3-Iodo-2-propynyl butyl carbamate	
KHDO	N-cyclohexyldiazeniumdioxy potassium	
MOE	modulus of elasticity	
MOR	modulus of rupture	
MSDS	Material Safety Data Sheet	
OSB	oriented strandboard	
РСР	pentachlorophenol	
PF resin	phenol formaldehyde resin	
pMDI-resin	polymeric diphenylmethane diisocyanate resin	
TGA	thermogravimetric analysis	
ZnB	zinc borate	

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#### Chapter 1

#### Background

#### **1.1 Introduction**

Waferboard is a wood composite typically made from strands, which may be oriented to produce greater board strength in which case it is known as Oriented Strand Board (OSB). The strands are prepared from small dimension timber, for example trees harvested during plantation thinning, or branches, as well as timber cut from fast-growing species, such as eucalyptus, and aspen. Because of its use of lower quality, less expensive wood supply and also the fact that recovery of fibre in the stranding process is high and its properties are similar to plywood, it has replaced plywood for many sheathing uses (Howard, 2001). It is widely used for roof, wall, and floor sheathing in residential construction in North America. Wood strands are coated with either phenol formaldehyde (PF) resin or polymeric diphenylmethane diisocyanate (pMDI) resin, and wax, then hot-pressed to produce the waferboard.

However, when used outdoors or in applications where the material may be exposed to high humidity or continual contact with water, untreated waferboard, like other untreated wood products, is susceptible to attack by decay fungi and insects. The principal reason is that neither the phenolic resin nor p-MDI once cured provides any biocidal efficacy. Although the free components of phenol and formaldehyde have been known to enhance wood durability, particularly in laboratory tests, once the polymerization has taken place and any free residual chemical has been lost from the composite, the durability is the same

as the untreated wood (Schmidt et al., 1978; Motoki et al., 1985). In practice, untreated waferboard bonded with PF-resin is susceptible to fungi and insect attack, since leaching of non-condensed phenol occurs. In addition, the release of formaldehyde from composite products is not desirable, due to harmful effects on humans. It is therefore important that all residual chemicals have been lost from waferboard prior to its use. The problems of termite attack, especially Formosan subterranean termite (FST) damage to wooden building in the southern USA and Hawaii, is increasing. It has been estimated that the FST causes some \$300 million damage annually in the Greater New Orleans Metropolitan Area (McClain, 1999). In 1993, the Wood Protection Council of the National Institute of Building Sciences (NIBS) estimated the annual cost of replacing wood damaged by the FST to be \$2 billion, up from \$750 million in 1988 (Ring, 1999). There are also increasing problems of decay, especially brown rot and white rot in untreated wall construction in condominiums on the west coast of North America, which are causing millions of dollars in repairs annually.

With the increasing problems of termite attack and fungal decay of untreated wafer board and OSB in residential construction, it is necessary for researchers to develop effective preservatives and procedures for protecting waferboard against biodeterioration. The main wood preservatives used in North America are chromated copper arsenate (CCA), pentachlorophenol, and creosote. Of these, only the waterborne CCA could be considered for treatment of the waferboard. However, as researchers have shown (Hall et al., 1979 and 1982) the pressure treatment of waferboard with waterborne preservatives after manufacture leads to significant swelling problems, as well as added cost due to the need to

redry the board. Therefore, even treatment with the newer environmentally friendly preservatives, such as alkaline copper quat (ACQ) will not overcome these two difficulties. An alternative approach may be to incorporate the wood preservative into the resin or board, during its manufacture (Hall et al., 1982). This would reduce the cost of the final treated waferboard and also provide a superior product in which the waferboard has a constant loading of preservative throughout its thickness rather than the "shell" treatment commonly present in treated solid wood products. The preservative-containing waferboard can then be cut into smaller compounds without loss of biological resistance. Another added benefit is that the need to handle wood preservatives is limited to a single manufacturing site.

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### **1.2 Objectives**

The principal objective of the current research was to examine the feasibility of incorporating selected industrially approved novel termiticides or fungicides supplied by Dr. Wolman GmbH, Germany, into PF- or pMDI-resin during waferboard manufacture, and spray-treating strands with the mixture during board manufacture. The waferboard was manufactured by Weyerhaeuser Company using data generated from the prior phase of the project. This main objective was supported by several sub-objectives:

- 1. Investigate the compatibility of the selected novel termiticides and fungicides with different liquid (core and surface) PF-resins, and with a pMDI-resin.
- 2. Assess the effect of the termiticides and fungicides on the mechanical properties of finished waferboard.
- 3. Assess the decay resistance of the fungicide treated waferboard against the selected white rot and brown rot fungi species.

### **Chapter 2**

#### **Literature Review**

During the past decade a relatively large number of wood preservatives have been identified as potential wood preservatives (Table 2.1), and since a high proportion are organic compounds, they also could be useful in protecting composite products. While post treatment of waferboard can be done with both organic and inorganic wood preservatives, the inclusion of the preservative mixed in with the liquid resin would favor on organic chemical. Wood preservatives can be incorporated into waferboard in three ways:

- 1. Pretreatment-treatment of the flakes before gluing by spraying first with a preservative solution or blending the flakes with a powdered wood preservative.
- 2. Glue-line treatment-mixing the wood preservatives with the adhesive, which is subsequently applied to the flakes in the blender.
- 3. Spraying wood preservative solution on the flakes simultaneously as adhesives.

Currently there are no published reports on the simultaneous application of wood preservatives and resin using separate spray systems in the published literature. The best method to use for a particular application will depend on the properties of the wood preservative and the adhesive. These include the heat stability of the wood preservative especially if it is an organic preservative, its diffusivity during consolidation, the presence of emulsifiers in the formulated wood preservative, the interaction of any additives with the adhesive, the method of incorporation, and the state of the additive (solid or liquid). Not all wood preservatives can be adapted to all these strategies to protect waferboard. Treating wood furnish prior to bonding (pre-treatment), and addition of preservatives to resin (glue-line treatment), are options which must be experimentally confirmed for a given composite-preservative combination. For example, the pH of the preservative may affect the resin cure, and thus be incompatible with the resin. It is possible that the hydroxyl groups present in wood that are necessary for resin bonding may be blocked by the pre-treatment (Schmidt 1983). The preservative may not withstand the conditions of pressing. Any such potential deleterious effects by the preservative on the bonding property of adhesive or mechanical properties of the waferboard are likely to prevent its use. The detailed effects of the selected preservative treatments on adhesive bonding properties, mechanical properties of manufactured waferboards, and preservatives' efficacy against fungi will be discussed in the following sections.

Principal biocidal action		Combined	
Fungicide	Insecticide	Fungicide/insecticide	
DDAC	Chlordane	Copper naphthenate	
DDAC + Cu	Fenvalerate	CCA	
DDAC+carbamate	Fenitrothion	Trimethyl borate	
Azaconazole	Pirimiphos-methyl	Sodium fluoride	
Tebuconazole		Ammonium hydrogen bifluoride	
IPBC		Borates	
Cu-8		Chromated copper fluorine	
PCP		Copper + borates	

Table 2.1 Wood preservatives used for composite protection

#### 2.1 Pre-treatment

The limitations placed on pre-treatment preservatives of waferboard are severe. In particular, preservatives must not interfere with the adhesive bonding properties, deteriorate the static bending properties of manufactured waferboard, or reduce the preservative efficacy against fungi or termites. Successful pre-treatment of strands prior to gluing can be achieved by the diffusion of aqueous solutions of inorganic and organic wood preservatives or the addition of powdered wood preservatives.

#### 2.1.1 Interaction with the adhesive

The most obvious way in which a preservative additive can have a detrimental effect on the properties of the waferboard is through interference with bond formation. An excellent example of this is the interaction of water-soluble borates with phenol-formaldehyde (PF) resins. Bond strengths of PF-bonded waferboard containing "biologically effective" levels of sodium borates or boric acid are unacceptably low (Laks et al, 1988). This is most likely due to gelling of the phenolic adhesive by the borate before the glue droplet can transfer to, wet, and penetrate into wood on the adjacent strands (Vick et al, 1990).

Another example of this is the interaction of chromated copper arsenate (CCA) with PF-resin. Pre-treatment of aspen (*Populus tremuloidus*) flakes with CCA can lead to a large loss in the internal bonding strength (IB) of PF resin-bonded waferboard. This observation was found both for the aged according to ASTM D1037-99 or unaged waferboard (Table 2). However, an exception was treatment of flakes with ammoniacal copper arsenate (ACA)

where the IB strength was not significantly reduced. This difference in the interaction of the preservative with the resin is mainly due to the fact that ACA solutions are basic and CCA solutions are acidic, and this influences PF resin bonding reaction kinetics. In addition, the fixation of CCA involves the reaction of  $Cr^{6+}$  with carbon-carbon double bonds and the phenolic protons of lignin, which partially blocks the reaction of the active groups of wood with PF-resin (Cameron and Pizzi, 1985). Other studies (Bryant, 1968; Thompson, 1961) also found that various chromium-complex solutions, such as acid copper chromate and chromated zinc chloride, impaired the glue-bond strength of phenolic adhesives.

Pesin	Treatment	Treatment	
type	$(ka/m^3)$	Non-aged	After aging
type	(kg/m)	(kPa)	(kPa)
	0.0	606.74	186.16
Parala	3.2 ACA	572.26	179.26
DE rosin	6.4 ACA	551.58	172.37
r r tesm	3.2 CCA	406.79	48.28
	6.4 CCA	317.16	41.37
	0.0	475.74	82.74
Nevelae	3.2 ACA	413.68	144.79
Novolac DE regin	6.4 ACA	393.00	186.16
rr tesin	3.2 CCA	303.37	103.42
	6.4 CCA	234.42	62.05

Table 2.2 IB strength of PF-bonded waferboard.(Boggio and Gertjejansen, 1982)

The available evidence generally suggests that the pMDI adhesives are less prone to interference problems when the strands are pretreated with an aqueous solution of an inorganic salt, than PF resins. For example, borates and CCA pretreated strands exhibited incompatibility with PF resin, but showed better compatibility with pMDI-resin (Laks and Palardy, 1993). Borates such as disodium octaborate tetrahydrate (DOT) have been studied for use in pre-treatment of strands prior to pMDI application. The results showed that borates can be successfully used for pre-treating wafer for pMDI-resin bonded waferboard (Table 2.3). Data presented in Table 2.3 shows that CCA does not interfere with the bonding strength produced by pMDI-resin, since the IB of treated waferboard (434.37 or 503.32 kPa) was equal to or greater than the corresponding value for the control samples (434.37 kPa) (Mengeloglu and Gardner, 2000; Laks and Bruce, 1988).

Table 2.3 IB strength of DOT, CCA-treated waferboard bonded with pMDI-resin

Treatment	IB	Treatment	IB
(%)	(kPa)	(%)	(kPa)
control	1,585.79	control (2 %pMDI)	434.37
0.5 DOT	1,716.79	0.4 CCA (2 %pMDI)	434.37
5.0 DOT	2,061.53	0.4 CCA (2.5 %pMDI)	503.32

One way to minimize the gelling effect of inorganic wood preservatives on PF resin is to change their state of application from liquid to powder. A patent issued to MacMillan Bloedel Ltd (Knudson and Gnatowski, 1989) claims that powdered zinc borate (low water solubility) and anhydrous borax (slow rate of solubilization) can be successfully incorporated into a particleboard bonded with a powdered PF adhesive.

Another solution is to employ the mixed solution of inorganic and organic wood preservatives. Effective treatment with the above formulations is indicated in work by Vick *et al.* (1990), and Vick (1990). These include copper naphthenate, copper octanoate, and zinc naphthenate.

As mentioned earlier, the water-soluble borates have a strong negative effect on the bonding performance of PF resin, but, in contrast, there was no adverse effect on pMDI-resin. Some researchers have tried to incorporate powdered borates into strands prior to the addition of pMDI-resin. Laks and Mark (1995) reported that, DOT and zinc borate (ZnB) at a loading of less than 0.5 % BAE caused minimal loss of IB strength (Figure 2.1). The IB of DOT waferboards remains reasonably constant as the additive content increased, while there was a decrease in IB as the ZnB content increased.

In looking at the effect of inorganic wood preservatives' pretreatment on the bonding property of waferboard, dry powdered preservatives demonstrate better compatibility with PF resin while the pretreatment of the strands with inorganic aqueous solutions show better compatibility with pMDI-resin. To minimize the gelling effect caused by the pretreatment of inorganic wood preservative solution on PF resin, they may be formulated with organic wood preservatives to reduce their content in the formulation.





#### 2.1.2 Interference with the static bending strength or shear strength

Modulus of elasticity (MOE) and modulus of rupture (MOR) usually express static mechanical properties (stiffness and strength) of manufactured wood composites. The shear strength is also significant for panels (Winandy and River, 1986). Preservative treatments generally affect the static bending strength of waferboards or the shear strength of veneer panels. The effects of preservative treatment on static bending strength or the shear strength appear to be directly related to resin type, (i.e. PF- and pMDI- resin), preservative type, (i.e. inorganic and organic), and the form of preservative application, (i.e. powder and liquid).

As described above, solutions of borates or chromium-based preservatives are not compatible with PF resin. Their treatment resulted in a significant reduction in IB. As to their effect on the static bending strength, the situation is different. Their treatment reduced MOR, but produced no negative effect on MOE. The reduction in the MOR may be due to a bending strength loss in the wood itself and a problem in the bonding of the flakeboard as mentioned in Section 2.1.1. Ruddick *et al.*, (1991) observed a increased surface hardness in pine poles treated by CCA. The surface hardness would likely decrease the fracture toughness of the wood, which would decrease MOR. They attributed this to the reaction of chromium with the lignin and/or with cellulose (Ruddick *et al.*, 1994). Draganov (1968) also observed a similar embrittling and hardness tendency in borate diffusion-treated wafers. ACA caused minimal reduction of MOR of PF resin bonded wafer board, although ACA is compatibile with PF resin (Table 2.4) (Hall and Gertjejansen, 1979).

Treatment	MOR (MPa)		MOE (GPa)		
$(kg/m^3)$	Control	Treatment	Control	Treatment	
8.0 DOT	41.2	34.2	5.47	5.52	
6.4 ACA	26.0	24.3	4.89	5.67	
6.4 CCA	26.0	19.3	4.89	5.14	

Table 2.4. Mechanical properties of PF resin bonded aspen waferboard (Hall and Gertjejansen, 1979)

In the case of the impact of inorganic wood preservative' pretreatment on bonding properties, dry powdered preservatives, especially zinc borate (ZnB), demonstrate better compatibility with PF resin. Sean *et al.* (1999) reported that ZnB at a loading of less than 1.17 % based on oven-dry furnish weight caused a slight, but not significant reduction of MOE and MOR of PF bonded OSB. This adverse effect on bonding strength of PF resin can be reduced by adding an organic flowing agent containing hydroxyl groups such as polyethylene glycol (Lee et al, 2001) or applying additional PF resin (Laks and Palardy, 1993).

As recommended before, the gelling effect of the solution of inorganic wood preservatives on PF resin can be minimized by the addition of organic wood preservatives. The shear strength results (Table 2.5) further confirmed the successful marriage between inorganic and organic wood preservatives, for examples, copper naphthenate, copper octanoate, and zinc naphthenate (Vick *et al.*, 1990; Vick, 1990).

Preservative	Retention $(1 \times 10^{3})$	Shear st asse	Shear strength (kPa) for three assembly times (min.)		
	(kg/m)	10	15	20	
Untreated control	0.0	4792.0	4240.4	4385.2	
Copper naphthenate	3.2	2530.5	3006.2	3171.7	
	6.4	3089.0	2902.8	3144.1	
	10.8	3040.7	2806.3	3164.8	
Copper octanoate	3.2	3764.7	3847.4	3964.6	
	6.4	3392.3	3916.4 ·	3599.2	
·	10.8	3613.0	3578:5	3592.3	
Zinc naphthenate	3.2	3468.2	3633.7	4033.6	
	6.4	3537.1	3330.3	3902.6	
	10.8	3123.4	3613.0	2254.7	

Table 2.5 Mean shear strengths of PF bonded preservative treated aspen plywood(Reproduced from Vick *et al.*, 1990)

As mentioned earlier, compared to PF resin, pMDI-resin shows better compatibility with water-borne inorganic preservatives, especially borates and chromates (Deppe, 1971). Table 2.6 indicated that borates caused significant reduction of MOE, MOR of pMDI bonded particleboard.

Table 2.6 Mechanical properties of preservative-treated pMDI-resin bonded particleboard(Deppe, 1971)

Resin type	Treatment	MOR (kPa)		MOE (kPa)	
	$(kg/m^3)$	Control	Treatment	Control	Treatment
pMDI-resin	8.0 DOT	65,162.35	55,130.47	7,418,538.22	6,475,693.95

In looking at pre-treatment, the treatment with dry powdered preservatives or an aqueous solution or wax emulsion of organic wood preservatives could be better choices for waferboard bonded with PF resin where inclusion of a water-borne inorganic preservative treatment is considered to be unacceptable. Based on current literature data of pMDI bonded waferboard, the pretreatment of the strands with an aqueous solution of an

inorganic preservative would be more successful than powdered inorganic wood preservative.

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#### **2.2 Glue-line treatment**

Incorporating wood preservatives with the wax is also a good choice, however the wax distribution is often not as good as that of the glue. This in turn may also influence the effectiveness of the wood preservatives. In contrast, glue-line treatment with wood preservatives has been more widely researched.

A general disadvantage of water-soluble preservatives for pre-treatment is that the water needed for dissolving the salts involves a second drying process, which limits its widespread industrial application and further research. Glue-line treatment does not involve the redrying problem. By contrast, glue-line treatment is a simpler, more economical way to protect waferboard with wood preservatives. However, the performance requirements of such preservatives are extremely demanding. The formulation of an adhesive is a finely balanced system. Minimal change of pH, viscosity, molecular weight of adhesive from the induction of preservatives may result in its bonding failure. The effects of wood preservative glue-treatment on bonding properties of adhesive and static bending strength of wood composites are closely related to wood preservative type: oil-borne, water-borne, and powdered preservatives.

#### 2.2.1 Oil-borne preservatives

Pentachlorophenol (PCP) was the first glue-line, oil-borne preservative widely used for the protection of particleboard in the European community as early as 1950s (Becker 1959; Stolley 1956; Klauditz and Stolley 1954). However, the permanence of this compound is limited (Monsalud 1964). The studies by Deppe and Petrowitz (1969)

indicated that a major amount of the PCP added to the glue evaporates during the hot pressing process. As a result, the residual concentration may be insufficient for the level of protection.

Modern organic wood preservatives are designed to be environmentally friendly, leach-resistant, water-proof, and efficient fungicidal wood preservatives. Some of them are widely used as glue-line additives. For example, carbamates including fenobcurb, carbaryl, and propoxur are recommended for use as commercial glue-line additives in plywood. Currently, chloropyrifos is still used as a PF glue-line additive to produce plywood industrially in North America and India although Laks et al., (1996) reported chlorpyrifos may not be suitable for treating furnish before hot pressing, because 40 % of the chlorpyrifos will be lost during hot-pressing.

Dimri et al., (1998) noted that the incorporation of 1 % chlorpyrifos based on oven-dry furnish in PF resin did not adversely affect the glue shear strength of plywood. Some studies in the USA revealed that water-based emulsions of 2-(thiocyanomethylthio)benzothiazole, chloronapthalene and tributyltin oxide can be added to liquid resole PF resin for making particleboard, since they did not cause an significantly adverse effect on mechanical strength of particleboard and their antifungal ability was not impaired (Hall and Gertjejansen 1982).

#### 2.2.2 Water-borne preservatives

Usually copper is formulated with co-biocides when designing a wood preservative

based on amine or ammonia aqueous solutions because when used alone, copper has limited protection against termites and copper-tolerant fungi. Aqueous copper and fluoride solution and amine-based copper naphthenate are examples of copper-cobiocide complex preservatives. When the aqueous copper and fluoride solution was incorporated into a PF resin, it caused at least a 17 % loss of IB, and a 38 % increase in thickness. For unaged waferboard, this treatment did not significantly affect either MOR or MOE. However, accelerated aging resulted in a 44 % reduction in MOR and at least a 16 % reduction in MOE (Hall et al., 1982). For amine-based copper naphthenate, the situation was opposite. The PF glue-line treatment at a loading of 0.1 % copper improved the IB by 10 %, the MOR by 15 %, and the MOE by 8 % without negative impact on thickness swelling. However, this glue-line treatment resulted in a small loss of fungicide efficacy (Schmidt 1991). This indicated that amine-based copper naphthenate seemed to be compatible with resole PF resin, in contrast to the incompatibility demonstrated by ammonia-based copper naphthenate with resole PF resin. The different compatibility between amine-based and ammonia-based copper naphthenate and PF-resin is probably due to the fact that ammonia based copper solutions can form ammonia copper wood complexes (Ruddick, 2002). The ammonia can function as a donor ligand and can not form sigma bonds to the copper. These are formed between copper and wood or the naphthenate. The copper can also form more stable complexes with ammonia and phenol. For ethanolamine the amine can form sigma bonds to the copper leaving less bonding available to naphthenate or wood or resin. So an ethanolamine solution is less likely to allow the copper to react with phenol than an

ammonia based solution (Ruddick, 2003).

#### 2.2.3 Powdered preservatives

Fungicide FNG containing copper and sulfur powder, the only dry powdered preservatives, was added to PF- and pMDI- resin. The results (Table 2.7) indicated that fungicide FNG at any loading caused significant reduction of the mechanical strength of aspen plywood and poor bonding of PF and pMDI-resin (Schmidt and Gertjejansen 1988).

Table 2.7 Strength properties of FNG-treated, PF or pMDI-resin bonded waferboard.

Resin type	Treatment	IB (kPa)		MOE (MPa)	
	$(kg/m^3)$	Control	Treatment	Control	Treatment
PF resin	1.6 FNG	611	597	5,910	5,410
pMDI-resin	1.6 FNG	363	310	4,520	3,970

It would seem that the use of dry powdered preservatives as glue-line additives will be difficult as they could interfere with the glue wood interaction by precipitating on the surface of the wood. They would also be difficult to include in any spray system.

In looking at the strategies to protect waferboards with preservatives, powdered preservatives such as ZB offer the fundamental change to pre-treatment of waferboards. In contrast, glue-line treatment is simpler, more economical and more easily implemented in existing plant and equipment. However, it is less suited to the use of inorganic salt-based preservative, or those having high or low pHs (Vick, 1990), as they can influence the curing and gelation of PF resin (Lee and Wu, 2001). Organic wood preservatives seem to be a better choice to solve both of these problems. An additional challenge will be to ensure

that the wood preservatives are compatible under all operating conditions in a waferboard plant. In addition, potential exists for losses of the wood preservative during the hot pressing process. This will also need to be investigated.

#### Chapter 3

# The compatibility of selected wood preservatives with eight phenol formaldehyde resins and one diphenylmethane diisocyanate resin

#### **3.1 Introduction**

Phenol formaldehyde (PF) and polymeric diphenylmethane diisocyanate (pMDI) resins are widely used as adhesives for wood composites. While pMDI is preferred for bonding the strands in the core of waferboard and agrofiber boards such as wheat straw, PF-resin is preferred for bonding the strands at the surface of waferboard. This preference for PF-resin at the surface and pMDI- resin in the core is partly because of the affinity of pMDI to bond well in metal oxides when used for bonding the face strands in wafer board. Special precautions must be taken to protect the platens of the press. The inclusion of pMDI for the core strands takes advantage of the more rapid curing of the pMDI-resin and reduces the energy and time needed for the hot pressing process. However, pMDI- resin is more expensive and is more moisture sensitive than PF-resin. As a result, a considerable amount of waferboard is still manufactured using PF-resin for bonding both the core and surface layers.

Although pMDI- resin reduces the thickness swelling of boards, neither pMDI- resin nor PF-resin enhances the durability of waferboard. To do this, wood preservatives must be used. They can either be applied after board manufacture, or during board manufacture as a pretreatment of the strands or as a component of the resin. However, if they are to be incorporated during board production, they must be compatible with the resin.

It is important to understand the sensitivity of the PF- and pMDI-resins not only to the wood preservatives, but also to any solvent or other components present in the wood preservative formulation. For example, it is known that pMDI- resin is sensitive to water, amines, alcohols, and strong bases, and if any of these chemicals are present in the wood preservative, they may affect the curing reaction. PF-resin has been observed to be sensitive to oxidizing agent such as hydrogen peroxide, as well as quaternary ammonium compounds such as didecyldimethylammonium chloride (DDAC), and if any of these chemicals are present in the wood preservative, they will accelerate the curing reaction.

The impact of adding wood preservatives with the resin during board manufacture can be determined by examining the resulting boards in terms of strength (MOR) and stiffness (MOE) and the internal bond strength (IB) (Winandy and River, 1986). However, it is possible to estimate the likely impact of various wood preservatives by examining the changes in the resin properties as they are added. One of the most obvious and easy properties to measure is viscosity. Another is the gelation time which is related to the rate of polymerization. This section focused on examining the impact of wood preservative addition to both PF- and pMDI- resins. The methods used were both rheological (changes in viscosity) and physical (changes in gelation time) (Cagle, 1973).

#### Viscosity

Viscosity is the internal friction of a liquid that offers resistance to flow. Viscosity is an important property of the adhesive because it influences the spread and distribution of resin on wood strands during blending. Viscosity is directly related to the molecular weight of resin, the higher the molecular weight, the higher the viscosity. Organic wood preservatives
containing amines may enhance the polymerization of PF- and pMDI- resins at room temperature, causing an increase in the viscosity of the resin. The inert solvent in the wood preservative formulation may reduce the viscosity of PF or pMDI-resin, causing overpenetration into wood and result in less resin being available for bonding at the surface. *Gelation time* 

The gelation time is a measure of the reactivity or curing rate of a resin. It is the time required for a resin to convert from a liquid to a gel (A gelled resin is one where all monomers have reacted to form one large molecule). Gelation time is closely related to the cure rate of the resin. The higher is the cure rate, the shorter is the gelation time. When the formulated wood preservatives are added to resin, the active ingredients may affect the cure rate, either accelerating it or retarding it, thus changing the gelation time. The solvents can also affect gelation time; if a solvent can not be dissipated at the right stage of cure, it will extend the gelation time, resulting in weaker bonds (Northcott et al., 1962).

In this research the compatibility of three termiticides (LP15406A, LP15406B and LP15447) and two fungicides (LP15396A and LP15396B) with eight phenol formaldehyde (PF) and one diphenylmethane diisocyanate (pMDI) resins was examined by measuring changes in gelation time and viscosity in order to identify desirable resins and wood preservatives combination for making waferboard.

## **3.2 Materials and Methodology**

## **3.2.1 Wood preservatives**

Three termiticides, LP15406A, LP15406B, LP15447, and two fungicides, LP15396A and LP15396B, were obtained from Dr. Wolman GmbH, Germany. The general description of each wood preservative taken from their Material Safety Data Sheet (MSDS) is given in Table 3.1. (An easy way to differentiate between termiticides and fungicides in the table to note is that termiticides contain the number 4 for the third digit and fungicides the number 3).

Trade name	Solvent	pH .	Chemical name	Active ingredient (%)	Function
LP 15406A	organic	9.8	Bifenthrin	25	termiticide
LP 15406B	organic	5.9	Chlorfenapyr	20	termiticide
LP 15447	organic	7.0	5-amino-1-[2,6-dichloro-4- (trifluoromethyl)phenyl]-4- [(1R,S)-(trifluoromethyl) sulfinyl]-1H-pyrazol-3- carbonitrile	1-5	termiticide
LP 15396A	water	8.3	K-HDO fenpropimorph	20 8.35	fungicide
LP 15396B	water	10.5	K-HDO	30	fungicide

Table 3.1 Wood preservative system.

## 3.2.2 Resins

The amounts of eight liquid PF-resins from several different companies and one pMDI- resin were used for this study. Their properties are compiled from the Material Safety Data Sheet (MSDS) and are listed in Table 3.2.

## **3.2.3 Formulation preparation**

The amounts of each preservative added to  $60.00 \pm 0.001$  g of PF- and pMDI- resin are shown in Table 3.3. These aliquots were calculated from the required loading of the formulated product provided by Dr. Wolman GmbH. The details of the conversion of the loading levels specified by Dr. Wolman Company to the concentrations of wood preservatives used here are shown in Appendix A. After the addition of the wood preservative, the mixture was stirred until a uniform solution was obtained, and the viscosity and gelation time immediately measured.

## 3.2.4 Viscosity determination-Gardner-Holt tubes

The viscosity was measured for each sample using Gardner-Holt tubes (ASTM D-1545). Gardner-Holt tubes are based on a series of tubes filled with liquids of different known viscosity. Each of the tubes is sealed and contains small air bubble. When the tubes are inverted the bubbles in each of the tubes rise at different rates depending on the viscosity of the liquids. Bubbles in liquids of greater viscosity rise at slower rates. The liquid to be tested is placed in a small test tube and sealed with a cork, being sure to leave enough room in the tube for an air bubble of similar size to the standard tubes. The sample

				······································	
Trade name	Description	Solid content (%)	Viscosity (cps)	pН	Source
GP-45	liquid face PF-resin	44.5-45.5	100-125	10.28	Borden Chemical, Inc., OR, USA
W 132D	liquid face PF-resin	46.1-46.6	75-125	9.6-10	Borden Chemical, Inc., OR, USA
WD01	liquid face PF-resin	46.2-47.2	50-100	9.8-10.2	Borden Chemical, Inc., OR, USA
PD-115	liquid PF-resin	35	5-35	9-10	Borden Chemical, Inc., OR, USA
BB7010	Liquid PF-resin	51.49	150	8.7-12.8	Dynea Ltd. Canada
BB7028	liquid PF-resin	48	125-140	9-11	Dynea Ltd. Canada
GP 265C54	liquid PF-resin	51	100-120	11.5	Georgia-Pacific Resins, Inc., GA, USA
GP 70CR66	liquid PF-resin	53	125-140	10.5	Georgia-Pacific Resins, Inc., GA, USA
Mondur 541 light	pMDI	100	140-165	NA	Bayer polymers LLC, PA., USA

Table 3.2 Resin systems

NA: not applicable.

Table 3.3 Wood preservative concentrations (µg of formulated product/mg of resin)

Concentration of formulated product in resin (µg wood preservative/ mg resin)							
LP 15406A	LP 15406B	LP 15447	LP 15396A	LP 15396B			
7.0	4.0	26.4	220	250			
12.0	6.5	46.3	340	370			
16.0	9.3	66.2	500	550			
	16.0		750	830			

examined.

tube is then inverted along with the standard tubes and the tube with the most similar rate of rise of the bubble is noted. If the viscosity of the sample falls between that of two tubes, record the average value of the two tubes. Two measurements were performed for each sample.

## 3.2.5 Gelation time

A 25 g aliquot of pure resin or a mixture of the preservative and resin was added to a 50 ml test tube. A glass stirring rod was placed into the tube. A clamp was added to the test tube, which was then placed in the spout of a rapidly boiling kettle so that the steam heated the tube and the resin. The mixed solution was stirred using the glass stirring rod at a rate of approximately 1.5 rotations per second while being heated by the steam. The time for a wood preservative/resin mixture to undergo a change from a liquid to a gel (indicated by the resin mass sticking to the glass rod) was recorded as the gelation time. Two measurements were performed for each sample.

## 3.3 Results and Discussion

The properties of the PF- and pMDI-resins before and after adding different types of wood preservatives are described in detail below. For the purpose of these experiments, wood preservatives, which produced precipitation of solids when added to the resins, were considered to be incompatible with resins. Wood preservatives were considered compatible with the resins if they did not change the gel time by + 2 minutes and the viscosity by + 35cps. When the wood preservative addition caused larger changes in the gelation time or viscocity, it was uncertain whether the combination could be used and further research would be needed to ensure that they are sufficiently compatible to still allow boards having strength similar to that of untreated waferboard to be produced. If the viscosity of the resin wood preservative/mixture changed by more that 35 cps they may significantly affect the flow properties of the resin on the furnish, thus affecting bond strength. In addition, such changes in viscosity may also affect its atomization as it is sprayed onto the furnish and may required further modifications to the equipment that supplies the resin to the spray nozzle. It may be possible to cope with changes outside these values, but that may require changes in the operating parameters of the spray system or the spray equipment. For the purpose of this work, changes larger than 35 cps would require more research of the chemistry of the interaction of the resin and the wood preservative to determine whether they are sufficiently compatible for pilot plant trials of waferboard production. Changes in the gelation time are more problematic since this could require changes in the press schedule, i.e., longer or shorter press times, in order to use the mixture. While it is possible for a plant to use a resin/wood preservative combination which change the gelation time by more than 2 minutes, this may require changes to their operation in order to use such a resin. So in these cases more research is needed to better understand the implications of changes to gelation time greater than 2 minutes. For these reasons, resin/wood preservative mixtures that change the viscosity by more than 35 cps or gelation time by more than 2 minutes would require more research to determine whether they could be used to manufacture waferboard.

## 3.3.1 The effect of wood preservatives on eight liquid PF-resins.

There are two types of PF-resins; novolaks which are catalyzed in acidic conditions, and resoles catalyzed by alkaline conditions. Resol PF-resins are normally used for wood composite products. Eight PF-resins used in the current research are water-based resol PF-resins (Table 3.2). Resin flow capability was an important parameter controlling the performance of the composite panels. In general, high-flow resins developed larger bonding areas and provided better panel performance as compared to the low-flow resins. If the addition of a wood preservative to a PF-resin caused the resin state to change, for example, to crystallize or flocculate, that wood preservative is unsuitable for addition to the PF-resin since it will lead to poor bonding. The introduction of a wood preservative with too much water is also unacceptable. Too much water from other sources, either introduced from wood preservatives or in the wood, may cause washout of the resins. Washout occurs when water affects the concentration, viscosity and gelation time of the resin enough to weaken the adhesion to the wood fibres or permit over-absorption into the strand surface.

## **3.3.1.1 Solid formation**

When soluble wood preservatives are added to a solvent they usually combine with solvent molecules to form a solvated complex. This complex is often unstable to changes in either the solvent or properties such as solution pH. Thus, when mixed with resins of high or low pH or with resins that can react with the wood preservative, the resulting addition will often lead to precipitation of the wood preservative from the resulting wood preservative-resin mixture. The addition of wood preservatives, especially inorganic preservatives, into liquid PF-resin usually causes crystallization. For example, one of the termiticides, LP 15396B (K-HDO solution), caused a crystalline solid to be precipitated, when added to all of the PF-resins tested, except for the PF-resin PD-115 (Table 3.4). Although LP 15396B produced stable solutions when added to PD-115 resin, the gelation time was increased by at least 9 minutes. The significant change in gelation time is mainly due to the dilution of water in LP 15396B to PD-115 resins. To overcome the influence of water in LP 15396B on the gelation time, powdered K-HDO was added at the loading level of 0.075:1 based on the weight ratio of wood preservative and resin. However, it can not completely dissolve in PD-115 PF-resin at room temperature. When PD-115 PF-resin was heated to 70 °C, powdered K-HDO at the higher loading level of 0.225:1 based on the weight ratio of wood preservative and resin can be added to form a uniform clear solution. The gelation time of the mixed solution of PD-115 PF-resin with powdered K-HDO at the highest loading level of 0.225:1 was 30 minutes, not significantly different from the

Resin	Wood preservative Concentration	Viscosity Change	Gel time Change	Observation	Compatibility
	(μg/mg)		(mm)		
	250	100	5	Cravatala	***
GP-45	250	-100		Crystals prescipitated in	no
PF-resin	570	-115	±15	increasing	no
	830	-03	±13 ±24	concentrations	no
	0.00	-23	·····		
	0	-435	0	0	
W132D	250	-135	+4	Crystals	no
PF-resin	370	-1/0	+/	precipitated in	no
	550	-195	+11	increasing	no
	830	-200	+17	concentrations.	no
	0	0	0	~	
WD01	250	-90	+4	Crystals	no
PF-resin	370	>-90	+8	precipitated in	no
	550	>-90	+12	increasing	no
	830	>-90	+18	concentrations.	no
	0	0	0		
PD-115	250	-35	+9		likely
PE-resin	370	-35	+15		likely
11-10311	550	-35	+20		likely
	830	-35	+34		likely
	0	0	0		
DD7010	250	0	+11	Crystals	no
BB/010 DE rogin	370	0	+14	precipitated in	no
rr-resin	550	÷ • 0	+19	increasing	no .
	830	-100	+22	concentrations.	no
	0	0	0		
	250	-165	+4	Crystals	no
BB7028	370	-140	+8	precipitated in	no
PF-resin	550	-140	+12	increasing	no
	830	-125	+18	concentrations.	no
	0	0	0		
GP	250	-115	+11	Crystals	<b>n</b> 0
265054	370	-115	+15	precipitated in	10
PF-resin	550	-115	+10	increasing	no
11 1000	830	-115	+26	concentrations.	10
	0.00	-115			
CD	0	U 40	U 1 4	Cravetala	
GP	230	-40	+0		no
JUCK00	370	-00	+0	precipitated in	no
rr-iesiii	550	-75	+14	ncreasing	no
	830	-100	+24	concentrations.	no

Table 3.4 The effect of LP15396B concentration on the viscosity and gelation time of PF-resins

Concentration in terms of formulated product.

gelation time of neat PD-115 PF-resin, 29 minutes. This indicated that at high temperature of more than 70 °C, powdered K-HDO in place of LP 15396B could be added to PF-resin to minimize the impact of water in LP 15396B on the gelation time and viscosity of PF-resin.

To minimize the impact of the crystallization of neat inorganic wood preservatives on PF-resin at room temperature, the incorporation of organic preservatives into inorganic wood preservatives was employed. For example, another termiticide LP 15396A, aqueous solutions of K-HDO and fenpropimorph, was added to eight PF-resins. LP 15396A caused crystallization of only four PF-resins rather than the seven PF-resins by LP 15396B (Table 3.5). LP 15396A produced stable solutions with GP-45, WD01, PD-115, and W132D PF-resin except at the highest concentration of 750  $\mu$ g/mg. The impact of LP 15396A on the gelation time and viscosity was significantly decreased when compared with LP 15396B.

All the observations indicated that, LP 15396A was a much more suitable additive for PF-resins than LP 15396B since LP 15396B contained 30 % K-HDO, and LP 15396A contained only 20 % K-HDO. The more K-HDO the solution contains, the more easily crystals precipitated from the solution during addition to the PF-resin. With respect to most PF-resins, when LP 15396A was added at room temperature, crystals formed immediately in the resulting mixture. However, when the solution was heated to  $70^{\circ}$ C, the crystalline solid completely dissolved to form a clear uniform solution. Upon allowing the solution to cool down, crystals re-precipitated. Thus, the use of a temperature of  $\geq 70^{\circ}$ C, LP 15396A could be incorporated into GP-45, W132D, BB7028, GP 265C54 and GP 70CR66

	Wood procorrective	Viscosity	Galtima		
Resin	Concentration	Change	Change	Observation	Compatibility
Resin	(ug/mg)	(cns)	(min)	Observation	compationity
·	0	0	0		
	220	-65	+3		likely
GP-45	340	-85	+8		likely
PF-resin	500	-90	+12		likely
	750	-90	+12 $+17$		likely
	0		0		
	220	-310	+1		Librate.
W132D	340	-335	+3		likely
PF-resin	500	-555	+3 ⊥4		likely
	500 750	-350	.⊥12	Crystals precipitated	ncery
	/ 50	-330	⊤15 ∩		
	220	- 55	<u></u>	2 X	likely
WD01	240	-55	+5		likely
PF-resin	540	-73	+0		
	500	-90	+ 1 2		likely
	/50	-95	+13	· · · · · · · · · · · · · · · · · · ·	пкету
	0	0, -	0		1:1 1
PD-115	220	-35	+4		likely
PF-resin	340	-35	-+-4		likely
	500	-35	+5		likely
	750	-35	+9		likely
	0	0	0	<b>a</b>	
BB7010	220	0	+8	Crystals	no
PF-resin	340	0	+11	precipitated in	no
	500	0	+16	increasing	no
	750	-100	+19	concentrations.	no
	0	0	0		
DD7028	220	+25	+3	Crystals	no
DD/020 DE resin	340	+50	+5	precipitated in	no
11-105111	500	+75	+9	increasing	no
	750	+100	+14	concentrations.	no
	0	0	0		
GP	220	-185	+4	Crystals	no
265C54	340	-35	+6	precipitated in	no
PF-resin	500	0	+9	increasing	no
	750	+35	+15	concentrations.	no
	0	0	0		
GP	220	-60	+1	Crystals	no
70CR66	340	-70	+7	precipitated in	no
PF-resin	500	-25	+11	increasing	no
	750	+15	+15	concentrations	no
	/ 30	+15	115	concentrations.	

Table 3.5The effect of LP15396A concentration on the viscosity and gelation time of<br/>PF-resin

Concentration in terms of formulated product.

- -

PF-resins.

PF-resins have been observed to be sensitive to oxidizing agent such as hydrogen peroxide, as well as tertiary amine and quaternary ammonium compounds such as didecyldimethylammonium chloride (DDAC), and if any of these chemicals are present in the wood preservatives, when they are added to liquid PF-resin, they may speed up the glue curing reaction, and resulting in solids being formed. For example, one of termiticides, LP 15406B, its main active ingredient of LP 15406B is chlorfenapyr, which belongs to the pyrrole class of compounds. Like tertiary amine, pyrrole usually acted as catalyst to improve the curing rate of PF-resin so that, when added to certain PF-resins such as GP-45, WD01 and PD-115 PF-resins, LP 15406B caused solids to come out from these liquid PF-resins (Table 3.6). At the highest concentration of 16 µg/mg, LP 15406B reacted with W132D, GP265C54 and GP 70CR66 PF-resins to form white solids, which floated on the surface of PF-resin solution. When all the above solutions were heated to 70°C, the white solids completely dissolved to form uniform clear solution. Upon allowing the solutions to cool down, solids reformed. This suggested that at temperatures of above 70 °C, LP 15406B could be a suitable additive for the GP-45, WD01 and PD-115 PF-resins at all concentrations or the W132D, GP265C54 and GP 70CR66 PF-resins at the highest concentration of 16 µg/mg.

The remaining two wood preservatives LP 15406A and LP 15447 did not produce solids when added to PF-resin.

	Wood preservative	Viscosity	Gel time		
Resin	Concentration	Change	Change	Observation	Compatibility
<u>.</u>	(µg/mg)	(cps)	(min)		
	0	0	0		
CD 45	4	0	0	White thin film	no
OP-45 PF_resin	6.5	0	0	was formed on	no
11-10311	9.3	0	0 .		no
	16	0	0	the surface	no
	0	0	0		
W122D	4	0	0		yes
WI32D PF_resin	6.5	0	0		yes
r r-resin	9.3	0	0		yes
	16	0	-1	Solid formation	no
	0	0	0		
WD01	4	+10	0	White thin film	no
WD01 DE regin	6.5	+25	0		no
FF-lesin	9.3 +25 0 V	was formed on	no		
	16	-40	+1	the surface	no
	0	0	0		
	4	0	-4	White thin film	no
PD-115	6.5	0	-4	was formed on	no
PF-resin	9.3	0	-4		no
	16	0	-4	the surface	no
	0	0	0		
	4	0	0		yes
BB7010	6.5	0	. 0		yes
PT-resin	9.3	. 0	0		yes +
	16	0	0		yes
	0	0	0		
	4.	0	0	· .	ves
BB/028	6.5	0	· 0		yes 👻
PF-resin	9.3	0	0		yes
	16	0	0		yes
	0	0	0		
GP	. 4	+35	-1		ves
265C54	6.5	+50	-2		likely
PF-resin	9.3	+65	-3		likely
	16	+65	-4	Solid formation	no
	0	0	0		
GP	4	ů 0	+1		Ves
70CR66	6.5	õ	+1		ves
PF-resin	0.3	ñ	+1		ves
	16	0	+1	Solid formation	no
	10	v	' 1		

## Table 3.6The effect of LP15406B concentration on the viscosity and gelation time of<br/>PF-resin

Concentration in terms of formulated product.

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## 3.3.1.2 Gelation time and viscosity

As observed in section 3.3.1, two fungicides, LP 15396A and LP 15396B (aqueous solutions of K-HDO or K-HDO and fenpropimorph) showed incompatibility with most PF-resins since they caused crystallization. One of three termiticides, LP 15406B (organic solvent-based emulsion of chlorfenapyr) exhibited incompatibility with three PF-resins GP-45, WD01 and PD-115 at all concentrations, and three other PF-resins W132D, GP265C54 and GP 70CR66 at the highest concentration of 16  $\mu$ g/mg since it caused solids to form in the mixture. In contrast, two other termiticides, LP 15406A and LP 15447 did not cause any crystallization or solids to be formed, but they did cause some changes in gelation time and viscosity of some PF-resins.

## 3.3.1.2.1 LP 15406B

At room temperature, BB7010 and BB7028 PF-resins were the only two of eight PF-resins that did not react with LP 15406B at any concentration. The effect of LP 15406B on their viscosity and gelation time is compiled in Figures 3.1 and 3.2 and Table 3.6. At all concentrations, LP 15406B is compatible with the BB7010 and BB7028 PF-resins.

As mentioned earlier, at the highest concentration of 16  $\mu$ g/mg, LP 15406B reacted with W132D, GP265C54 and GP 70CR66 PF-resins to form solids. At the other concentrations, LP 15406B did not react with W132D, GP265C54, or GP 70CR66 PF-resins. However, with increasing LP 15406B content, the viscosity of its mixture with GP 265C54 PF-resin gradually increased from 435 cps to 500 cps, and the gelation time decreased from 19 minutes to 16 minutes (Figure 3.3). At room temperature, at the

concentrations of 4  $\mu$ g/mg, 6.5  $\mu$ g/mg, and 9.3  $\mu$ g/mg, LP 15406B was considered to be incompatible with GP 265C54 PF-resin. With respect to W132D PF- and GP 70CR66 PF-resins, at the concentrations of 4  $\mu$ g/mg, 6.5  $\mu$ g/mg, and 9.3  $\mu$ g/mg, LP 15406B were compatible with them since their additions did not cause the change of more than 35cps in viscosity and the change of more than 2 minutes in gelation time (Table 3.6).

The variation of the impact of LP 15406B on eight liquid PF-resins indicated that the working properties of PF-resins closely depended on their constituents. Different PF-resin elements resulted in varied compatibilities with LP 15406B.

In summary, at room temperature, BB7010 and BB7028 PF-resins were the most promising PF-resins for the incorporation of LP 15406B. Also, the GP70CR66 and W132D PF-resins look promising for the LP 15406B at loading levels less than 16  $\mu$ g/mg. Care should be taken when adding LP 15406B to GP265C54 PF-resin since LP 15406B may change the viscosity or gelation time of the resin to produce a board of low bond strength or lead to the loss of its bonding property.



Figure 3.1 The effect of the LP 15406B concentration on the viscosity and gelation time of BB7010 PF-resin



Figure 3.2 The effect of the LP 15406B concentration on the viscosity and gelation time of BB7028 PF-resin.







## 3.3.1.2.2 LP 15406A

The effect of LP15406A concentrations on the viscosity and gelation time of eight PF-resins was compiled in Table 3.7. The addition of LP 15406A to GP-45 PF-resin caused a gradual increase in the viscosity with increasing wood preservative concentration. The viscosity change at wood preservative concentrations of 7  $\mu$ g/mg and 12  $\mu$ g/mg were 0 cps and 25 cps respectively, while the viscosity change at the wood preservative concentration of 16  $\mu$ g/mg was 60 cps, above the 35 cps limit for compatibility. The addition of LP 15406A to GP-45 PF-resin reduced gelation time by only 1 minute. LP 15406A, at concentrations of 7  $\mu$ g/mg and 12  $\mu$ g/mg and 12  $\mu$ g/mg and 12  $\mu$ g/mg is probably compatible with GP-45 PF-resin.

In contrast to GP-45 PF-resin, the viscosity of the WD01 PF-resin was decreased with the addition of LP 15406A. Especially so at the lowest wood preservative concentration of 7  $\mu$ g/mg, its viscosity only decreased 40 cps. At the higher concentrations of 12  $\mu$ g/mg and 16  $\mu$ g/mg, its viscosity was 120 cps, approaching the viscosity of neat WD01 PF-resin, 140 cps. However, at the lower concentrations of 7  $\mu$ g/mg and 12  $\mu$ g/mg, the gelation time of WD01 PF-resin was not influenced by the addition of LP 15406A. At the concentration of 16  $\mu$ g/mg, its gelation time increased 1 minute, still below the 2-minute limit. LP 15406A at the concentrations of 12  $\mu$ g/mg was compatible with WD01 PF-resin. LP 15406A at the concentration of 7 $\mu$ g/mg was borderline compatible with the WD01 PF-resin.

Unlike either the GP-45 PF- or the WD01 PF-resins, when LP 15406A was added to

either the W132D or the PD-115 PF-resins, neither viscosity nor gelation time changed. LP 15406A was deemed compatible with GP-45 and WD01 PF-resins at all concentrations evaluated.

The addition of LP 15406A at all concentrations to either BB7010 or BB7028 PF-resins caused an increase of 25 cps in the viscosity, well below the 35 cps limit. In addition, the gelation time remained unaffected. LP 15406A was compatible with the BB7010 and BB 7028 PF-resins at all concentrations.

The addition of LP 15406A at the lower concentrations of 7  $\mu$ g/mg and 12  $\mu$ g/mg to the GP 265C54 PF-resin did not cause any change in viscosity or gelation time. However, at the highest concentration of 16  $\mu$ g/mg, the viscosity increased 35 cps while its gelation time was unaffected. LP 15406A was compatible with the GP 265C54 PF-resin at all concentrations examined.

At all concentrations, the addition of LP 15406A to the GP70CR66 PF-resin did not cause any change in viscosity, but it did increase the gel time by 2 minutes. For the GP70CR66 PF-resin, the LP 15406A was also compatible at all concentrations tested.

From the above results, the introduction of LP 15406A to eight liquid PF-resins did not cause the significant change in the viscosity and gelation time, suggesting that neither the main active ingredient bifenthrin or the additives/solvent system present in LP 15406A react with the PF-resins. This is supported by the prior observations of Kennedy *et al.* (2003) who observed that bifenthrin was exceptionally stable in alkaline PF-resins.

Resin         Concentration ( $\mu g/mg$ )         Change (cps)         Change (min)         Compatibility (min)           0         0         0         0         0           GP-45         7         0         0         yes           PF-resin         12 $+25$ $-1$ yes           16 $+60$ $-1$ likely           0         0         0         0           W132D         7         0         0         yes           0         0         0         yes           PF-resin         12         +25         0		Wood preservative	Viscositv	Gel time	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Resin	Concentration	Change	Change	Compatibility
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		$(\mu g/mg)$	(cps)	(min)	1
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0	0	0	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	GP-45	7	0	0	yes
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	PF-resin	12	+25	-1	yes .
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		16	+60	-1	likely
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0	0	0	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	W132D	7	0	0	ves
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	PF-resin	12	0	0	ves
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		16	0	0	yes
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0	0	0	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	WD01	7	-40	0	likely
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	PF-resin	12 .	-15	0	yes
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		16	-15	+1	ves
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0	0	0	••••*•••••••••••••••••••••••••••••••••
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	PD-115	7	0	0	yes
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	PF-resin	12	0	0	ves
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		16	0	. 0	ves
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0	0	0	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	BB7010	7	+25	0	ves
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	PF-resin	12	+25	0	yes
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		16	+25	0	yes
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0	0	. 0	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	BB7028	7	+25	0	ves
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	PF-resin	12	+25	0	yes
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		16	+25	0	yes
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0	0	0	
$\begin{array}{c ccccccc} 265C54 & 12 & 0 & 0 & yes \\ PF-resin & 12 & 0 & 0 & yes \\ \hline 16 & +35 & 0 & yes \\ \hline GP & 7 & 0 & +2 & yes \\ 70CR66 & 7 & 0 & +2 & yes \\ PF-resin & 12 & 0 & +2 & yes \\ \hline 16 & 0 & +2 & yes \\ \hline \end{array}$	GP	7	0	0 0	ves
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	265C54	12	0	0	ves
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	PF-resin	16	+35	Ū	yes
GP         7         0         +2         yes           70CR66         7         0         +2         yes           PF-resin         12         0         +2         yes           16         0         +2         yes			0		····
$\begin{array}{ccccccc} 70CR66 & 1 & 0 & -2 & ycs \\ PF-resin & 12 & 0 & +2 & yes \\ 16 & 0 & +2 & yes \end{array}$	GP	° 7	0 0	+2	ves
$\begin{array}{cccc} \text{PF-resin} & 12 & 0 & 12 & \text{yes} \\ \hline 16 & 0 & +2 & \text{ves} \end{array}$	70CR66	12	0 0	+2	ves
	PF-resin	16	Õ	+2	yes

Table 3.7 The effect of LP15406A concentration on the viscosity and gelation time of<br/>PF-resin

Concentration in terms of formulated product.

## 3.3.1.2.3 LP 15447

The addition of LP 15447 caused a decrease of 50 cps in the viscosity of GP-45 PF-resin and 15 cps for the WD01 PF-resin, but slightly increased the gelation time of GP-45 and WD01 PF-resins (Table 3.8). Combining LP 15447 with W132D PF-resin reduced the viscosity substantially more than 200 cps, and increased the gelation time to over 3 minutes. Conversely, LP 15447 did not affect the viscosities of BB7010 and PD-115 PF-resins, and only slightly increased their gelation times. LP 15447 had little effect on BB7028 PF-resin, increasing viscosity from 200cps to 225cps, and decreasing gelation time from 32 minutes to 30 minutes. In contrast, GP 265C54 PF-resin is the only PF-resin whose viscosity increased (more than 60 cps) by LP 15447, but gelation time was unaffected. LP 15447 caused GP 70CR66 PF-resin the slight increase of 25 cps in viscosity, and the gain of 5 minutes in gelation time.

LP 15447 is a more compatable additive for PF-resin compared to LP 15406B, since it did not react with any of the PF-resins tested to form insoluble solid at room temperature. The main active ingredient of LP 15447 is 5-amino-1-[2,6-dichloro-4-(trifluoromethyl) phenyl]-4-[(1R,S)-(trifluoromethyl)sulfinyl]-1H-pyrazol-3-carbonitrile, which is classed as a phenylpyrazole. Like tertiary amines, phenylpyrazoles can catalyze the polymerization reactions of some PF-resins, and then increase their curing rate. When added to certain PF-resins such as GP 265C54 and GP 70CR66, LP 15447 increased their viscosity. PD-115, BB 7010 and BB7028 PF-resins are the most compatible PF-resins when formulating LP 15447 as an additive, for all of the concentrations examined. For other PF-resins, care should be taken since LP 15447 can change their viscosity or gelation time.

## 3.3.2 The effect of wood preservatives on the viscosity of pMDI- resins

The chemical properties of pMDI-resin are quite different from those of PF-resin. The pMDI-resin is solubilized in an organic solvent, and is more sensitive to water, amines, alcohols and strong bases than PF-resins. As such, pMDI-resin is not compatible with the fungicides of LP 15396A and LP 15396B since they contain at least 70 % water. When these fungicides were added to pMDI-resin, even at the lower concentrations of 220  $\mu$ g/mg or 250  $\mu$ g/mg, they reacted with pMDI-resin to form a hard foam, especially so for the LP 15396A, which foamed immediately upon the addition of the fungicide. Compared with LP 15396A, the reaction rate of LP 15396B was much slower. This is almost certainly because the surfactants and co-solvents present in the LP 15396B are less reactive with pMDI-resin. The higher pH of the LP 15396B may also reduce the reactants reactivity with the pMDI-resin.

Compared with the LP 15396A and LP 15396B fungicides, the termiticides of LP 15406A, LP 15406B and LP 15447 are more compatible with pMDI-resin since their formulations are based on organic solvents rather than water. This is especially so for the LP 15406B and LP 15447 termiticides where, with increasing termiticide content, they caused only a gradual decrease in viscosity due to the lower viscosity of their solvents (Figures 3.4 and 3.5). The addition of LP 15406A to pMDI-resin at the recommended

Resin	Wood preservative	Viscosity	Gel time	
Resin	Concentration			
	Concentration	Change	Change	Compatibility
	(μg/mg) (cps)		(min)	
	0	0	0	
GP-45	26.4	0	+1	yes
PF-resin	46.3	-50	+1	likely
	66.2	-50	+3	likely
	0	0	0	
W132D	26.4	-135	+1	likely
PF-resin	46.3	-210	+2	likely
	66.2	-270	+3	likely
	0	0	0	
WD01	26.4	-15	+2	yes
PF-resin	46.3	-15	+3	likely
	66.2	-15	+6	likely
	0	0	0	
PD-115 、	26.4	0	0	yes -
PF-resin	46.3	.0`	+1	yes
· · ·	66.2	0	+1	yes
	0	0	0	
BB7010	26.4	0	0	yes
PF-resin	46.3	0	+1	yes
	66.2	0	+2	yes
	0	0	0	
BB7028	26.4	+25	-2	yes
PF-resin	46.3	+25	-2	yes
	66.2	+25	-2	yes
~~~	0	0	0	
GP	26.4	+65	0	likely
265C54	46.3	+65	0	likely
rr-resin	66.2	+65	0	likely
	0	0	0	
GP	26.4	0	0	ves
70CR66	46.3	+15	+2	ves
PF-resin	66.2	+15	+5	likelv

Table 3.8 The effect of LP15447 concentration on the viscosity and gelation time of<br/>PF-resin

Concentration in terms of formulated product.

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concentrations by Dr. Wolman GmbH caused a slight increase of the viscosity from 500 cps to 550 cps (Figure 3.6). However, the large changes in the viscosity suggested that there may be difficulties in terms of compatibility, for all the termiticides with pMDI-resin. However, the actual compatibility of pMDI with these termiticides needs to be proved in further mechanical tests.



Figure 3.4 The effect of the LP 15406B concentration on the viscosity of pMDI-resin.



Figure 3.5 The effect of the LP 15447 concentration on the viscosity of pMDI- resin.



Figure 3.6 The effect of the LP 15406A concentration on the viscosity of pMDI- resin.

The results on the compatibility of 5 wood preservatives with 8 liquid PF- and 1 pMDI-resins are summarized in Table 3.9, and suggested that, at room temperature, the BB7010 and BB7028 PF-resins are the most compatible resins for the LP 15406A, LP 15406B and LP 15447 termiticides. Also, the GP70CR66 PF-resin may be compatible with these termiticides. As was the case for pMDI-resin, these termiticides are considered to be likely compatible.

Compared with the LP 15406A, LP 15406B and LP 15447 termiticides, the LP 15396A and LP 15396B fungicides are more difficult to incorporate into PF-resins and pMDI-resin. No fungicides can be added to pMDI-resin. Only PD-115 PF-resin could be suitable for these two fungicides. LP 15396B can not be added to any other PF-resins. For LP 15396A, GP-45, W132D and WD01 PF-resin could be suitable for it to be added.

D	Concen-	PF-resin						pMDI		
Preservative	tration	GP-45	W132D	WD01	PD-115	BB7028	BB7010	GP265C54	GP70CR66	-resin
	7	yes	yes	likely	yes	yes	yes	yes	yes	likely
LP15406A	12	yes	yes	yes	yes	yes	yes	yes	yes	likely
	16	likely	yes	yes	yes	yes	yes	yes	yes	likely
	4	no	yes	no	no	yes	yes	yes	yes	likely
I D15406D	6.5	no	yes	no	no	yes	yes	likely	yes	likely
LP13400D	9.3	no	yes	no	no	yes	yes	likely	yes	likely
	16	no	no	no	no	yes	yes	no	no	likely
	26.4	yes	likely	yes	yes	yes	yes	likely	yes	likely
LP15447	46.3	likely	likely	likely	yes	yes	yes	likely	yes	likely
	66.2	likely	likely	likely	yes	yes	yes.	likely	likely	likely
	220	likely	likely	likely	likely	no	no	no	no	no
I D15206A	340	likely	likely	likely	likely	no	no	no	no	no
LF15590A	500	likely	likely	likely	likely	no	no	no	no	no
	750	likely	no	likely	likely	no	no	no	. no	no
	250	no	no	no	likely	no	no	no	no	no
I D15206D	370	no	no	no	likely	no	no	no	no	no
Lr 15590D	550	no	no	no	likely	no	no	no	no	no
	830	no	no	no	likely	no	no	no	no	no

Table 3.9Summary of the compatibility of preservatives and PF-, and pMDI-resins at<br/>room temperature

Concentration in terms of formulated product.

## **3.4 Conclusions**

The results of this phase of the research suggests that, at room temperature, wood preservatives based on inorganic aqueous solution, for examples, the two fungicides LP 15396A and LP 15396B, are difficult to combine with PF-resins and pMDI-resin since they often caused crystallization or polymerization. Even if they did not cause these changes, they significantly changed the gelation time and viscosity. These observations indicated that, they are not suitable as glue-line additives.

Compared with the LP 15396A and LP 15396B fungicides, termiticides based on organic solvent emulsion, especially LP15406A and LP15447, showed much better compatibility with all eight PF-resins. However, LP 15406B caused the formation of solids with GP-45, WD01 and PD-115 PF-resins at all concentrations, and W132D, GP265C54, and GP 70CR66 PF-resins at 16 µg/mg (the highest concentration examined). At room temperature, BB7010 and BB7028 PF-resins were the most promising PF-resins to incorporate the LP 15406B termiticide. Also, GP 70CR66 PF-resin looks the desirable combinations with LP 15406B except the highest loading level of 16 µg/mg. These results suggested that BB7010 and BB7028 PF-resins are the most suitable PF-resins for the LP15406A, LP 15406B and LP15447 termiticides. GP 70CR66 PF-resin can also be considered. Because of the large changes in viscosity the compatibility of the termiticides with the pMDI-resin was considered to be uncertain, with further experimental work on mechanical strength required to confirm their incompatibility.

## **Chapter 4**

# The effect of preservative treatment on the mechanical properties of waferboard

## 4.1 Introduction

The mechanical properties of OSB are important since it is widely used for roof and wall sheathing, as well as the subfloor in residential construction. The three characteristics most often measured are the bending or modulus of rupture (MOR), the stiffness or modulus of elasticity (MOE), and the internal bond strength (IB). These are the key strength properties that characterized waferboard and OSB. Considerable research has been reported which investigates the various factors influencing these properties.

The key difference between wafer board and OSB is the strand alignment and layer structure of OSB. In waferboard, the mat may consist of more than 1 layer (due to different resins used in the face and core layers) but the strands are randomly oriented on each other. OSB has layers of aligned strands that simulate the alternating orientations of veneer sheets in plywood. In the lab, it is difficult and time-consuming to make OSB lab boards, wherever possible, researchers of OSB use randomly oriented mats to reduce the amount of effort needed to make the boards.

An important consideration for waferboard is its durability. The two major biological hazards are termites and decay fungi. Termites are a major pest in south eastern USA (as well as in states like Hawaii. In the Greater New Orleans Metropolitan Area alone, it has been estimated that termites cause some \$300 million in damage per year (McClain, 1999). They are found in most tropical countries, where they are the major source of problems in timber structures. The protection of a building against termites involves several strategies including, soil poisoning, physical barriers, building maintenance, and the eradication of termite nests close to buildings. However, when all of these fail, the use of preservative treated wood in the structure provides an important defense mechanism to extended service life of the building components. Plywood has traditionally been used for the sheathing and subfloor of buildings, but today much of that market has been replaced by waferboard or OSB. A key difference between these two products is that while plywood and sawnwood can be pressure treated with preservative, due to the significant swelling of wafer board or OSB when exposed to water, the post manufacture treatment of waferboard or OSB is not practical. Consequently, to enhance the durability of waferboard, the wood preservatives must be added during the manufacturing process. This may be done either by incorporating the wood preservative in with the resin or alternatively by spraying the flakes with a solution of the wood preservative prior to gluing. However, there are some drawbacks with these approaches since the wood preservatives may interfere with the quality of the glue bond and reduce the strength properties.

The incorporation of solid wood preservative with the resin can also produce problems of microdistribution, as the movement of the wood preservative will often be limited to that of the resin. However, this approach remains the most popular method with zinc borate being the most widely used wood preservative in North America. It is added as a powder

either with the resin or often by tumbling the wafers in the powdered zinc borate together with the solid resin or prior to spraying with the liquid resin. The resulting strength reductions have been reported to be minor. However, several reports suggest that the microdistribution of the wood preservative has a significant impact on its durability. Laks and Palardy (1993), Barnes and Amburgey (1993) have postulated that powdered preservatives remain as small particles between the wood wafers, and so are not able to protect the wood matrix. Emulsified solutions of organic preservatives could provide superior penetration into the wafer. In addition, emulsifiers or surfactants in solution could promote the movement of relatively inert organic preservatives.

This research project examined the impact of incorporating emulsified solutions of novel termiticides and a fungicide during the manufacture of waferboard, on its strength properties in terms of the MOR, MOE, and IB. The termiticides were bifenthrin, chlorfenapyr, and 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(1R,S)-(trifluoromethyl)sulfinyl]-1H-pyrazol-3-carbonitrile, while the fungicide was formulated from K-HDO and fenpropimorph.

## 4.2 Materials and Methodology

## **4.2.1 Panel preparation**

## 4.2.1.1 Adhesives

Prior to Weyerhaeuser undertaking the production of the test boards at their pilot plant, the compatibility of the three termiticides and two fungicides with eight PF-resins and a pMDI-resin were assessed. The results of this analysis were presented and discussed in Chapter 3. The selection of the PF- resins for the board production was based on those used commercially to produce OSB in the Weyerhaeuser waferboard mills. The two PF-resins chosen were GP 70CR66 liquid PF-resin (Georgia-Pacific Resins, Inc., GA, USA) with 53 % solids as the surface resin, and BB7028 liquid PF-resin (Dynea Ltd. CA) with 47.6 % solids for the core. In addition, a preliminary screening of waferboard that had the wood preservative mixed in pMDI-resin was also performed. Due to the great sensitivity of the pMDI to moisture, only the solvent-based termiticides were incorporated into the test boards. When pMDI-resin was used, the face resin remained GP 70CR66 liquid PF-resin, while the core resin was changed to Mondur 540 pMDI-resin (Bayer polymers LLC, PA, USA).

## **4.2.1.2 Preservative formulations**

Discussion with Weyerhaeuser confirmed that the waferboard commercially produced with zinc borate generally has high hardwood content. Because of this, and based on information from Dr. Wolman GmbH it was decided to proceed only with the incorporation of the fungicide formulated with both KHDO and fenpropimorph which can resist both brown and white rot attack. Building components produced from hardwoods are known to frequently be attacked by white rot fungi in service. Four concentrations of the formulated fungicide were included during PF-resin waferboard production. Three concentrations of the three termiticides were incorporated during the PF-resin waferboard manufacture. Since the study with the boards bonded with pMDI-resin was considered to be preliminary, after consultation with Weyerhaeuser and Dr. Wolmann GmbH, it was decided to use only the median termiticide concentration.

## 4.2.1.3 Furnish

Dried strands were obtained from Weyerhaeuser's Grayling, Michigan mill. The composition of these strands was 65 % aspen, 10 % pine, 20 % soft maple and 5 % hard maple. The length of the strands ranged from fines (less than 0.32cm) to 7.62cm. The moisture contents of the blended surface and core strands were 8.5 % and 7.0 % respectively.

## 4.2.1.4 Panel manufacture

The waferboard was manufactured by Weyerhaeuser Company, Washington, USA, in their pilot plant. Both the face and core strands received target applications of 5 % liquid PF-resin based on the oven-dry weight of furnish. For waferboard manufactured from pMDI the core strands received a target application of 2.75 % resin. The application weight ratio of core and surface PF-resin was 1:1. Each termiticide was mixed with liquid PF- or pMDI-resin and was sprayed onto wafers using atomizing nozzles, after spraying the wafers with 1.00 % wax based on the oven-dry weight of furnish. LP 15396A, the only

fungicide, was sprayed onto wafers using a separate nozzle, but was applied at the same time as the core and surface liquid PF-resin. The strands were formed into mats by hand with a random flake orientation. Two replicate panels were produced for each treatment and control. The pressing time was 4 minutes at 204 °C (400 °F). The highest pressure was up to 4.6 MPa (670 psi). The target thickness and panel density were 11.1 mm and 631.127 kg/m<sup>3</sup>, respectively. The actual target loadings are shown in Table 4.1.

Table 4.1 The preservative active ingredient concentration in waferboard (% m/m total active ingredients/oven dried wood strands).

Board type	LP 15406A	LP 15406B	LP 15447	LP 15396A
PF-resin	0.003 0.0052	0.0044 0.0073	0.003 0.0052	0.21 0.29 0.44
	0.0074	0.01	0.0074	0.44 0.67
pMDI-resin	0.0052	0.0073	0.0052	· · ·

#### 4.2.2 Specimen testing

Following production of the 610 mm x 610 mm x 11.1 mm thick waferboard panels at Weyerhaeuser, approximately 38.1mm was trimmed from all four edges prior to shipping to Vancouver to eliminate edge effects. The moisture content of the board, as determined from the oven-dry weight, was found to be 4.6 %. Six 76.2 mm by 533.4 mm long sections were cut from each replicate panel and labeled as outer, middle, or inner to indicate their position within the panel. Thus, there were two outer, middle, and inner sections from each panel. These sections were then further cut into the various test samples required for the static bending testing, internal bonding testing, termite and decay testing, using the cutting patterns shown in Figures 4.1.

## 4.2.2.1 Static bending testing

Six unaged replicates (340 mm length  $\times$  76 mm width  $\times$  11 mm thickness) from each panel were prepared from each waferboard for testing. All specimens were conditioned for one week to constant weight and moisture content (10.5 %) in a conditioning chamber maintained at 20 °C and 65 percent relative humidity (RH). The MOR and MOE of the experimental panels were evaluated in 3-point bending on a Sintech 30D test machine in accordance with American Society for Testing and Materials Standard D 1037 (ASTM 1992). The span for each specimen was 282 mm. The specimens were loaded at the center of the span with the loading speed of 5.65 mm/min applied to the face at a constant rate (Figure 4.2). The maximum load, modulus of rupture and modulus of elasticity were recorded.

## **4.2.2.2 Internal bonding testing**

Eighteen unaged replicates (51 mm $\times$ 51 mm $\times$ 11mm thickness) from each fungicide treated panel and twelve replicates (51 mm $\times$ 51 mm $\times$ 11 mm thickness) from each termiticide treated panel were prepared for the determination of the internal bonding strength. Specimens were bonded to a 50 mm square aluminum base plate with hot melt glue. These specimens were then conditioned for one week to attain constant weight and moisture content (10.5 %) in a conditioning chamber maintained at 20 °C and 65 percent relative humidity (RH). Internal bonding of the experimental panels were evaluated on a

Sintech 30D test machine in accordance with American Society for Testing and Materials Standard D 1037 (ASTM 1992). The crosshead speed of the testing machine was 0.094 cm/cm per minute (Figure 4.3).

## **4.2.3 Control samples**

The control samples in this study were untreated boards manufactured at the same time as those which were manufactured with wood preservative. Control boards were produced for both the total PF waferboard as well as those boards which incorporated a pMDI-resin core. For reference, commercially produced zinc-borate (0.83 %) treated waferboard was also studied to determine its properties for comparison with the pilot plant produced waferboard.

## **4.2.4 Statistical analysis**

The statistical analysis of the mechanical strength test results was a one-way analysis of variance (ANOVA) using JMP statistical software. The statistical model was designed to detect significant differences in the mean value for each treatment. Tukey-Kramer Significant Difference multiple-range test was employed to determine which mean values were different at the 95 percent confidence level.
IB	IB	IB	MOR/MOE			IB
	FFF					
IB		MOR	/MOE	IB	IB	IB
				FF		
IB	IB	IB	MOR/MOE			IB
FF	EEF	FF			l	
BE		MOR/	MOE	IB	IB	IB
IB	IB	IB	MOR/MOI	3	<u></u>	IB
					Į	
IB	<u>r i r il r</u>	MOR/	MOE	IB	IB	IB
				EFI	<u>UEE</u>	EE



(a MOR/MOE TT TT IB IB IB TT MOR/MOE TT TT IB IB IB TT ПТ MOR/MOE TT TT IB IB IB TT TT MOR/MOE TT TT IB IB IB TT TT MOR/MOE TT TT IB IB IB TT MOR/MOE TT TT IB IB IB тт TT

(b)

Figure 4.1 Cutting patterns: (a) fungicide, (b) zinc borate, and (c) termiticides. Sample abbreviations:

IB: internal bond,

MOR/MOE: modulus of rupture/elasticity,

TT: termiticides,

F: fungicides.



Figure 4.2 Static bending testing



Figure 4.3 Internal bonding testing

#### 4.3 Results and discussion

#### 4.3.1 Mechanical properties of commercial ZnB treated PF-resin waferboard

The results on mechanical strength of commercial control and zinc borate treated waferboard supplied by Weyerhaeuser Company, Washington, USA, are summarized in Table 4.2. The IB strength of the treated boards is 21 % lower than the controls, which indicates that ZnB is interfering with the development of the PF glue-line strength. This was consistent with previous results obtained with waferboard, where IB strength of ZnB treated PF-resin waferboard generally decreased with increasing ZnB content (Sean et al., 1999). The adverse effect of ZnB on bonding strength is mostly due to the fact that, powdered ZnB stays on the flake surface, thereby reducing the bond efficiency of the adhesive.

Waferboard treated with 0.83 % ZnB also had a 7 % reduction in MOE and a 15 % reduction in MOR. This observation was not a surprise. The same pattern with MOE and MOR of 0.83 % ZnB treated waferboard was also observed by Sean *et al.*, (1999). The loss in MOR and MOE reflected a problem in the bonding of the flakeboard.

Property	Control	0.83 % ZnB	Strength loss (%)
IB(MPa)	0.38	0.30	21
MOE(MPa)	2999.32	2785.58	7
MOR(MPa)	17.72	15.06	15

Table 4.2 Mechanical strength of ZnB treated waferboard.

## 4.3.2 Effect of fungicide on mechanical properties of PF-resin experimental waferboard

The fungicide, LP 15396A, an emulsified aqueous solution of K-HDO and fenpropimorph, was sprayed onto the strands using a separate spraying line but at the same time as PF-resin. A series of waferboards were made with target active ingredients of K-HDO and fenpropimorph of 0.21 %, 0.29 %, 0.44 %, and 0.67 % based on oven-dry weight strands. The distribution of the MOR, MOE and IB results were all normal (Table 4.3), and thus the results can be analyzed using an ANOVA.

Table 4.3 Test for Normality of density, MOR, MOE and IB of fungicide treated PF-resin waferboard.

Property	W	Prob < W	
Density	0.9725	0.3848	
MOR	0.9730	0.4021	
MOE	0.9649	0.1789	
IB	0.9821	0.4975	

The results of the analysis are listed in Table 4.4, (the ANOVA analyses are listed in Appendix B) and show that, the fungicide treatment significantly increased the density of treated waferboard (p = 0.0009) but did not affect the static bending strength (p = 0.2981 for MOR and p = 0.0561 for MOE). As expected, the static bending strength of the fungicide treated waferboard was not impaired since the increase in moisture content of flakes introduced from fungicide may change the vertical density profile, produce more densified board, and then enhance MOR/MOE (Andrews *et al.*, 2001). All MOR and one MOE value were above the minimums (17.2 MPa for MOR and 3.10GPa for MOE) established by the Canadian Standards Association (CSA 1993). These results were also

consistent with previous findings obtained with waferboards, where the pretreatment of strands with wood preservatives such as 3.4 % IPBC, 0.71 % tubuconazole or 0.71 % propiconazole), water-repellent agents, and emulsion systems did not have a significant negative effect on the static bending properties (Baileys et al., 2003).

Fungicide Concentration in board (%)	Density (kg/m <sup>3</sup> )	MOR (MPa)	MOE (MPa)	IB (MPa)
0	645.83(26.01)A	19.17(2.23)A	2735.50(289.63)A	0.303(0.061)A
0.21	645.81(19.47)A	17.73(2.25)A	2868.67(453.56)A	0.235(0.069)B
0.29	661.48(15.75)AB	19.26(2.79)A	3031.50(269.93)A	0.251(0.069)B
0.44	670.20(25.57)B	20.25(4.24)A	3219.50(487.03)A	0.251(0.062)B
0.67	679.48(22.06)B	20.15(3.57)A	3031.50(424.36)A	0.252(0.062)B
Prob>F(Total)	0.0009	0.2981	0.0561	0.0002

Table 4.4 Mechanical properties of fungicide treated experimental PF-resin waferboard.

Values followed by the same capital letter are not significantly different (p=0.05). Values in parentheses are standard deviations.

The fungicide had a significant effect on the IB strength (p = 0.0002). The addition of fungicide into waferboard generally caused at least a 17 % reduction in IB strength of finished waferboard. Lower IB strength for fungicide treated waferboards could be attributed to fungicide residues in the wood cells or surface-active agents in the fungicide. Vick (1990) reported that chemically inert preservative residue in the wood cells can block the attraction between wood and PF-resin. Surface-active agents in the fungicide emulsion may also cause PF-resin to over-penetrate the wood. The lower IB strength is also likely due to the increase in moisture content of flakes introduced from fungicide, which may

cause washout of the resins, and reduce the bonding property. However, the adverse effect of fungicide on IB strength could be minimized by the application of more PF-resin (Laks and Palardy, 1993) or the addition of organic flowing agents containing hydroxyl (-OH) groups such as polyethylene glycol (PEG) (Sean et al., 1999).

# 4.3.3 Effect of termiticides on mechanical properties of PF-resin experimental waferboards.

The three termiticides, LP 15406A, LP 15406B and LP 15447, the organic emulsified solution based on bifenthrin, chlorfenapyr, and 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(1R,S)-(trifluoromethyl)sulfinyl]-1H-pyrazol-3-carbonitrile respectively, mixed with PF-resin, were sprayed onto strands. The probability for test for Normality of density, MOR, MOE and IB is presented in Table 4.5. It is generally accepted that, if probability is more than 0.05, the data distribution is normal. In view of the criterion, we observed that the data distribution of density, MOR, MOE and IB is normal. One-way ANOVA was conducted for identifying the statistically significant differences for density, MOR, MOE and IB.

Table 4.5 Test for Normality of density, MOR, MOE and IB of termiticide treated PF-resin waferboard.

Items	W	Prob < W
Density	0.9911	0.9690
MOR	0.9836	0.6826
MOE	0.9832	0.6589
IB	0.9874	0.8247

A one-way ANOVA shown in Table 4.6 (the ANOVA analyses are listed in Appendix B) indicates the presence of significant interactions between termiticide type and MOR (p = 0.029), especially between termiticide type and MOE (p = 0.0035). It was therefore necessary to analyze for these effects separately for each termiticide. There was no strong evidence that showed an effect of termiticide type on IB strength (p = 0.3583). This observation was expected from the results of the compatibility experiment discussed in Chapter 3, where the addition of these three termiticides to GP 70CR66 and BB7028 liquid PF-resins did not cause significant changes in either gelation time or viscosity. Hall et al. (1982) investigated the effect of the addition of the stock solution of chloronapthalene and tributyltin oxide into liquid PF- resin on IB strength of aspen waferboard. Their results are consistent with these findings.

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-	Termiticide	Density	MOR	MOE	IB
_	type	$(kg/m^3)$	(MPa)	(MPa)	(MPa)
	Control	669.13(25.94)A	19.17(2.23)AB	2735.58(289.63)A	0.303(0.061)A
	LP 15406A	658.20(41.88)A	18.25(3.28)A	2970.23(363.68)AB	0.289(0.076)A
	LP 15406B	670.30(39.46)A	19.94(2.93)AB	3137.61(343.62)B	0.282(0.069)A
	LP 15447	674.32(36.66)A	20.01(2.20)B	3018.06(285.29)AB	0.300(0.070)A
	Prob>F(Total)	0.0717	0.029 0.00	0.3583	

Table 4.6 Mechanical properties of termiticide treated experimental PF-resin waferboard.

Values followed by the same capital letter are not significantly different (p=0.05). Values in parentheses are standard deviation

#### 4.3.3.1 LP 15406A

With LP 15406A, the emulsion of bifenthrin, Figure 4.4 shows that the MOR values tended to decrease slightly with increasing concentration, but the trend was not statistically different for any concentration. The reductions in the mean MOR varied from 1 to 10 percent. Mean MOR did not decrease proportionally with increasing bifenthrin content.

The change in MOE as a function of LP 15406A loading level is presented graphically in Figure 4.5. There is no clear indication that the MOE of the treated waferboards was adversely affected by the inclusion of LP 15406A. Furthermore, the MOE values of the waferboards treated with 0.003 percent bifenthrin were 12 percent higher than the untreated control. No further increase in MOE with higher bifenthrin content was noticed.



\*Error bars represent a standard deviation.



\*Error bars represent a standard deviation.

#### 4.3.3.2 LP 15406B

As indicated in Figure 4.6, the treatment of LP 15406B, the emulsion of chlorfenapyr, did not have any detrimental effect on MOR. Indeed, the addition of LP 15406B slightly increased the mean MOR values. The increase in mean MOR ranged from 1 % to 7 %, but the increase in MOR was not statistically significant. Considering the changes in the MOE, a similar trend was observed as for the MOR (Figure 4.7). The treatment with LP 15406B significantly improved MOE (p = 0.001) by at least 8 %. There was an immediate increase when including the termiticide at the lowest concentration, and a further increase was noted when increasing the concentration of LP 15406B to 0.0073 %. Further increases in the termiticide content produced no addition increase in the mean MOE.





#### 4.3.3.3 LP 15447

Clearly, the MOR of the treated waferboard was not significantly affected by mixing LP 15447 with the PF-resin (p = 0.28). However, LP 15447 treatment with 0.003 % and 0.0074 % active ingredient increased the MOR an average of 8 % and 5 % respectively, when compared to untreated controls (Figure 4.8). Figure 4.9 shows the significant positive effect of LP 15447 treatment on MOE (p = 0.021). The addition of LP 15447 at 0.003 % active ingredient caused a 14 % increase in the MOE. Higher loading levels (0.0052 % and 0.0074 %) increased the MOE compared to controls to a less degree of 8 % and 9 % respectively.

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\*Error bars represent a standard deviation.

4.3.4 Effect of termiticides on mechanical properties of pMDI-resin experimental waferboards.

The three termiticides, LP 15406A, LP 15406B and LP 15447, after mixing with pMDI-resin, were sprayed onto strands. The data distribution of density, MOR, MOE and IB of pMDI-resin waferboard samples is normal (Table 4.7). A one-way ANOVA was conducted in order to identify the statistically significant differences for density, MOR, MOE and IB.

Table 4.7 Test for Normality of density, MOR, MOE and IB of termiticide treated pMDI-resin waferboard.

Items	W	Prob < W
Density	0.9624	0.2186
MOR	0.9873	0.9463
MOE	0.9602	0.1797
IB	0.9741	0.2708
•	· · · · · · · · · · · · · · · · · · ·	

The effects of different termiticide treatment on MOR, MOE and IB strength of waferboard bonded with pMDI-resin are given in Table 4.8 (the ANOVA analyses are listed in Appendix B). Obviously, different termiticides significantly positively affected MOR (p = 0.0027). Especially LP 15406B treatment with 0.0073 % chlorfenapyr caused a 30 % increase in MOR compared with the untreated controls. Waferboards treated with LP 15406A provided similar MOR as waferboards treated with LP 15447. Their mean MOR values were 18 % more than those of the untreated controls. In the case of MOE, the similar positive trend as MOR was observed. All termiticide treatment caused at least a 14 %

increase in MOE compared with the untreated controls. These higher MOR and MOE values of termiticide treated waferboard suggest that these termiticides at contents tested did not impair the static bending strength.

There is strong evidence that shows the effect of termiticide treatment on IB strength (p = 2.47E-07). The IB results (Table 4.8) show that, LP 15406B had no effect on IB strength, LP 15406A caused a 12 % drop in IB. However, the reduction caused by LP 15406A was not statistically significant (95 % confidence level). LP 15447 had a significantly negative effect on IB strength with a 37 % drop. The IB loss caused by LP 15447 was expected from the results of the compatibility studies discussed in Chapter 3, where the addition of LP 15447 at concentrations tested with pMDI-resin caused at least a 20.0 % reduction in viscosity. The lower viscosity of pMDI caused over-penetration into wood, resulted in less resin being available for bonding.

Termiticide Concentration	Density	MOR	MOE	IB
in board (%)	$(kg/m^3)$	(MPa)	(MPa)	(MPa)
0	662.33(24.74)A	17.99(2.94)A	2922.26(446.94)A	0.330(0.087)B
0.0052(LP 15406A)	673.76(20.09)A	21.13(3.15)AB	3333.79(368.44)AB	0.289(0.086)B
0.0073(LP 15406B)	714.23(79.32)A	23.29(2.39)B	3644.87(273.36)B	0.328(0.065)B
0.0052(LP 15447)	687.29(28.85)A	21.13(4.15)AB	3333.79(481.61)AB	0.209(0.063)A
Prob>F(Total)	0.053	0.0027	0.00092	2.47E-07

Table 4.8 Mechanical properties of termiticide treated experimental pMDI-resin waferboard

Values followed by the same capital letter are not significantly different (p=0.05). Values in parentheses are standard deviation.

#### **4.4 Conclusions**

The comparison of the mechanical strength of commercial waferboard supplied by the Weyerhaeuser Company, suggested that 0.83 % powdered ZnB pre-treatment significantly impaired the mechanical strength of PF-resin waferboard. It caused a 21 % loss in IB strength, a 7 % loss in MOE and a 15 % loss in MOR.

Compared with ZnB, the experimental wood preservatives, especially termiticides, caused much less adverse effect on PF-resin waferboard. The incorporation of fungicide, LP 15396A, into PF-resin waferboard within the range of concentrations tested did not negatively affect the bending strength, but caused a 17 % reduction in IB strength. However, the adverse effect of fungicide on IB strength could be minimized by the application of more PF-resin or addition of organic flowing agents containing hydroxyl (-OH) groups such as polyethylene glycol (PEG). These results on mechanical strength suggest that, the novel fungicide, the emulsified aqueous solution of K-HDO and fenpropimorph, could be effectively spray-applied to furnish simultaneously as PF-resin for manufacturing waferboard.

The addition of three termiticides into PF-resin had no significant effect on IB strength. However, the effects on static bending strength were different. LP 15406A did not negatively affect MOE, but did reduce the MOR. However, the reduction in MOR was not statistically significant. LP 15406B had no any effect in MOR, but significantly increased MOE. With LP 15447, the similar trend on MOR and MOE was observed as LP 15406B. These results suggest that, all three termiticides are desirable additives to be successfully

incorporated into PF-resin for making waferboard within the range of concentrations tested.

As with pMDI-resin waferboard treated with termiticides, the results on mechanical strength indicate that, LP 15406B, with 0.0073 % chlorfenapyr content in waferboard, is the most promising termiticide to be added to pMDI-resin for waferboard since this treatment had no effect on mechanical properties. LP 15406A, with 0.0052 % bifenthrin content in waferboard, could be added to pMDI-resin. Although the mean IB values were not found to be significantly different, caution must be used since the mean IB values for this treatment were 12 % lower than controls boards. LP 15447, with 0.0052 % 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(1R,S)-(trifluoromethyl)sulfinyl]-1H-pyrazol-3-carbonitrile content in waferboard, can not be added to pMDI-resin since its treatment caused a 37 mean IB loss.

#### Chapter 5

### Decay resistance of novel fungicide modified waferboard 5.1 Introduction

The chemical treatment of waferboard to enhance its durability against bio-deterioration is becoming increasingly important for the wood preservative industry. Waferboard, like other wood products, is susceptible to decay by basidiomycetes when exposed to high relative humidities for prolonged periods of time or to liquid water. There are two kinds of basidiomycete fungi. These are commonly known as brown rot and white rot fungi.

Brown-rot fungi degrade the carbohydrates (cellulose and hemicellulose) converting them to biomass, carbon dioxide and water, leaving a modified lignin residue. In the early stages of decay, the wood surface lacks luster. The strength properties of wood attacked by brown-rot fungi decrease rapidly, even in the early stages of decay. For example Eaton and Hale (1993) reported losses in strength of up to 50 % for only 2 % loss in mass. As decay progresses, the wood acquires an abnormal brown color, often appearing as if it has been charred. It also develops "cubical cracking" problems when the decayed wood dries, due to the fracture of the fibers caused during the decay process.

White-rot fungi can degrade all the components of wood cell walls, including lignin. In the early stages of decay, the wood tends to turn off-white and sometimes appears bleached. In hardwoods, black zone lines may develop in the light areas. Unless severely degraded, the wood does not crack across the grain or develop an abnormal shrinkage or collapse like the brown rotted wood. A white fibrous mass may occur in the late stages of decay. With the exception of toughness, strength properties decrease gradually. The losses in strength are generally lower than those occurring in brown rotted wood, typically ranging from 10 to 30 %. Toughness can however decrease dramatically to losses of 70 % in hardwoods with only 4 % mass loss (Eaton and Hale, 1993).

Decay resistance of wood-based composites has been studied (Behr and Wittrup, 1969), and as expected treated products show a greater resistance to decay, than untreated composites (Curling and Murphy, 1999). Previous work in combining wood preservatives with waferboard has mainly focused on inorganic systems such as ammoniacal copper arsenate (Hall and Gertjejansen, 1979) and zinc borate (Brunette et al., 1999). Relatively little research is available regarding the efficacy of formulated inorganic/organic preservatives which are added to glue to protect composites such as waferboard, against decay fungi attack.

In this chapter the efficacy of an emulsified solution of a novel fungicide containing the potassium salt of N-cyclohexyl-diazeniumdioxide (K-HDO) and fenpropimorph was examined. The treatment was applied to the furnish using a separate nozzle, but at the same time as the liquid PF resin. The main objective of this durability research component is to find the toxic threshold of the formulation with respect to standard wood decay fungi. This threshold will then be compared with that observed in commercial waferboard containing zinc borate to determine the concentration of the novel wood preservative that provides the equivalent protection to the zinc borate.

#### 5.2 Materials and methodology

#### 5.2.1 Wood samples

Three different aspen waferboards - waxed and unwaxed untreated waferboard and commercially manufactured zinc borate treated, waxed waferboard, were obtained from the Weyerhaeuser Company. In order to observe any deleterious effects of the phenol formaldehyde residue in the waferboard, the extent of decay was measured in aspen sapwood control blocks exposed to white rot fungi and southern pine sapwood control blocks exposed to brown rot fungi.

Waferboard treated with an aqueous solution of LP 15396A (K-HDO and fenpropimorph), at four different loading levels was prepared by the Weyerhaeuser Company, Washington, USA. The detailed manufacturing process was described in Section 4.2.1.4. Commercially produced, waxed waferboard with no wood preservative additives was used as the control.

#### 5.2.2 Wood decay fungi

#### 5.2.1.1 Brown-rot fungi

Two standard brown rot fungi, *Gloeophyllum trabeum* (Pers. Ex Fr.) Murr. (Madison 617, ATCC 11539) – which is particularly tolerant to phenolic and arsenic compounds, and *Postia placenta* (Fries) M. Larsen et Lombard (Madison 618, ATCC 11538) – which is particularly tolerant to copper compounds, were used.

#### 5.2.1.2 White-rot fungi

Two standard white rot fungi, Trametes versicolor (L.) Quel (FP-101664-Sp, ATCC

42462) - commonly found in decayed hardwood products, and *Pleurotus ostreatus* (Jacq. ex Fr.) Kummer (CBS 342.69) - reported on hardwoods and plywood and chipboards by Lea and Bravery (1986), were used. *P. ostreatus* has been proposed as a standard test fungus for waferboard in Europe.

#### 5.2.3 Decay evaluation

The assessment of the decay resistance imparted by the preservative treatments was conducted in accordance with AWPA E-10 method (AWPA, 2004). The fungi were grown and maintained on malt extract agar (MEA) - 2 % malt extract and 1.5 % agar by weight. Cultures of the test fungi were selected from those in the culture collection obtained from the US Forest Products Laboratory. They had been stored at -20 °C. A small plug containing fungal inoculum was removed and placed on MEA in Petri plates which had been sterilized for 30 min in steam at 103 kPa, and cooled to room temperature before inoculation. All manipulation of fungi was done under sterile conditions maintained on a laminar flow air bench. Prior to use the bench surfaces were wiped with a sterile cloth soaked in alcohol and sterilized with ultraviolet light overnight. Petri plates of the four test fungi were prepared and incubated at 25 °C for one week prior to inoculating the soil jars.

To prepare the soil jars, commercial, sterilized horticultural soil, was screened through a U.S. No. 6 sieve. The water holding capacity of the soil was determined as described in the standard. The method involved placing soil in a Buchner funnel and saturating the soil with distilled water using capillary action. The soil was then subjected to a vacuum for 15 minutes after which it was weighed and then oven dried and reweighed. The water holding capacity is defined as the weight of the water in the soil after the suction compared to the oven dry weight of the soil, expressed as a percentage. The water-holding capacity of the soil was more than 240 %.

To each cylindrical 450 ml culture jar was added 220 grams of the screened loamy soil. To increase the moisture of the soil to 130 % of the water holding capacity the required amount was determined from the above water holding capacity together with the existing moisture content of the soil. Following the addition of the distilled water, one sterile untreated southern pine (*Pinus* sp.) sapwood feeder strip (60 x 26 x 3 mm) was added to all culture jars being prepared for addition of brown rot fungi. For culture jars receiving white-rot fungi an aspen (*Populus* sp) feeder strip of similar dimensions was placed on the top of the soil in each jar. The soil jar was closed with a plastic cap. The loosely capped, soil filled jars were then, autoclaved for 30 min with steam at 103.4 kPa

After cooling the jars were transferred to a sterile laminar flow bench for the addition of the test fungi and feeder strips. Each feeder strip was then inoculated diagonally at opposite corners with a mycelial plug. The plug was cut from the actively growing edge of the seven day old culture of either a white or brown rot fungus. After inoculation, the plastic cap of each jar was immediately replaced by a sterilized metal screw lid. A small hole (approximately 3 mm in diameter) had been drilled in the metal lid and had been sealed on the inside by a Gelman 0.2 micron metrical autoclavable filter which was 25 mm in diameter (AWPA, 2004). Each inoculated bottle was then incubated at 26 °C for three weeks at which time the feeder strip had become heavily colonized by the test fungi. Culture jars of distilled water were placed in the incubator to minimize drying of the soil during incubation. This was confirmed by monitoring the weight changes in selected soil jars.

All decay tests were done with 19 x 19 x 11 mm blocks which were sawn from each waferboard (Figures 4.1 to 4.3). Two boards had been prepared for each preservative retention (See Section 4.2.4.1). Six replicate soil blocks for each fungal species were cut from each waferboard. The labeled test blocks were oven-dried and weighed to the nearest 0.001g. They were then wetted with distilled water to achieve a moisture content of approximately 30 % after which they were placed in aluminum foil and steam sterilized for 20 min. They were transferred to a laminar flow bench, where they were added to the soil jars containing the actively growing fungus. Two soil blocks from different locations in the same board were placed on the surface of the feeder strip colonized by a fungus. The jars were incubated for 12 weeks at 26 °C.

At the end of the exposure period, the test blocks were removed from the jars. The mycelium on the block surfaces was carefully removed by brushing, taking care not to lose any surface wood. After weighing, the blocks were oven-dried and weighed again. The weight loss was calculated as the percentage loss of the oven-dry sample weight before and after decay, compared to the original oven dried weight.

In determining the amount of chemical required to control decay, the toxic threshold is the concentration of total preservative active ingredients which reduces the mass loss to less than 3 %. The toxic limits are the actual concentrations of the active ingredients which

straddle the toxic threshold. The two concentrations are the lower retention which just allows a weight loss greater than 3 % and the first concentration which reduces the weight loss to 3 % or less.

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#### 5.3 Results and discussion

#### 5.3.1 Decay resistance of commercial aspen waferboard

The decay resistance of commercial, untreated and zinc borate treated, aspen waferboard is presented in Table 5.1. The data presented is the mean value of 6 blocks prepared from a commercially produced board (waxed controls and zinc borate) and a laboratory produced board (unwaxed controls). The values in parenthesis represent the standard deviation. It is possible that some component present in the resin or additives may increase the durability of the aspen waferboard compared to corresponding solid wood. To identify any enhanced durability even in untreated waferboard, solid aspen (white rot) and southern pine (brown rot) sapwood blocks were also included for reference

The southern pine sapwood blocks had an average weight loss of 39.6 % with a standard deviation of 4.5 % for *G. trabeum* and an average weight loss of 48.5 % with a standard deviation of 5.3 % for *P. placenta*. Similarly, the aspen sapwood blocks recorded an average mass loss of 50.5 % (S.D. of 11.6 %) for *T. versicolor* and an average mass loss of 18.4 % (S.D. of 8.2 %) for *P. ostreatus*. These results demonstrate excellent decay capacity for all four fungi under the conditions of the incubation for these non-durable wood species.

Waferboard test samples that received no chemical treatment were also heavily decayed when exposed to both white rot and brown rot fungi. From the data in Table 5.1 it is clear that the ability of the fungi to decay the waferboard was not influenced by the

presence of the wax. For example the mean weight loss produced by the brown rot fungus G. trabeum was 43 % in blocks prepared from unwaxed boards and 38 % in blocks cut from waxed boards. Similarly P. placenta caused a mass loss of 51 % in blocks from unwaxed waferboard and 57 % in blocks from waxed waferboard. A similar picture emerged for the white rot fungi with the mass losses of the blocks cut from an unwaxed and waxed boards being identical (29 %) when decayed by *P. ostreatus* and slightly higher at 53 % for unwaxed boards exposed to T. versicolor compared to waxed boards (48 %) for blocks cut from unwaxed boards exposed to the same fungus. Clearly the presence of wax did not prevent the fungus from decaying the waferboard. This might have been suspected since the wax could only slow the wetting of the blocks during the experiment. This clearly did not happen as the moisture contents at the end of the test were all above the 30 % needed for the blocks to decay (Table 5.1) In addition, the average moisture contents for blocks prepared from the waxed boards were in two cases higher than those for blocks prepared from the corresponding unwaxed boards, while the remaining two sets of blocks were similar. As would be expected in the presence of the zinc borate the lack of decay. inhibited any significant increase in the permeability of the wood and so the moisture content remained slightly above 30 %.

For both of the brown rot fungi, there were no significant differences in the mean weight loss between solid southern pine blocks and blocks cut from untreated waferboard. This confirmed that the presence of the phenol-formaldehyde resin does not impart any

durability to the composite. A similar comparison was also found for the white rot fungus *T*. *versicolor*. However, the second white rot fungus, *P. ostreatus* produced slightly lower weight losses in the solid wood compared to the waferboard. This may be due to the ability of the P. ostreatus to decay the other wood species present in the waferboard furnish more readily. It may also be due to the fact that the waferboard being composed of wafers with considerable end-grain may be easier to colonize than the solid wood blocks. In addition, the greater end-grain would allow a more rapid uptake of moisture than in solid wood blocks and this may also facilitate the decay.

The addition of zinc borate at 0.83 % zinc borate into aspen waferboard completely prevented fungal degradation of aspen waferboard. The average weight loss of zinc borate treated waferboard exposed to white rot and brown rot fungi ranged from 1.2 % for *P* ostreatus to 2.4 % for *G* trabeum (Table 5.1). It is generally recognized by users of the AWPA soil block method that small mass losses of up to 3 % can occur due to loss of soluble components in wood during the exposure in the soil jar. Consequently, mass losses of less than 3 % are often considered to be insignificant and that control of the fungus has been achieved at a loading of 0.83 % zinc borate (0.7 % BAE). This result is in agreement with the observations for zinc borate treated waferboard reported by Wu et. al. (2003), and, Laks and Manning (1995). Wu et al. (2003) showed that the toxic threshold for *T versicolor* and *G* trabeum for zinc borate treated waferboard made from mixed hardwoods was between 0 and 0.97 % BAE, Laks and Manning (1995) were able to establish the toxic

threshold against G. trabeum and T. versicolor more precisely as 0.45 BAE for both fungi.

Fungi type		Species Group	Moisture	Weight loss (%)
		-	content(%)	
		Aspen sapwood	46.3 (4.2)	50.5 (11.6)
	Typergianlar	Waxed waferboard	42.2 (5.9)	53.2 (6.3)
		Unwaxed waferboard	44.7 (7.1)	48.4 (5.5)
White rot		0.83 % ZnB waferboard	34.1 (3.1)	2.3 (0.8)
fungi		Aspen sapwood	35.5 (4.5)	18.4 (7.2)
	P. ostreatus	Waxed waferboard	49.6 (4.7)	29.8 (4.4)
		Unwaxed waferboard	41.3 (8.7)	29.5 (8.9)
		0.83 % ZnB waferboard	57.3 (9.3)	1.2 (0.4)
	G. trabeum	Southern pine	60.8 (5.9)	39.6 (4.5)
		Waxed waferboard	49.0 (4.5)	38.3 (4.5)
		Unwaxed waferboard	56.2 (3.7)	42.6 (2.8)
Brown rot		0.83 % ZnB waferboard	34.9 (4.2)	2.4 (0.7)
fungi		Southern pine	53.1 (7.7)	48.5 (5.3)
	D placenta	Waxed waferboard	53.5 (4.9)	56.5 (4.0)
	P. placenta	Unwaxed waferboard	47.5 (2.7)	51.2 (6.4)
		0.83 % ZnB waferboard	34.2 (8.7) <sup>-</sup>	2.1 (0.5)

Table 5.1 Decay resistance of commercial aspen waferboard

#### 5.3.2 Decay resistance of experimental waferboard incorporating the novel fungicide

Plots of the average weight loss versus target fungicide content in the waferboard exposed to two white rot fungi (*T. versicolor* and *P. ostreatus*) and two brown rot fungi (*G. trabeum* and *P. placenta*) are shown in Figures 5.1 and 5.2. A higher average weight loss corresponds to a lower resistance to fungal degradation of the wood. Where the average weight loss is less than 3 %, it is generally considered that fungal protection has been achieved since small losses of wood components can occur when the wood becomes wet. The toxic threshold was determined as that preservative retention that gave a 3 % weight loss. With all four fungi this toxic threshold was achieved at a target retention of 0.44 % or

less. This is the threshold, the minimum amount of fungicide, which is effective in preventing significant decay under the test conditions by these particular fungal species.

As shown in Figure 5.1a clear dose response relationship was observe for both of the white rot fungi (*T. versicolor* and *P. ostreatus*). The generally lower mass losses found in these experiments compared to those done earlier, can be attributed to a lack of aging in the blocks which were cut from newly prepared waferboards. The waferboards used for the first study involving waxed and unwaxed boards, as well as commercial waferboard incorporating zinc borate, were allowed to age for in excess of 6 months prior to processing to produce the blocks used for the soil block study. This would allow the any residual unreacted phenol or formaldehyde remaining in the boards to gradually dissipate. However, in the boards with the LP15396A a small amount of residual resin would slightly enhance the durability of the board reducing the overall mass losses. However, those observed are still acceptable and allow a clear dose response to be observed. Schmidt et al. (1978) have observed previously that PF-resin residues may confer some enhanced durability to particleboard resistance because of its high pH and the presence of uncondensed phenol residues. For the white rot fungi the toxic threshold was determined to be 0.44 % of LP 15396A.

The control blocks exposed to the brown rot fungus *G trabeum* also showed only moderate mass losses but again a dose response relationship was observed. In this case the toxic threshold was lower, being approximately 0.29 % LP 15396A. However, the other brown rot fungus *P. placenta* produced very large mass losses in the control blocks and the

toxic threshold was close to 0.29 % LP 15396A (Figure 5.2). The *P. placenta* was markedly affected by the fungicide, with even small amounts causing a dramatic decrease in the amount of decay found.

The ability of *G trabeum* to decay both untreated and treated waferboard is shown in Figure 5.3. It is noted that the weight loss produced in the blocks cut from the hand made control boards is lower than those produced in the commercial material. However, they are comparable to those reported by Schmidt et al., (1983). The slight difference in decay resistance of these controls is not significant and probably arises from the fact (discussed earlier) that the waferboards were not aged before the soil blocks were cut. In addition, in the experimental boards, the furnish was composed of mixed non-durable hardwoods with some southern pine. Generally, low density hardwoods such as aspen are none durable. However, the presence of any southern pine heartwood will enhance the decay resistance slightly as it is rated as moderately durable. This may also increase the variability of the mass losses observed for different boards.

The commercially produced waferboard with a zinc borate content of 0.83 % (0.7 % BAE) produced an acceptable protection with a mass loss ranging from 1.2 % for *P. ostreatus* to 2.4 % for *G trabeum*. It may then be observed from the data in Figures 5.1 to 5.3 that 0.29 % of LP 15396A can provide equivalent protection against the brown rot fungi while 0.44 % LP 15396A is needed to protect the waferboard from decay by the white rot fungi.

It is also possible to compare the efficacy of the zinc borate and the LP 15396A against

the individual fungi. For example 0.83 % zinc borate reduced the mass loss of the waferboard produced by *T. versicolor* to 2.3 % compared to 2.2 % with 0.44 % of LP 15396A. Similarly, *P. ostreatus* caused a mass loss of 1.2 % in the zinc borate treated waferboard (0.83 %) which may be compared to a mass loss of 2.2 % at 0.44 % LP 15396A. Clearly the LP 15396A is a more effective preservative against white rot fungi than zinc borate. However, for successful implementation of a new system the cost effectiveness has also to be considered.

Turning to the brown rot fungi, *G. trabeum* produced a mass loss of 2.4 % in the zinc borate (0.83 %) blocks while the LP 15396A at 0.29 % reduced the mass loss to 2.0 %. The other brown rot fungus *P. placenta* caused a weight loss of 2.1 % in the (0.83 %) zinc borate treated blocks while 0.29 % of LP 15396A limited the mass loss to 1.3 %. So again the LP 15396A is a more effective preservative.

Comparing the efficacy of the LP 15396A it appears from the data that the formulation is most active against brown rot fungi, as illustrated by the lower amount required to reach a toxic threshold corresponding to a 3 % mass loss.

It is interesting to note the variation present in the degree of decay in blocks cut from the same waferboard. This is illustrated by the standard deviations. These are generally similar for the two treatments although occasionally the standard deviation increases for blocks cut from the LP 15396A blocks. The variations in weight loss are typical of those observed in standard decay tests and can arise due to variations in fungal vigor, changes in the microclimate in the blocks, as well as uneven distribution of the fungicide in the board

during manufacture. However, the limited number of boards produced during this research (two) prevents any extended discussion of the variability.

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Figure 5.2 Average weight losses due to decay by brown rot fungi



Figure 5.3 Weight loss of waferboard tested against G.trabeum

#### **5.4 Conclusions**

A zinc borate retention of 0.83 % (0.7 % BAE) provided complete protection for commercial aspen waferboard against two brown rot fungi (*G trabeum* and *P. placenta*) and two white rot fungi (*T. versicolor* and *P. ostreatus*). Untreated unwaxed and waxed aspen waferboard was susceptible to decay. Wax on the waferboard surface had no effect on fungal decay when the waferboard blocks were exposed to high decay environment.

The results for both the brown- and white-rot soil block decay experiments confirmed a clear dose response relationship, i.e. the weight loss was proportional to the LP 15396A content. In the case of the brown-rot fungi, the toxic threshold was achieved at 0.29 % LP 15396A (active ingredient). For the white rot fungi higher LP 15396A retention of 0.44 % (active ingredient) was required to achieve the toxic threshold. The novel fungicide LP 15396A, (an emulsified aqueous solution of K-HDO and fenpropimorph) at active ingredient loading level of greater than or equal to 0.44 %, provided waferboard with complete protection from all four fungi. This is approximately 50 % of the amount of zinc borate required to provide equivalent protection. However, the cost effectiveness of the LP 15306A is not known.

#### Chapter 6

#### **Summary and conclusions**

The results on compatibility based on changes in gelation time and viscosity indicated that preservative type, preservative retention level, and adhesive type affect their mutual compatibility. Generally, the wood preservative formulation based on inorganic based active ingredients, especially the fungicide LP 15396B (K-HDO aqueous solutions), were incompatible with PF- and pMDI-resins. The solvent-based wood preservatives, for example, the termiticides LP 15406A, LP 15406B and LP 15447, showed better compatibility with PF- and pMDI-resin. Among the eight liquid PF-resins, BB7028 showed the best compatibility with the termiticides. Two other PF-resins GP70CR66 and GP265C54 and pMDI-resin showed some compatibility with all three termiticides although some changes in viscosity or gelation time were recorded.

Zinc borate is now used in North America as a commercial additive to waferboard to enhance its durability. This strategy is supported by the available research data. The observations in the current research of the mass losses produced in a soil block test are consistent with these previous results. A wood preservative retention of 0.83 zinc borate (0.7% BAE) provided complete protection for commercial aspen waferboard against two brown rot fungi (*G trabeum* and *P. placenta*) and two white rot fungi (*T. versicolor* and *P. ostreatus*).

The examination of the test fungicide LP 15396A against the same four fungi also confirmed a clear dose response relationship, between the weight loss and the active
ingredient content of the novel fungicide. LP 15396A (an emulsion of KHDO and fenpropimorph) at an active ingredient loading level of greater than or equal to 0.44%, provided the aspen waferboard with complete protection from all white rot and brown rot fungi tested. At this concentration there was no adverse effect on static bending strength, but there was a slight (15%) loss in IB strength. The amount of LP 15396A required to provide protection against all four fungi is approximately 50 % of the amount of zinc borate required to provide equivalent protection. The LP 15396A was more effective against the brown rot fungi (toxic threshold 0.29 %) than against white rot fungi (0.44 %). The results on decay testing and mechanical strength both suggested that, the LP 15396A could be effectively spray-applied to furnish simultaneously with PF resin GP70CR66 and GP265C54 for manufacturing waferboard to improve its fungal resistance properties.

The addition of three termiticides into PF resin had no significant effect on IB strength. However, the effects on static bending strength were different. LP 15406A did not negatively affect MOE and MOR. LP 15406B had no effect on MOR, but significantly increased MOE. With LP 15447, the similar trend on MOR and MOE was observed as LP 15406B. These results reflect that all three termiticides are desirable additives to be successfully incorporated into PF resin for making waferboard within the range of contents tested. As with pMDI-resin waferboard treated with termiticides, the results on mechanical strength indicate that, LP 15406A, with 0.0052% bifenthrin content in waferboard, is the most promising termiticide to be added to pMDI-resin for waferboard because its treatment did not cause any negative effect on mechanical properties. LP 15406B, with 0.0073%

chlorfenapyr content in waferboard, could be added to pMDI-resin. However, care should be taken since its treatment did cause a 14.1% mean IB loss although the IB loss was not statistically significant. LP 15447, with 0.0052%5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(1R,S)-(trifluoromethyl)-sulfinyl]-1H-pyrazol-3-carbonitrile content in waferboard, can not be added to pMDI-resin since its treatment caused a 57.9% mean IB loss.

# Chapter 7

# Recommendations

The impact of the fungicide, LP 15396A, on mechanical strength requires further work. The current research on mechanical strength indicated that LP 15396A caused a 15% loss in IB strength which was lower than that for the zinc borate treated waferboard. Such changes can be minimized in practice through the application of more PF resin or addition of organic flowing agents containing hydroxyl (-OH) groups such as polyethylene glycol (PEG) and further research should examine these aproaches.

An important extension of this research is to determine the laboratory and field termite thresholds for the three termiticides. These are now being initiated in Hawaii. It would also be useful to determine the uniformity of the chemical in the waferboard. This will require significant chemical analysis which is beyond the scope of the current project. Some analytical data is now in progress and should confirm the role of preservative distribution on the variation in the resistance to fungal degradation as determined by the standard deviations in the soil block test.

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## **Appendix A**

# The conversion of the loading levels from Dr. Wolman GmbH to the wood preservative concentrations (5 % resin)

The conversion of the loading levels recommended from Dr. Wolman to the concentrations of wood preservatives was based on 720 kg/m<sup>3</sup> OSB density, 5 % resin of OSB product. For example, for 150 g/m<sup>3</sup> loading level of LP 15406A, and 5 % resin with a board density of 720 kg/m<sup>3</sup> equates to 36 kg/m<sup>3</sup> of formulated preservative. So, the concentration of LP 15406A for the resin was 4.2  $\mu$ g of LP 15406/mg of resin (150 g/m<sup>3</sup> : 36 kg/m<sup>3</sup> = 4.2 g:1 kg = 4.2  $\mu$ g:1 mg resin). For 0.73 % m/m loading level of LP 15396B, the concentration of LP 15396B for the amount of  $\mu$ g wood preservative per mg resin was 250  $\mu$ g/mg (0.73 % m/m : 5 % m/m = 146 g:1 kg =146 $\mu$ g: 1mg). The detailed concentration for each sample is listed in Table A. The concentration conversion from g wood preservative/kg resin to g wood preservative/kg oven-dry furnish is based on 5 % resin, 1 % wax of OSB product. For example, for 0.73 % m/m loading level of LP15396B, the concentration of LP 15396B for the amount of  $\mu$ g wood preservative per mg furnish was 7.83  $\mu$ g/mg (0.73 % m/m : 93.27 % m/m = 7.83 g:1 kg=7.83  $\mu$ g:1 mg).

	1 4010 7		i preservative e	oncentrations.	
Trade name	Loading level from Dr Wolman	Resin Content	Concentrations (µg wood preservative/m g resin)	Concentrations (g wood preservative/kg oven-dry furnish)	Concentrations (g active ingredient /kg oven-dry furnish)
	$150 \text{g/m}^3$		4.2	0.22	0.045
I P 15406A	$250 \text{ g/m}^3$	$36000  a/m^3$	7.0	0.37	0.074
LI 15400A	$350 \text{ g/m}^3$	50000g/III	10.0	0.53	0.106
LP 15406B	80g/m <sup>3</sup> 140 g/m <sup>3</sup> 200 g/m <sup>3</sup> 350 g/m <sup>3</sup>	36000g/m <sup>3</sup>	2.2 3.9 5.6 9.7	0.12 0.21 0.30 0.52	0.029 0.052 0.074 0.129
I P 15447	$570 \text{g/m}^3$ 1000 \text{g/m}^3	36000g/m <sup>3</sup>	15.8 27.8	0.84 1.48	0.042 0.074
LI 13447	1430g/m <sup>3</sup>	30000g/m	40.0	2.13	0.107
	0.66 %m/m 1.00 %m/m		132 200	7.07 10.75	2.005 3.048
LP 15396A	1.5 %m/m 2.25 %m/m	5 %m/m	300 450	16.22 24.52	4.597 6.952

# **Appendix B**

This appendix lists the results for ANOVA analyses for results contained in Chapter 4. Listed below are headings that denote the treatment and the properties of concern for each analysis.

#### Fungicide LP 15396A (Table 4.4)

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Treatment: Fungicide LP 15396A Property: IB Density

Analysis of Variance					
source	degrees of	sum of	mean	E Ratio	Prob>F
	freedom	squares	square	T Ratio	1100-1
model	4	0.096434	0.024108	5.732	0.0002
error	173	0.727628	0.004206		
c total	177	0.824062	0.004656		

treatment	fungicide concen- tration	n	mean	standard deviation	standard error
Control-PF	0	36	669.131	25.9401	4.3233
396A-1	0.21	36	668.494	33.9504	5.6584
396A-2	0.29	36	662.839	45.8776	7.6463
396A-3	0.44	36	685.522	43.8581	7.3097
396A-4	0.67	36	677.761	41.4639	6.9106
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#### Treatment: Fungicide LP 15396A Property: IB Strength

	10 L				
Analysis of Variance					
source	degrees of	sum of	mean	E Ratio	Proh>F
Source	freedom	squares	square	i nato	1100-1
model	4	0.096434	0.024108	5.732	0.0002
error	173	0.727628	0.004206		
c total	177	0.824062	0.004656		

treatment	fungicide concen- tration	n	mean	standard deviation	standard error
Control-PF	0	36	0.303003	0.061424	0.01024
396A-1	0.21	36	0.228219	0.078623	0.0131
396A-2	0.29	36	0.250856	0.069303	0.01155
396A-3	0.44	36	0.244233	0.074331	0.01239
396A-4	0.67	-36	0.252231	0.061567	0.01026

# Treatment: Fungicide LP 15396A Property: MOE/MOR Density

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Analysis of Variance					
source	degrees of	sum of	mean	E Ratio	Prob>F
	freedom	squares	square	T Malio	1100-1
model	4	10633.38	2658.35	5.4399	0.0009
error	55	26877.3	488.68		
c total	59	37510.68	635.77		· · · · ·

treatment	fungicide concen- tration	n	mean	standard deviation	standard error
Control-PF	0	12	645.833	26.0173	7.5106
396A-1	0.21	12	645.817	19.4629	5.6184
396A-2	0.29	12	661.483	15.7526	4.5474
396A-3	0.44	12	670.2	25.5593	7.3783
396A-4	0.67	12	679.483	22.0514	6.3657

#### Treatment: Fungicide LP 15396A Property: MOR

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		Analysis of	Variance		
source	degrees of	sum of	mean	E Ratio	Prob>E
source	freedom	squares	square	r Natio	
model	4.	48.96433	12.2411	1.2566	0.2981
error	55	535.7575	9.741		
c total	59	584.7218	9.9105		

treatment	fungicide concen- tration	n	mean	standard deviation	standard error
Control-PF	0	12	19.175	2.23774	0.646
396A-1	0.21	12	17.7333	2.25402	0.6507
396A-2	0.29	12	19.2583	2.8008	0.8085
396A-3	0.44	12	20.2417	4.24809	1.2263
396A-4	0.67	12	20.15	3.5674	1.0298

#### Treatment: Fungicide LP 15396A Property: MOE

		Analysis of	Variance		
0.011500	degrees of	sum of	mean	E Patio	ProbSE
source	freedom	squares	square	T Natio	
model	4	1617655	404414	2.5932	0.0463
error	55	8577467	155954		
c total	59	10195121	172799		
	fungicide			standard	standard
treatment	concen-	n	mean	deviation	orror
	tration			deviation	enoi
Control-PF	0	12	2735.5	289.607	83.6
396A-1	0.21	12	2868.67	453.586	130.94
396A-2	0.29	12	3031.5	269.867	77.9
396A-3	0.44	12	3219.5	487	140.58
396A-4	0.67	12	3031.5	424.452	122.53

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# Termiticides (Table 4.6)

Treatment:	Termiticides
Property:	IB Density

		Analysis of	Variance		
source	degrees of	sum of	mean	E Potio Proba	
	freedom	squares	square	1 IXalio	
model	9	22457.97	2495.33	1.7691	0.0748
error	241	339929.2	1410.49		
c total	250	362387.2	1449.55		

treatment	fungicide concen- tration	n	mean	standard error
Control-PF	0	36	669.131	6.2594
406A-1	0.003	24	652.196	7.6662
406A-2	0.0052	23	670.77	7.8311
406A-3	0.0074	24	652.158	7.6662
406B-1	0.0044	24	674.779	7.6662
406B-2	0.0073	24	664.842	7.6662
406B-3	0.01	24	671.283	7.6662
447-1	0.003	24	664.746	7.6662
447-2	0.0052	24	671.967	7.6662
447-3	0.0074	24	686.246	7.6662

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#### Treatment: Termiticides Property: IB Strength

Analysis of Variance						
source	degrees of	sum of	mean	E Ratio	Proh>E	
	freedom	squares	square	1 Malio	F100-1	
model	9	0.070399	0.007822	1.6088	0.1132	
error	241	1.171732	0.004862			
c total	250	1.242131	0.004969			

treatment	fungicide concen- tration	n	mean	standard error
Control-PF	0	36	0.303003	0.01162
406A-1	0.003	24	0.2779	0.01423
406A-2	0.0052	23	0.292552	0.01454
406A-3	0.0074	24	0.297687	0.01423
406B-1	0.0044	24	0.291504	0.01423
406B-2	0.0073	24	0.284904	0.01423
406B-3	0.01	24	0.270138	0.01423
447-1	0.003	24	0.264996	0.01423
447-2	0.0052	24	0.315454	0.01423
447-3	0.0074	24	0.3187	0.01423

#### Treatment: Termiticides Property: MOE/MOR Density

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		Analysis o	f Variance		
source	degrees of	sum of	mean	E Patio	DrobhE
	freedom	squares	square	r Raliu	
model	9	13143.24	1460.36	3.0652	0.0026
error	110	52408.36	476.44		
c total	119	65551.6	550.85		

treatment	fungicide concen- tration	n	mean	standard error
Control-PF	0	12	645.833	6.3011
406A-1	0.003	12	656.417	6.3011
406A-2	0.0052	12	654.017	6.3011
406A-3	0.0074	12	657.733	6.3011
406B-1	0.0044	12	675.375	6.3011
406B-2	0.0073	12	668.692	6.3011
406B-3	0.01	12	679.817	6.3011
447-1	0.003	12	673.067	6.3011
447-2	0.0052	12	672.233	6.3011
447-3	0.0074	12	669.85	6.3011

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#### Treatment: Termiticides Property: MOR

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Analysis of Variance						
source	degrees of	sum of	mean	E Ratio Probal		
	freedom	squares	square	i Ralio		
model	9	108.7624	12.0847	1.5409	0.1425	
error	110	862.7175	7.8429			
c total	119	971.4799	8.1637			

treatment	fungicide concen- tration	n	mean	standard error
Control-PF	0	12	19.175	0.80844
406A-1	0.003	12	18.8917	0.80844
406A-2	0.0052	12	17.3	0.80844
406A-3	0.0074	12	18.5833	0.80844
406B-1	0.0044	12	19.9583	0.80844
406B-2	0.0073	12	19.4	0.80844
406B-3	0.01	12	20.4833	0.80844
447-1	0.003	12	20.6333	0.80844
447-2	0.0052	12	19.2167	0.80844
447-3	0.0074	12	20.2	0.80844

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#### Treatment: Termiticides Property: MOE

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447-3

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		Analysis of	<sup>f</sup> Variance		
source	degrees of	sum of	mean	E Patio	ProbNE
source	freedom	squares	square	T Natio	
model	9	2579228	286581	2.7397	0.0063
error	110	11506221	104602		
c total	119	14085449	118365		
	fungicide			standard	
treatment	concen-	n	mean	Stanuaru	
	tration			enor	
Control-PF	0	12	2735.5	93.364	
406A-1	0.003	12	3070.67	93.364	
406A-2	0.0052	12	2839.67	93.364	
406A-3	0.0074	12	3000.33	93.364	
406B-1	0.0044	12	2966.17	93.364	
406B-2	0.0073	12	3216.58	93.364	
406B-3	0.01	12	3230.25	93.364	
447-1	0.003	12	3113	93.364	

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## Termiticides with pMDI resin (Table 4.8)

Analysis of Variance						
source	degrees of	sum of	mean	E Ratio	Prob>E	
	freedom	squares	square	T INALIO		
model	3	383.3	127.77	0.0725	0.9746	
error	92	162143.9	1762.43			
c total	95	162527.2	1710.81			

Treatment: Termiticides with pMDI resin Property: IB Density

treatment	fungicide concen- tration	n	mean	standard error
Control-pM	0	24	658.386	8.5694
406A	0.0052	24	662.203	8.5694
406B	0.0073	24	662.516	8.5694
447	0.0052	24	658.353	8.5694

Treatment: Termiticides with pMDI resin Property: IB Strength

Analysis of Variance					
source	degrees of	sum of	mean	E Ratio	Prob>E
	freedom	squares	square	I Matto	1100-1
model	3	0.229871	0.076624	13.3807	<.0001
error	92	0.526832	0.005726		
c total	95	0.756704	0.007965	· · ·	۰. <sup>۲</sup>

treatment	fungicide concen- tration	. N	mean	standard error
Control-pM	0	24	0.330333	0.01545
406A	0.0052	24	0.28997	0.01545
406B	0.0073	24	0.327955	0.01545
447	0.0052	24	0.209302	0.01545

#### Treatment: Termiticides with pMDI resin Property: MOE/MOR Density

Analysis of Variance						
source	degrees of	sum of	mean	E Ratio – Proha		
	freedom	squares	square	1 Matio	1100-1	
model	3	6390.698	2130.23	3.6198	0.0204	
error	43	25305	588.49			
c total	46	31695.69	689.04			

treatment	fungicide concen- tration	n	mean	standard error
Control-pM	0	12	662.342	7.0029
406A	0.0052	12	673.758	7.0029
406B	0.0073	11	692.182	7.3143
447	0.0052	12	687.3	7.0029

# Treatment: Termiticides with pMDI resin Property: MOR

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		Analysis of	Variance		
source	degrees of	sum of	mean	E Ratio	Prob>E
Source	freedom	squares	square	T Matio	
model	. 3	156.0977	52.0326	4.9302	0.005
error	43	453.8189	10.5539		
c total	46	609.9166	13.2591		

treatment	fungicide concen- tration	ņ	mean	standard error
Control-pM	0	12	18	0.93781
406A	0.0052	12	20.675	0.93781
406B	0.0073	11	23.1545	0.97951
447	0.0052	12	21.1417	0.93781

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#### Treatment: Termiticides with pMDI resin Property: MOE

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Analysis of Variance						
	degrees of	sum of	mean	E Potio	BrobsE	
source	freedom	squares	square	F Nalio		
model	3	3013780	1004593	6.1159	0.0015	
error	43	7063113	164258			
c total	46	10076893	219063			

treatment	fungicide concen- tration	n	mean	standard error
Control-pM	0	12	2922.42	117
406A	0.0052	12	3276.33	117
406B	0.0073	11	3642.64	122.2
447	0.0052	12	3333.67	117

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