In-process Protection of Wood Composites
An Industry Perspective

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Protection of Wood Composites

Key Attributes of an In-process Biocide Additive

1. Adhesive bond interference
2. Processing stability
3. Limited volatility
4. No negative impact on strength properties
5. Have relatively low immobility from wood composite.

} Safety, Technical, Regulatory, Environmental, Economics

P.E. Laks & R.D. Palardy. 1993. Properties and Process Considerations for Preservative Containing Waferboards. In Proceedings: Protection of Wood-Based Composite Products. Forest Products Society. Madison, WI. Pg. 12-17.

Key Attributes of an In-process Biocide Additive

Safety →

Technical

Regulatory

Environmental

Economics

- Toxicology Profile – biocide & treated wood composite
- Safe storage at manufacturing facility (containment)
- Dilution or other special handling before use?
- Will the use of the biocide produce unsafe volatiles during pressing?

Key Attributes of an In-process Biocide Additive

Safety

Technical →

Regulatory

Environmental

Economics

Stability of formulation in (bulk) storage

RTU or on-site tank mixing?

Are process equipment changes needed?

Can the biocide be uniformly applied?

Is biocide resistant to process variables?

Key Attributes of an In-process Biocide Additive

Safety

Technical

Regulatory

Environmental

Economics

- Is biocide compatible with adhesives being used?
- Is the biocide compatible with intended end use?
- Can the biocide be easily assayed on site?
- Will the supplier provide (ongoing) support?

Key Attributes of an In-process Biocide Additive

Safety

Technical

Regulatory →

Environmental

Economics

For the biocide: Applicable federal, state and local registrations

At the manufacturing plant: permits

For the finished product: building code (ICC) and association (WDMA, AWPA) approvals / recognitions

Key Attributes of an In-process Biocide Additive

Safety

Technical

Regulatory

Environmental →

Economics

Recycle / Re-use of manufacturing waste

Recycling considerations for job site downfall & OEM facility

Disposal

Key Attributes of an In-process Biocide Additive

Safety

Technical

Regulatory

Environmental

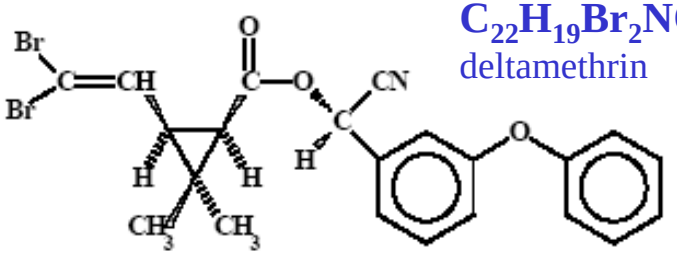
Economics →

Does treatment cost + delivered performance = value?

Will the market bear increased cost of product / recognize value of increased performance?

Is treated wood composite competitive with alternate material, like steel?

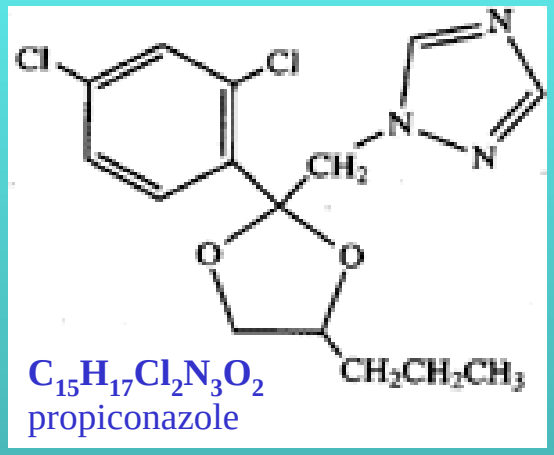
Organic & Inorganic Actives



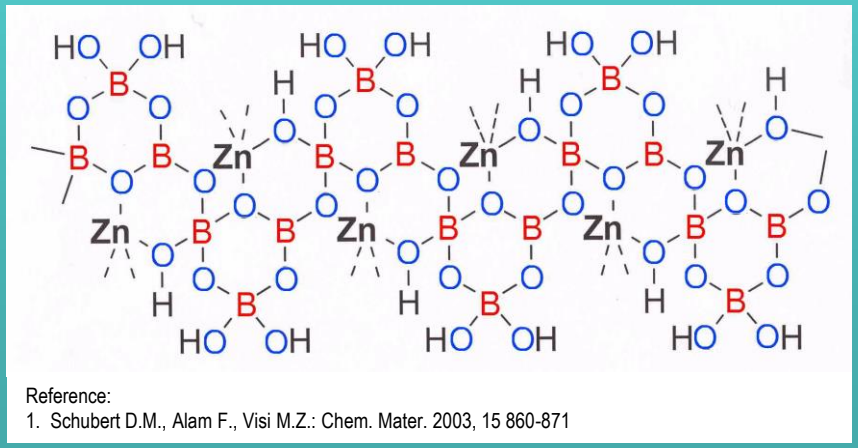
$C_{22}H_{19}Br_2NO_3$
deltamethrin

Copper Ammonium Acetate (CAA) – Comptec™

Copper Ammonium Carbonate (CAC) - Compsol™



$C_{15}H_{17}Cl_2N_3O_2$
propiconazole



Reference:
1. Schubert D.M., Alam F., Visi M.Z.: Chem. Mater. 2003, 15 860-871

$2ZnO•3B_2O_3•3.5H_2O$

1. Borogard® ZB

2. ZB-Shield

3. Storshield™ ZB2335

Borates for Wood & Wood Composites

Borates Evaluated or Considered for Wood Composites				
Common Name		Molecular formula	% B_2O_3	Water Sol.
Boric Acid		$B(OH)_3$	56.3	4.8 - 5.6
Zinc borate		$2ZnO•3B_2O_3•3.5H_2O$	48.2	**0.28**
Sodium Borate	decahydrate	$Na_2•B_4•O_7•10H_2O$	36.5	4.9
	pentahydrate	$Na_2•B_4•O_7•5H_2O$	47.8	4.5
	anhydrous	$Na_2•B_4•O_7$	77.8	5.8
	disodium octaborate	$Na_2•B_8•O_{13}•4H_2O$	67.1	9.5+
Calcium borate (colemanite)		$Ca_2B_6O_{11}•5H_2O$	~42	1.0

Ref:

Laks, P.E. and M.J. Manning. Inorganic Borates as Preservative Systems for Wood Composites Second Pacific Rim Bio-Based Composites Symposium. Vancouver, Canada. 1994

Product Data Sheets. US Borax, Valencia, CA.

Kirk-Othmer Encyclopedia of Chemical Technology 4th Edition. Volume No. 4. 1992.

Synthesis and Manufacturing of Zinc Borate

$$2ZnO + 6H_3BO_3 \rightleftharpoons 2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O + 5.5H_2O$$

- Zinc borate is a precipitate from a reaction mixture of zinc oxide & boric acid
- Variations in the process will yield slightly different types of reaction products
- 12 reaction products were identified by Schubert et. al.

Examples of Zinc Borate Products

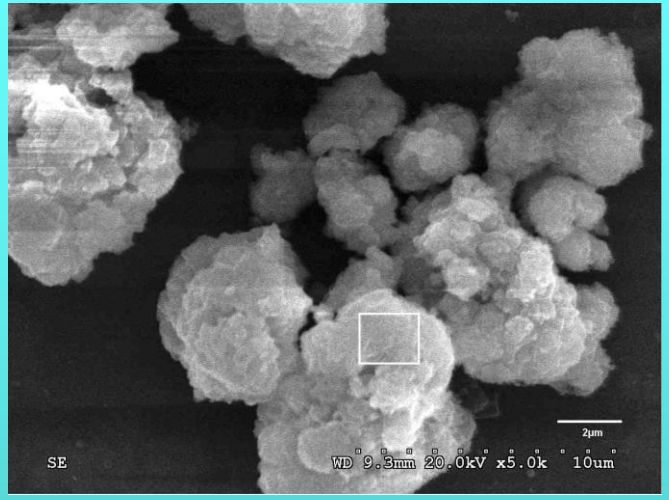
Examples of Zinc Borate Compounds					
Commercial Reference	Chemical formula	% ZnO	% B_2O_3	%H_2O	Water Sol.
ZB2335	$2ZnO•3B_2O_3•3.5H_2O$	38.2	48.2	13.6	0.28
ZB223	$2ZnO•2B_2O_3•3H_2O$	43.5	34.2	19.2	0.04

Note:
2335 form standardized by AWPA & registered by EPA for wood preservation
223 & 2335 forms used as a fire retardant & smoke suppressant in plastics industry.

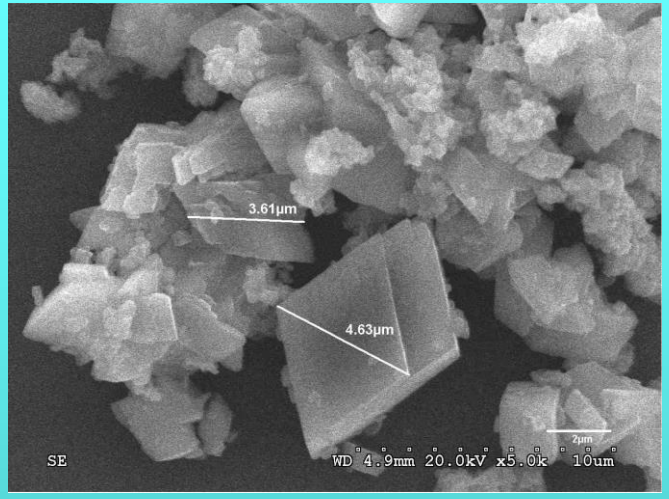
Important features to consider

- **Particle size & geometry**
- **Purity of product**

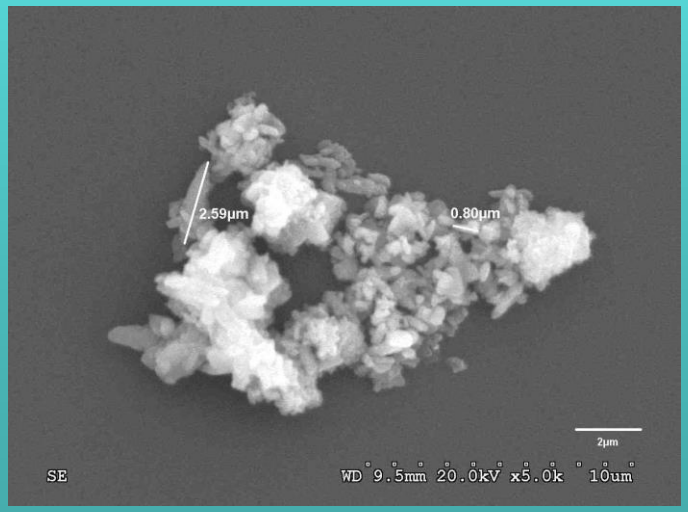
Zinc Borate 2335 Geometry (5000x)



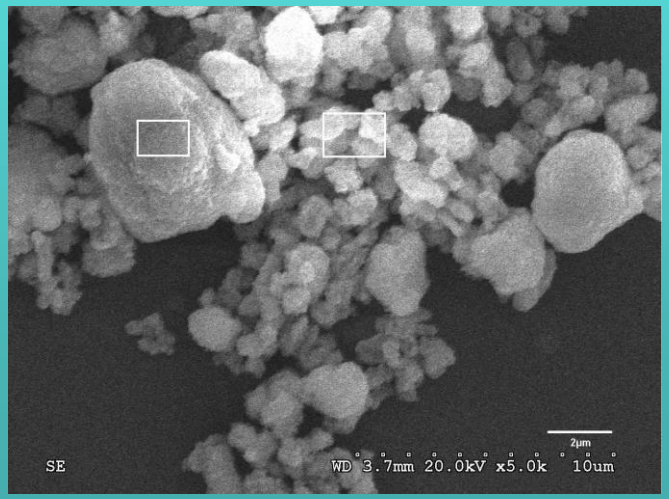
Zinc Borate 1



Zinc Borate 2



Zinc Borate 3



Zinc Borate 4

Commercial Zinc Borate Purity

Element	Concentration in Zinc Borate ppm				Detection Limit
	A	B	C	D	
Antimony	-	-	1660	-	0.2
Arsenic	-	-	16	6	0.2
Barium	-	-	2	234	0.2
Cadmium	0.5	0.7	5	9	0.04
Calcium	1060	1230	1330	1030	10
Chromium	0.6	2.3	-	-	0.2
Copper	12	6	8	7	0.2
Lead	3	4	45	434	0.2
Sodium	95	-	689	143	10
Strontium	0.5	-	19	34	0.2

Zinc Borate Application

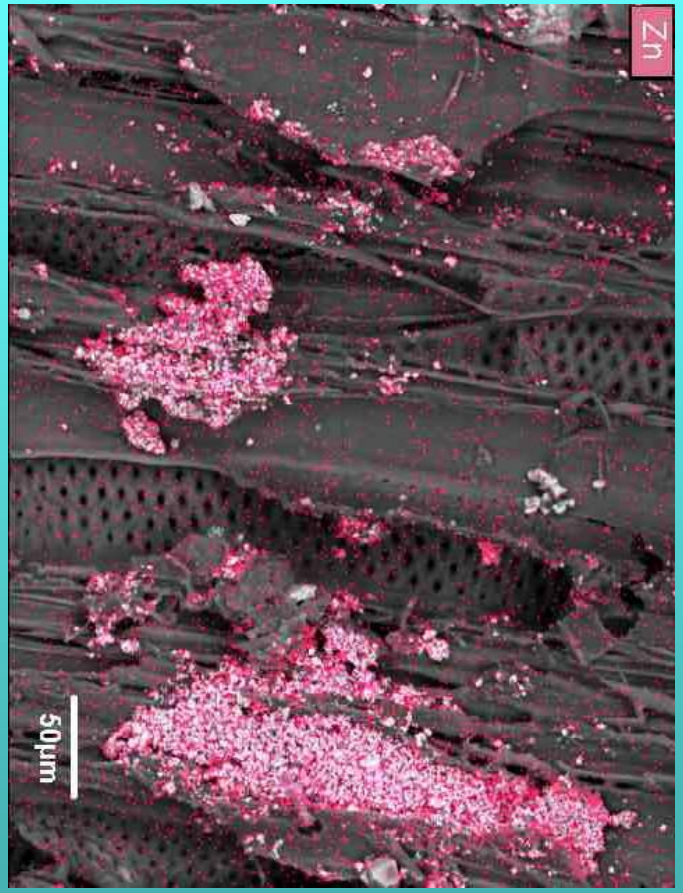
Powder

Liquid (high solids dispersion)

- **Zinc borate is stable in a concentrated, high solids dispersion**

References:
1. Fookes D., Gnatowski M., US Patent 5,972,266
2. Knudson R., Gnatowksi M., US Patent 4,879,083
3. Schubert D.M., Alam F., Visi M.Z.: Chem. Mater. 2003, 15 860-871
4. Gnatowski M.J., Unpublished report 2002

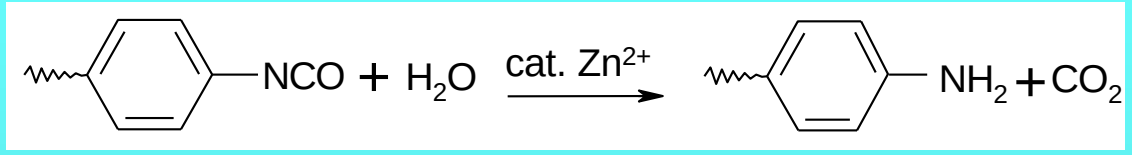
Zinc Borate in the LSL Wood Composite

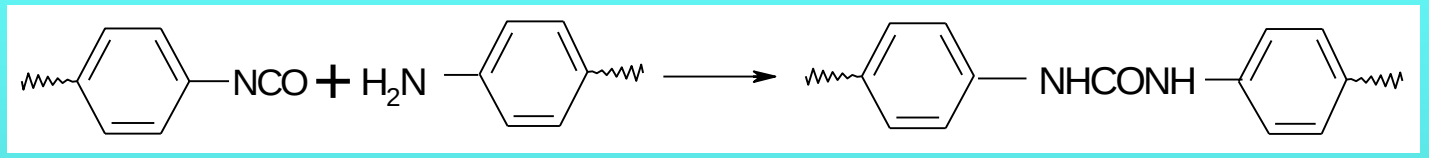


- **In the LSL process, additives like zinc borate, will be distributed between the wood strands, in the adhesive zone.**
- **A portion of ZB, or any additive, may be absorbed or otherwise bound in the adhesive itself.**
  - **Enough must be free to provide for bio-efficacy.**
- **Potential exists for negative physical & chemical interaction of the ZB with adhesive, resulting in lower IB**

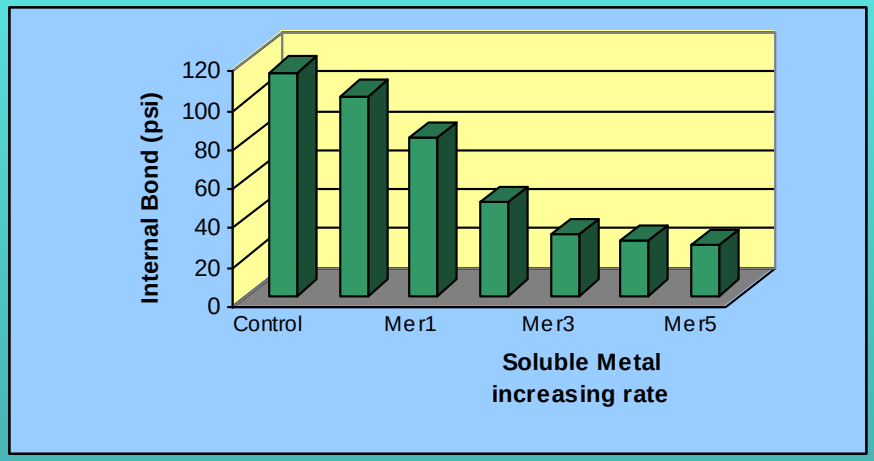
Larkin, G.M., P.E. Laks & M.P. Nelson. The Microdistribution of Borate Preservatives in Flake-Based Wood Composites. In proceedings: Enhancing the Durability of Lumber and Engineered Wood Products. Forest Products Society. 2002. pg. 115-118.

Isocyanate Adhesive Interaction





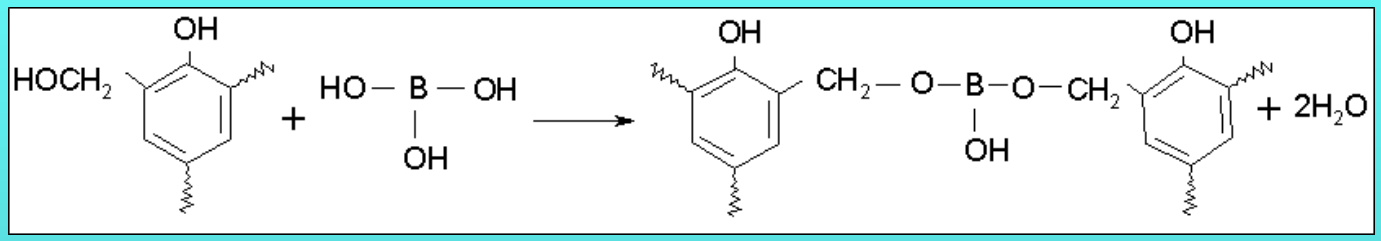
- Zinc (and many metal) ions have potential to catalyze the reaction leading to cross linking of MDI adhesive prior to bonding to wood substrate
- Commercially this is not experienced, because zinc borate is not appreciably soluble in MDI resin



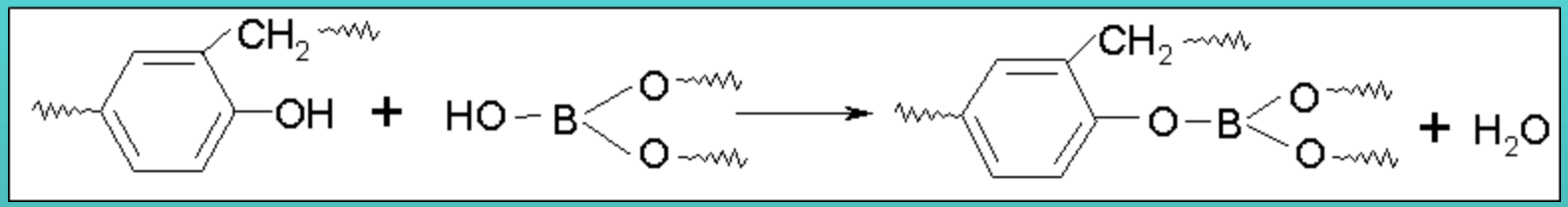
Reference:
1. Borsus J.M., Jerome R., Teyssie Ph., J. of Appl. Poly. Sc., 2003,26, 3027-3043
2. Trus Joist Research, unpublished.

Phenolic Adhesive Interactions

1 – boric acid reaction with methylol groups of PF



2 – boric acid reaction with phenol groups of PF



References:

1. Goa J.G., Liu Y.F., Wang F.L., Eur. Polym.J. 2001, 37, 207-210
2. Knudson R., Gnatowksi M., US Patent 4,879,083
3. Sean, S. T., US Patent 5,763,338
4. Xia Liya, Gou Jungang, Yu Zhenxia, 2004 www.chinachemistry.com
5. Knop A., Scher B.W., Chemistry and Application of Phenolic Resins, Springer-Verlag, Berlin, Heidleberg, New York , 1979

Hydrolysis of Zinc Borate

$$2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O + 7.5H_2O \rightleftharpoons 2Zn(OH)_2 \downarrow + 6H_3BO_3$$

- **Slow hydrolysis of zinc borate into boric acid & hydrated zinc oxide supplies active ingredients for protection of wood composite against insects and decay.**
- **Hydrolysis is important to enable active to move from glue line into wood fibers themselves.**
- **Hydrolysis & subsequent diffusion into the wood improves distribution of actives within the composite.**
- **Zinc borate hydrolysis mechanism in wood likely has some similarities to the hydrolysis of zinc borate in a diluted dispersion; as tested by Shubert et. al.[1]**

References:
1. Schubert D.M., Alam F., Visi M.Z.: Chem. Mater. 2003, 15 860-871
2. Gnatowski M.J., Unpublished report 2002
3. Fookes D., Gnatowski M.J., Pike R.L., Templeton D.A.: Pat. 5,972,266

Zinc Borate meets the key attributes….

- Safe for us to use in manufacturing
- Easy to store and apply
- Process compatibility: press & adhesive
- Real-time quality assurance testing using XRF
- Biological activity against both decay fungi & insects (up to UC3a)
- Cost effective
- Finished product is safe for our customers to use