Formaldehyde and standards in board products

Dr Morwenna Spear

Contents

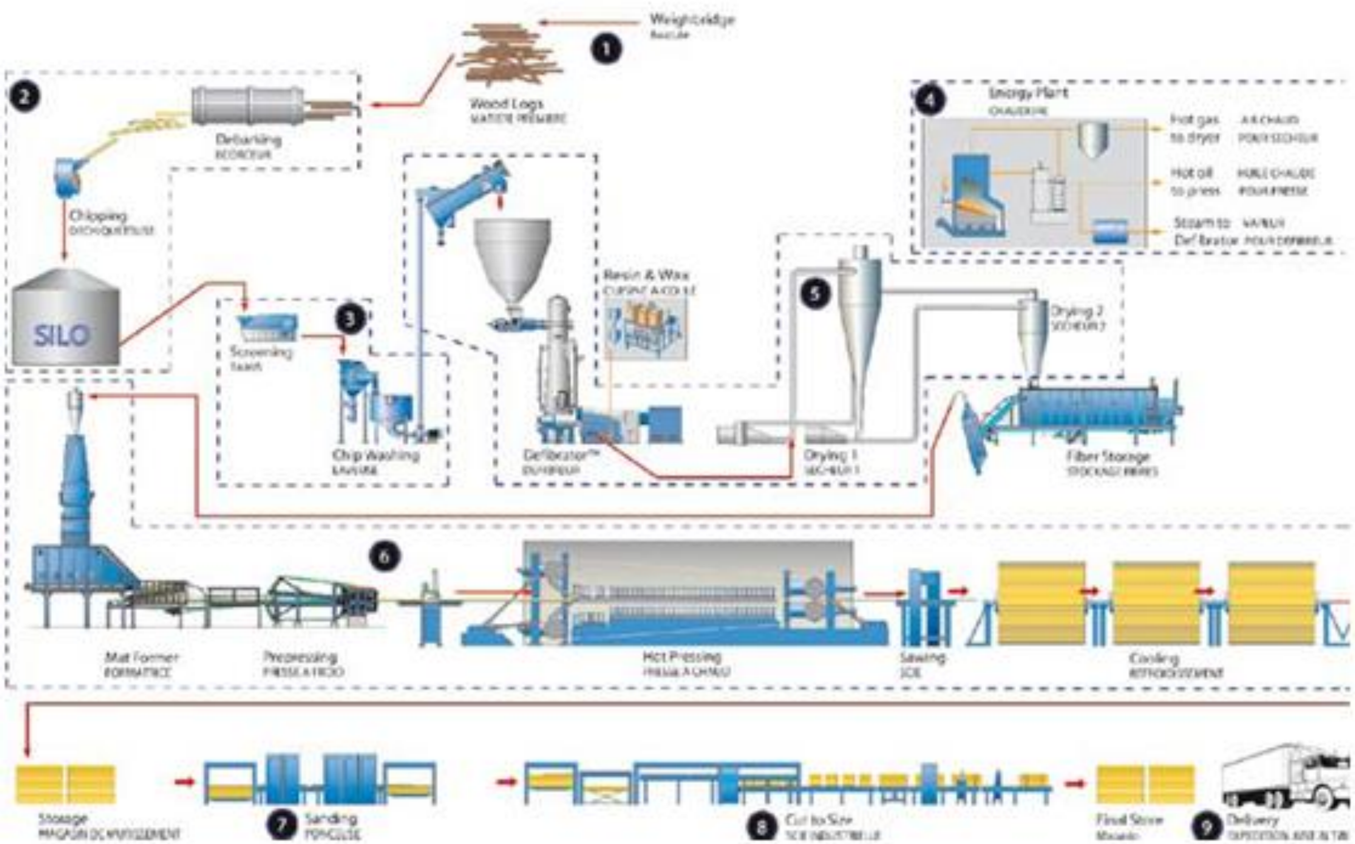
- VOCs in wood based panels
- Formaldehyde measurement
- What is going on in the panel?
- What can we do about it?
- What are the legislators doing about it?

VOCs in manufacture and in service

Workplace exposure limit 2 ppm time weighted average over 8 hours
Short term limit 2 ppm in 10 minutes

EPA no more than 0.016 ppm in new building constructions
Studies show typically 0.076 ppm in a new home, dropping to 0.045 ppm in 28 days

Production process



Individual VOC and their content at different manufacturing stages.

No.	RT (min)	MW (amu)	Compounds	Content (μg)				
				UFR	WC	WF	MDF	PFR
1	2.881	72.1	2-methylbutane	–	6.4 ± 0.5	–	–	–
2	3.227	72.1	Pentane	–	37.3 ± 4.6	26.4 ± 14.3	–	–
3	3.302	58.0	Acetone	1.8 ± 0.7	–	1.2 ± 0.1	–	–
4	3.457	68.1	2-methyl-1,3-butadiene		10.9 ± 1.3	–	–	–
5	3.680	76.1	Dimethoxymethane	51.1 ± 23.6	–	–	–	338.3 ± 156.9
6	4.052	84.0	Methylene chloride	–	11.4 ± 1.5	–	7.6 ± 2.4	–
7	4.405	86.1	2,3-dimethylbutane		8.1 ± 0.7	–	–	–
8	4.464	86.1	2-methylpentane	–	1161.1 ± 230.0	314.4 ± 203.6	–	–
9	4.787	86.1	3-methylpentane		9.8 ± 1.7	16.3 ± 7.2	–	–
10	5.108	60.0	Acetic acid	–	–	–	174.9 ± 10.9	–
11	5.153	86.1	Hexane	–	1399.8 ± 626.7	213.4 ± 134.1	46.5 ± 12.3	0.7 ± 0.1
12	5.370	72.1	2-Butanone	12.3 ± 0.2	–	–	–	–
13	5.732	88.1	Ethyl acetate	0.3 ± 0.2	101.1 ± 20.5	35.6 ± 0.1	–	–
14	5.959	84.1	Methylcyclopentane	–	5.2 ± 0.8	–	–	–
15	6.127	72.1	Tetrahydrofuran	–	–	–	95.3 ± 37.7	–
16	6.723	100.1	2-methylhexane	–	41.5 ± 10.5	11.6 ± 6.8	–	–
17	6.865	74.1	1-Butanol	–	–	–	–	88.1 ± 0.8
18	7.512	86.1	2-Pentanone	3.9 ± 0.1	–	–	–	–
19	7.736	86.1	3-Pentanone	3.3 ± 0.1	–	–	–	–
20	8.289	102.1	Butanoic acid methyl ester	1.3 ± 0.1	–	–	–	–
21	9.448	92.1	Toluene	–	21.7 ± 1.3	13.4 ± 5.5	–	–
22	10.328	128.2	2,4-dimethylheptane	–	94.0 ± 1.3	221.7 ± 69.1	–	–
23	11.552	106.1	Ethylbenzene	0.2 ± 0.1	58.0 ± 5.1	59.0 ± 16.3	–	–
24	11.704	106.1	p-xylene	–	241.2 ± 18.7	195.7 ± 58.1	21.9 ± 1.3	–
25	12.219	104.1	Styrene	–	75.1 ± 36.6	–	69.9 ± 18.2	–
26	12.992	136.1	α-pinene	–	187.0 ± 133.7	110.7 ± 43.9	75.9 ± 24.9	–
27	13.374	136.1	Camphene	–	39.0 ± 4.1	35.2 ± 4.9	27.4 ± 0.9	–
28	13.989	118.1	α-methylstyrene	–	–	–	–	0.7 ± 0.2
29	14.950	170.2	Dodecane	–	138.9 ± 9.1	87.7 ± 32.7	–	–
30	16.057	142.1	Nonanal	2.4 ± 0.8	–	–	–	–
31	16.973	162.1	1,3-dimethylbutylbenzene	–	–	–	–	3.3 ± 0.9
32	17.772	156.2	Decanal	5.4 ± 2.9	–	–	–	–
33	18.051	128.1	Naphthalene	–	13.0 ± 2.2	8.8 ± 0.6	6.2 ± 0.8	–
34	20.873	204.2	α-cubebene	–	5.9 ± 0.7	–	–	–
			Total	81.9 ± 28.9	3666.2 ± 1111.6	1351.2 ± 597.2	525.7 ± 109.4	431.1 ± 158.8

- Not detected.

VOCs in panel manufacture

- Study by He, Zhang and Wei (2012, Building and Environment 47(1):197-204)

UFR = UF resin
WC = wood chip
WF = resonated wood fibre
MDF = MDF panel
PFR = PF resin

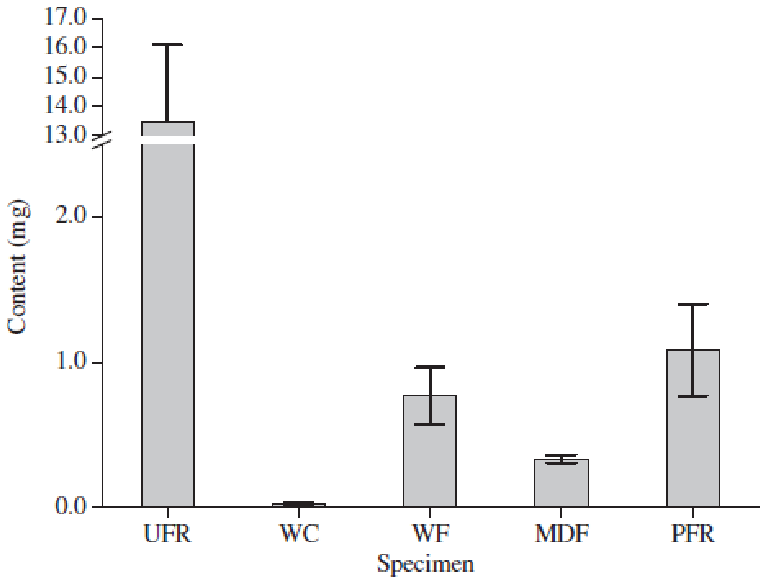


Fig. 5. Formaldehyde content at different manufacturing stages.

Methods for formaldehyde quantification

Analytical methods

- Detection / Derivatisation / Sensors

Materials testing approaches

- Perforator method
- Flask method
- Desiccator method
- Gas analysis

Climate controlled testing

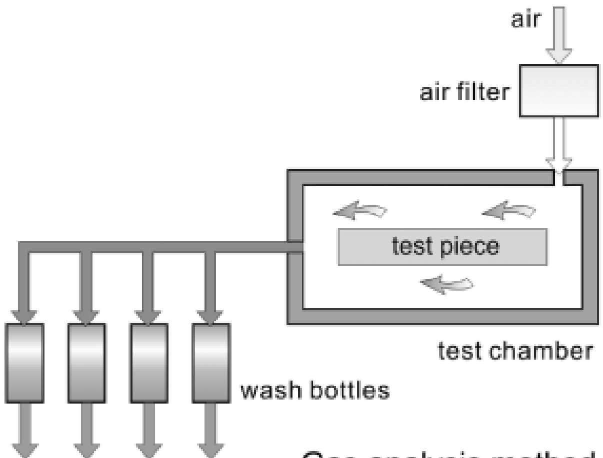
Field evaluation

More info: Review by Salthammer et al. 2010, *Chemical Reviews* 110:2526

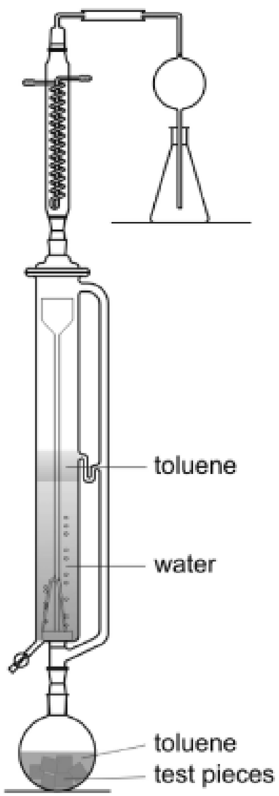
Methods for formaldehyde quantification

Perforator method

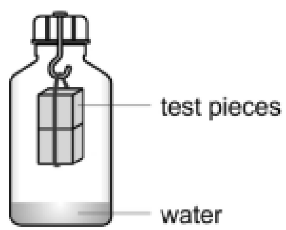
- Or TEF test (total extractable formaldehyde)
- EN 120:1992 Wood based panels. Determination of formaldehyde content. Extraction method called the perforator method.
- Now superseded by EN ISO 12460-5
- Cubes of wood in toluene are refluxed in special apparatus (perforator) to bubble the toluene through water.
- Water is analysed for formaldehyde content



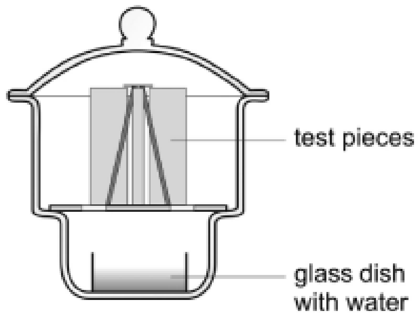
Gas analysis method



Perforator method



Flask method



Desiccator method

Methods for formaldehyde quantification

Flask method

- EN 717-3:1996 Wood-based panels. Determination of formaldehyde release. Formaldehyde emission by the flask method.
- Three board pieces (20g) in a flask of 400ml volume above 50ml of water
- Water is analysed for F content

Methods for formaldehyde quantification

Desiccator method

- Various iterations exist from different regions (America, Australia, Japan)
- ISO 12460-4
- Similar to the flask method, but with bigger volumes

Methods for formaldehyde quantification

- Gas analysis method
- EN ISO 12460-3:2015 Wood-based panels. Determination of formaldehyde release. Gas analysis method
- Previously: EN717-2:1995 Wood-based panels. Determination of formaldehyde release. Formaldehyde emission by the gas analysis method.

Formaldehyde in controlled climate

Chamber method

- EN 717-1: 2004 Wood-based panels. Determination of formaldehyde release. Formaldehyde emission by the chamber method.
- Material is enclosed in a chamber of fixed volume
- Temperature, relative humidity, air exchange rate, air velocity are controlled
- Measure the formaldehyde content of the air, and the specific emission rate (SER)

Specific Emissions Rate (SER)

- $SER = N\ C_s\ /L$

- Where N = air change rate (1/hr)
- L = loading factor (m^2/m^3)
- C_s = steady state concentration (mg/m^3)

- ISO 16000-10

Measurement VOCs from surfaces

- FLEC (Field Laboratory Emission Cell)
- ISO 16000-10 (emission test cell method)
- Stainless steel cell, with diameter 150mm
- Bolted to evaluation surface
- Gives surface area of 0.0177 m2 and volume of 35ml for analysis
- Controlled gas flow and analysis
- Collect a defined volume of air and analyse chemometrically

Resins

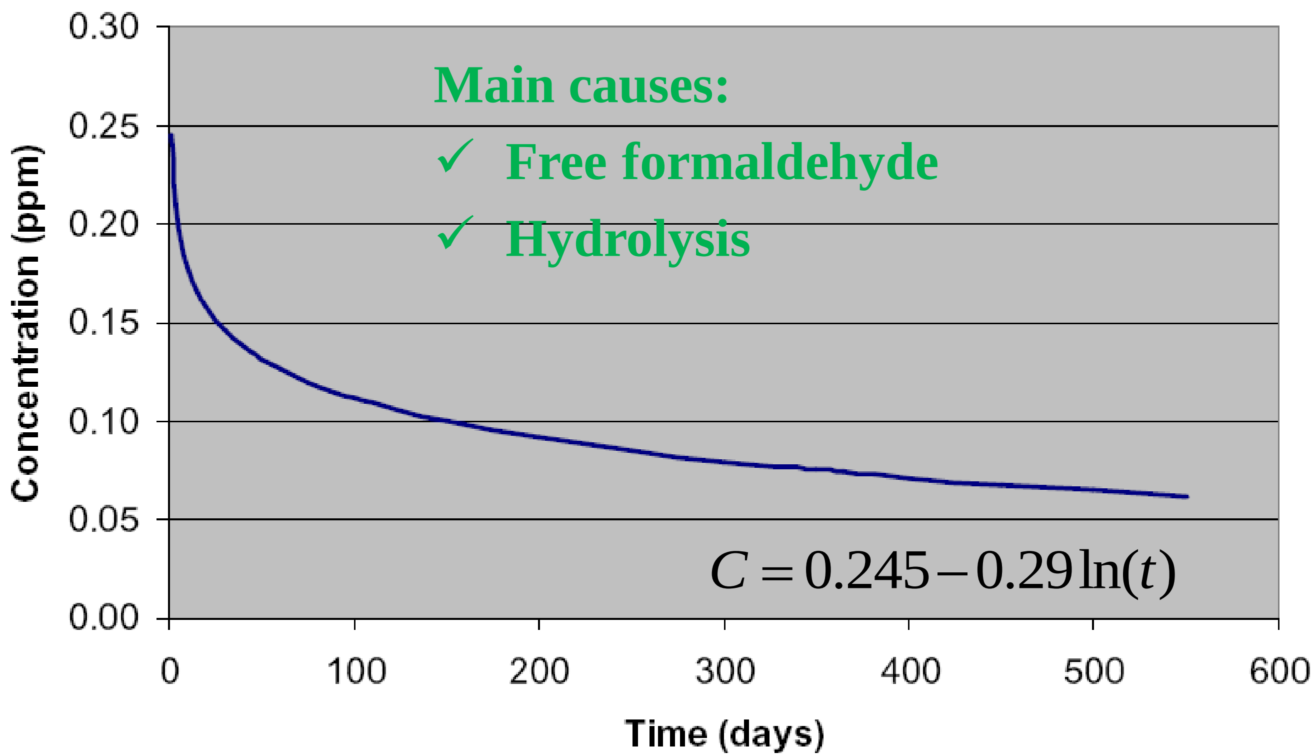
Urea formaldehyde resins

- Inexpensive
- Fast curing rate
- Good performance
- Well understood
- Resin manipulation easy
- Colourless

But:

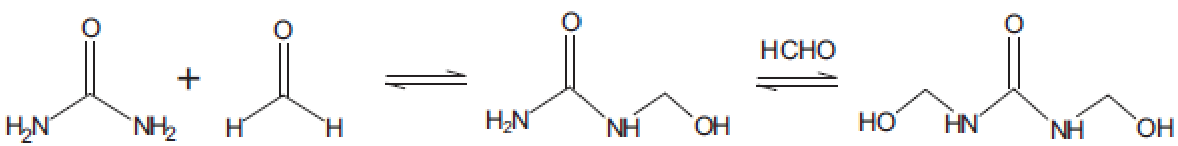
- Formaldehyde emissions
- Lower resistance to water
- Not suitable for exterior products

Formaldehyde emissions



Source: Zinn et al. (1990)

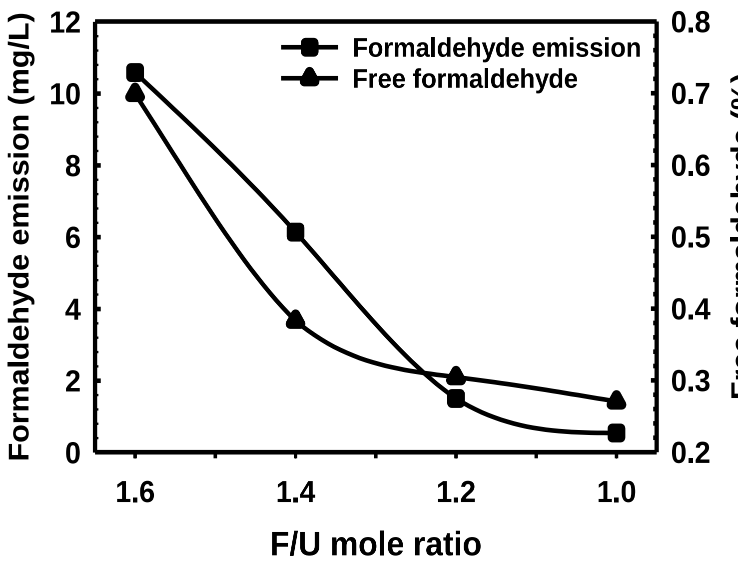
UF resin manufacture



Strategies for reducing free formaldehyde 1

Lowering the formaldehyde - urea ratio (F/U)

- Can reduce the free-F and F-emissions
- But this increases the gel time
- Pressing becomes less economic



Source: Park et al. (2015)

Strategies to reduce free formaldehyde 1

Lowering the formaldehyde - urea ratio (F/U)

- Also reduces UF susceptibility to hydrolysis
- But reduces the stiffness of the adhesive
- Has been related to altered number of cross links within the resin
- Can lead to lower performance boards

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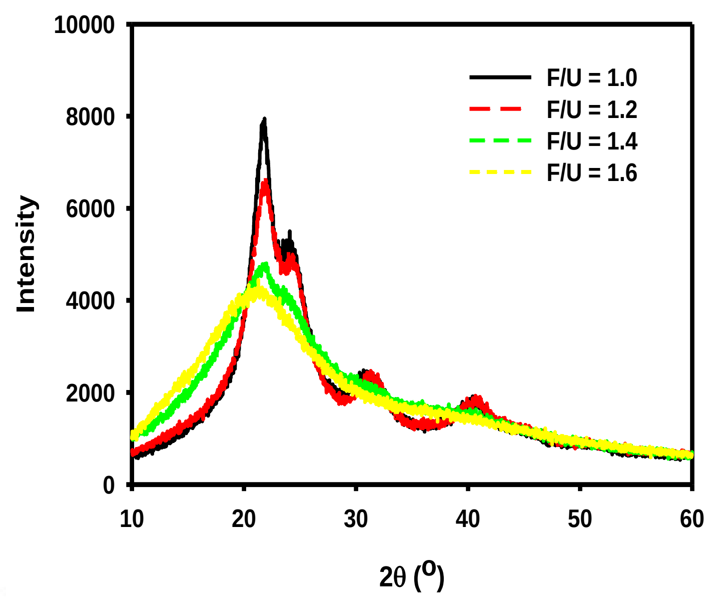
Strategies for reducing free formaldehyde 1

- Lowering the formaldehyde - urea ratio (F/U)
- Resin hardness is also reduced
- This can be related to a more crystalline resin forming at low F/U ratios (Park et al. 2011)
- Crystallinity approaches 45% at F/U ratio of 1.0



Int. J. Adhes. & Adhes., 2011, 31(6): 524-529

Strategies for reducing free formaldehyde 2

Scavengers:

- Urea and ammonium chloride
- Typically 20:1
- NH_4Cl acts as acid catalyst and scavenger
- Organic amines
- Formaldehyde binding paraffins

Strategies for reducing free formaldehyde 2

Scavengers:

- Ammonium bisulphite
- Ammonium bisulphite
- Ammonium chloride
- Pozzolan
- Charcoal

Strategies for reducing free formaldehyde 2

Scavengers:

- Altered UF chemistry, e.g. glyoxal
- Essentially swapping one aldehyde for another, with lower volatility
- React glyoxal with monomethylol urea
- Reasonable results in plywood tests

Strategies for reducing free formaldehyde 3

Alternative resins:

- Isocyanate resins platform
- pMDI
- Relatively expensive

Strategies for reducing free formaldehyde 3

Alternative resins:

- Protein based resins
- E.g. Soyad

Strategies for reducing free formaldehyde 3

Alternative resins:

- Starch based resins

Standards and regulations

- Standards for:
  - Classification
  - Quality Assurance
  - Physical properties
  - Mechanical properties
  - Decay resistance
  - Chemical release (VOC / formaldehyde)
  - Testing standards
  - Product standards (e.g. toys, flooring)
  - End of life disposal

Standards – formaldehyde content

- EN120 Perforator method

	Total extractable formaldehyde mg / 100g panel
E2	< 15
E1	< 6.5
E0	< 0.8

Standards – formaldehyde emission

- Desiccator method

Korea	Japan (JIS A 1460)	Formaldehyde mg / litre
E2	F*	< 5
E1	F**	< 1.5
E0	F***	< 0.5
S-E0	F****	< 0.3

Formaldehyde in indoor air - guidelines

- Threshold limit values (TLV)
- Time-weighted average values (TWA) 0.75ppm
- Short term exposure limits (STEL) 2ppm
- Ceiling values (C)

(OSHA)

Formaldehyde in indoor air - guidelines

- Threshold limit values (TLV)
- Time-weighted average values (TWA) 0.1ppm
- Short term exposure limits (STEL) 0.016ppm
- Ceiling values (C)

(NIOSH)

Formaldehyde in indoor air - guidelines

- Differences between workplace exposure and occupational are due to:
- Duration – 8 hrs vs potential 24 hours
- Age and frailty of people present (children, the elderly)
- Prevention of acute health effects versus prevention of development of chronic illnesses
- Occupational levels also address prevention of significant sensory irritation, and potential presence of individuals who are allergic to F

Table 5. International Guideline Values and Recommendations for Formaldehyde in Indoor Air

country	year issued	value		comments
Australia	1982[226]	0.1 ppm	120 µg m^{-3}	short-duration
	2006[227]	0.08 ppm	100 µg m^{-3}	
Canada	1987[220]	0.1 ppm	120 µg m^{-3}	action level
	1987	0.05 ppm	60 µg m^{-3}	target level
	2005[22]	0.1 ppm	123 µg m^{-3}	1 h
	2005	0.04 ppm	50 µg m^{-3}	8 h
China	2003[225]	0.08 ppm	100 µg m^{-3}	1 h average
Denmark	1990[207]		0.15 mg m^{-3}	
Finland	2001[209]		30 µg m^{-3}	S1
			50 µg m^{-3}	S2
			100 µg m^{-3}	S3
France	2008[213]		*50 µg m^{-3}*	*2 h (proposed)*
			10 µg m^{-3}	*long-term exposure (proposed)*
Germany	1977[216]	0.1 ppm		
Singapore	1996[224]	0.1 ppm	120 µg m^{-3}	8 h
Hong Kong	1999	0.025 ppm	30 µg m^{-3}	level 1 (8 h)
		0.081 ppm	100 µg m^{-3}	level 2 (8 h)
		0.3 ppm	370 µg m^{-3}	level 3 (8 h)
	2003[221]	0.025 ppm	30 µg m^{-3}	excellent
		0.081 ppm	100 µg m^{-3}	good
Japan	1997[223]	0.08 ppm	100 µg m^{-3}	0.5 h
Korea	2004[222]	0.1 ppm	120 µg m^{-3}	8 h
Norway	1990[210]	0.05 ppm	60 µg m^{-3}	24 h average
	1999[211]	0.05 ppm	100 µg m^{-3}	30 min average
Sweden	2000	0.08 ppm	100 µg m^{-3}	adopted from WHO
Poland	1996[215]	0.04 ppm	50 µg m^{-3}	category A: 24 h
		0.08 ppm	100 µg m^{-3}	category B: 8−10 h
U.K.	2004[208]		100 µg m^{-3}	0.5 h
USA (California)	1991[217]	0.1 ppm	120 µg m^{-3}	action level
		0.05 ppm	60 µg m^{-3}	target level (ALARA)[a]
	1999[203]	0.076 ppm	94 µg m^{-3}	1 h (acute REL)[b]
	2004[219]	0.027 ppm	33 µg m^{-3}	8 h (interim REL)
	2005[218]	0.002 ppm	3 µg m^{-3}	annual average (chronic REL)
WHO	1987[228]	0.08 ppm	100 µg m^{-3}	0.5 h average

[a] ALARA = as low as reasonably achievable. [b] REL = reference exposure limit.

Formaldehyde in indoor air - guidelines

Other schemes:

- US Green Building Council LEED
- Voluntary participation
- California Environmental Protection Agency (CARB)
- A state-wide regulation, but frequently referred to as a benchmark
- Set maximum level at 0.10 ppm in 1991
- And 0.05 ppm as target value

Formaldehyde in indoor air - guidelines

Finland has classification for indoor climate

- S1 individual indoor climate 30 µg m^{-3}
- S2 good indoor climate 50 µg m^{-3}
- S3 satisfactory indoor climate 100 µg m^{-3}

- Conversion factor: 60 µg m^{-3} is 0.05ppm

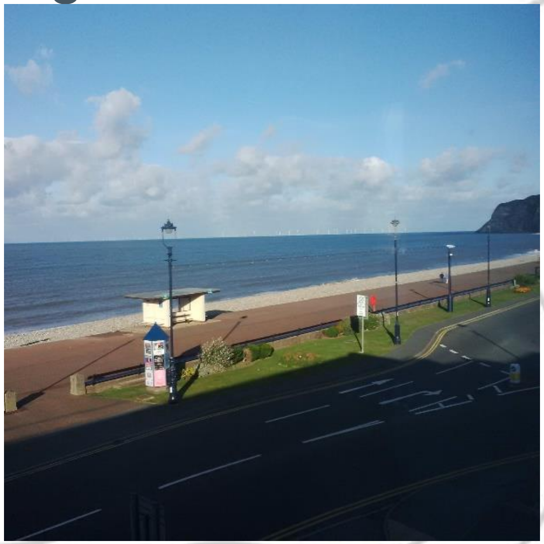
INNOVATION IN BIO-MATERIALS FOR INDUSTRY

International Panel Products Symposium

4th & 5th October 2017

Call for papers:

- Innovation in wood based panels
- Panel performance, durability, weathering
- Resins and bioresins
- Novel feedstocks and recycling
- Processing technologies
- VOCs and emissions in service



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