SUBSPORT Specific Substances Alternatives Assessment – Formaldehyde

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Table of content

1. Profiling formaldehyde to be included in the Specific Section of the Case Story Database

Characterising formaldehyde based on its inherent hazards is an essential component of conducting an alternatives assessment (see SUBSPORT methodology, 2012). This approach allows the reviewer to assess whether or not an alternative is indeed preferable from an environmental, health and safety perspective. The hazard properties are intrinsic to the chemical, which means that regardless of the way that a chemical is used, these characteristics do not change (Table 1 and 2). The goal of the substitution processes is to advance inherently safer chemicals and products, consistent with the principles of green chemistry .

Table 1: Classification of formaldehyde

Formaldehyde		
Chemical name (IUPAC)	Formaldehyde	
Identification number	CAS 50-00-0 EC 200-001-8	
Trivial names	Formalin (aqueous), Formol, Formic aldehyde, Methaldehyde, Methanal, Methyl aldehyde, Superlysoform, Methylene oxide, Lysoform, FYDE, Dormol, Formalith, Tetraoxymethalene, Oxomethane, Oxymethylene, Morbicid, Paraformaldehyde, Paraform, Metaformaldehyd (solid polymer of formaldehyde)	
Substance function	disinfectant, preservative, food additive fumigant, stabilizer, starch modifier, drying agent	
Classification	Carc Cat. 3 R23/24/25 R34 R40 R43 H351 H331 H311 H301 H314 H317	Source: ESIS - European chemical Substances Information System

Sources that have been checked for hazard characterisation:

1. SUBSPORT Hazardous Substance Database according to SUBSPORT Screening Criteria, SDSC, including:
   a. CLP Regulation (CMR 1A or 1B)
   b. IARC (group 1, 2A or 2B carcinogens)
   c. CLP Regulation (Sensitiser: H317, H334)
   d. EC PBT Working Group
   e. OSPAR List of Substances of Possible Concern (PBT)
   f. EC Endocrine Disruptors Database
   g. SIN List (endocrine disruptors)
   h. Vela et al. (neurotoxins, cat 2-4)

2. The ESIS database for R and H phrases

3. TOXNET/HSDB (hazardous substances database)

For green house gases and ozone depleting substances:
4. Greenhouse gases- Kyoto protocol- Annex A, as presented in IPCC (intergovernmental panel on climate change)
5. Ozone Depleting Substances List (Montreal Protocol)

6. Additional sources have been checked for information, especially for endpoints where no information is available in the previous mentioned sources, and also for getting the most up-to-date information. These sources include:

- REACH registration dossiers
- Search for scientific studies using the search resources Google scholar PubMed.
- The endocrine disruption exchange list of potential endocrine disrupting substances:
- Ordinary google search

Table 2: Hazard characteristics of formaldehyde

	Properties	Source of information
Physical Hazards		
Explosivity	Not applicable	GHS Classification
Flammability	conclusive but not sufficient for classification Cat. 1	ECHA registred substances, data dossier formaldehyde (2012) GHS Classification
Oxidizing	conclusive but not sufficient for classification	ECHA registred substances, data dossier formaldehyde
Other properties of reactivity	-	
Human Health Hazards		
Acute toxicity		
Highly toxic	Toxic if swallowed H301 Toxic in contact with skin H311 Toxic if inhaled H331	SDSC – (SUBSPORT 2013), CLP, List of harmonised classification and labelling of hazardous substances
Skin or eye corrosion / irritation	Skin Corr. 1B	SDSC (2012)
Chronic toxicity		
Carcinogenicity	Carc. 2 Carc. Cat 3 group 1, 2A or 2B carcinogens	CLP, List of harmonised classification and labelling of hazardous substances ESIS, Annex I to Directive 67/548/EEC IARC (2006)
Mutagenicity	Germ cell mutagenicity conclusive but not sufficient for classification	ECHA registered substances, data dossier formaldehyde (2013)
Reproductive toxicity (including developmental toxicity)	conclusive but not sufficient for classification	ECHA registered substances, data dossier formaldehyde (2013)
Endocrine disruption	-	
Respiratory or skin sensitization	Skin Sens. 1	SDSC (SUBSPORT, 2013)
Neurotoxicity	-	
Immune system toxicity	-	

	Properties	Source of information
Systemic Toxicity		
Toxic metabolites		
Environmental Hazards		
Acute/chronic aquatic toxicity	Cat 2 Toxic to aquatic organism	GHS classification PAN Pesticide Database (2013)
Bioaccumulation	Experiments performed on a variety of fish and shrimp show no bioconcentration of formaldehyde Not classified	OECD, ChemPortal (2012) TURI (2006)
Persistence	Not classified	
Greenhouse gas formation potential	Formaldehyde in the air breaks down in sunlight during the day into carbon monoxide and formic acid, a component of acid rain.	TURI (2006)

2. Identify functions and uses

2.1 Formaldehyde uses

A key first step in identifying appropriate alternatives is to determine the functions, uses and processes associated with formaldehyde, as potential feasible and safer alternatives are often differ particularly where a substance has numerous disparate applications. Table 3 provides an overview about formaldehyde uses.

Formaldehyde is a high volatile gaz and is soluble in water, ethanol and diethyl ether. It is mostly sold as aqeuos solution containing 37 to 50% formaldehyde and 10 to 15% methanol (afsset, 2004). It is also present in solid form as paraformaldehyde, a polymer of formaldehyde.

Formaldehyde is widely used in the industry. Annually 21 Million tones of formaldehyde are used all over the world in 2006, and 3 Million tones in Europe in 2007 (IARC, 2006). It has four basic uses: as an intermediate in the production of **formaldehyde based resins**; as an **intermediate in the production of industrial chemicals and plastics**; as a **bactericide or fungicide**; and as a component in the **formulation of end-use consumer items** such as cosmetics, shampoos and glues. Formaldehyde is also used as embalming fluid and in textile treating to impart wrinkle-resistance to clothing (United States Department of Labour, 1992).

Construction/remodeling activity, vehicle/motor and furniture production, and original equipment manufacture (OEM) account for most world consumption of formaldehyde (IHS, 2012). Formaldehyde is also used in health care sector for desinfection and as preserving agent for various vaccines and in laboratories and in funeral services to conserve biomaterials.

Resins

Urea-, phenol- and melamine-formaldehyde resins (UF, PF and MF resins) accounted for about 63% of world demand in 2011 (IHS, 2012).

The over-all main use is for the production of urea-formaldehyde resins (UF). UF is widely used in the industry as binding material for particle boards and medium density pfibreboard (MDF) and plywood, and as components of melamine-phenolic resins for production of laminated flooring board.

According to GlopbalInsight UF accounted for 55% (about 5.4 million metric tons) of EU25 +Norwegian formaldehyde consumption in 2004 (GlobalInsight, 2007).

Melamine formaldehyde (MF) has an excellent water and weather resistance, as well as chemical and heat resistance. It is used for the impregnation of paper for surfacing of wood-based panel products (e.g. laminate), as wood adhesives where improved water resistance is required (Pizzi, 2006), and also as molding compound. The automobile industry also uses MF resins such as clear coats and molding compound. MF consumption in the EU25 + Norway in 2004 was about 1.3 million metric tons.

The next largest formaldehyde consumption in EU25 + Norway in 2004 is for phenolic formaldehyde (PF) resins. PF is water resistant and has fire resistant properties. It is used in the automobile industry (e.g. brake linings, friction material, foundry resins), in the electroindustry (e.g. printed circuit boards and insulators), as well as in the construction industry as water resistant wood adhesive, and as binders in mineral wool insulation. Consumption in the EU25 + Norway in 2004 about 75,000 metric tons.

Intermediate in the production of industrial chemiclas
Formaldehyde is used as intermediate in the production of

- EDTA (Ethylenediaminetetraacetic acid)
- 1.4-butanediol (BDO)
- Pentaerythritol
- Isocyanates (MDI)

Biocide: Bactericide and Fungicide
HMTA (Hexamethylenetetramine) is used as biocide/preservative. Consumption in the EU25 + Norway in 2004 about 25,000 metric tons. Hexamethylenetetramine (Hexamine) is a crystalline, solid material, which is produced starting from Formaldehyde and Ammonia and which is mainly used in the resin and rubber industry.)
Formaldehyde as aequous solution (formalin) in health care, laboratory, funeral service as disinfectant, preservative, embalming solution.

Tabel: 3 Formaldehyde uses - overview

Sector	Function	Product, article	Source of information
Binding agents/resins/ adhesivs for different materials			
16. Manufacture of wood and of products of wood and cork, except furniture…. **16.21 Manufacture of veneer sheets and wood-based panels**	Binding agent • Binder for wood, plywood, chipboard • Binder for structural wood panels	Wood articles	http://www.formaldehydefacts.org/applications/common_uses/
16. Manufacture of wood and of products of wood and cork, except furniture….	surfacing of panels: laminats and surface coating	Wood articles	http://www.icis.com/v2/chemicals/9076013/formaldehyde/uses.html http://www.form

			aldehyde-europe.org/fileadmin/formaldehyde/PDF/Socio-Economic-Benefits-Study.pdf
31. Manufacture of furniture	Binding agent • Glue	Polymer preparations and compounds	
23. Manufacture of other non-metallic mineral products **23.14 Manufacture of glass fibers**	Binding agent • Binder for glass wool, mineral wool	Polymer preparations and compounds Stone, plaster, cement, glass and ceramic articles	http://www.icis.com/v2/chemicals/9076013/formaldehyde/uses.html
17. Manufacture of paper and paper products	Impregnation agent • paper impregnating resins for surfacing	Paper and board dye, finishing, impregnation and care products Paper articles	http://www.icis.com/v2/chemicals/9076013/formaldehyde/uses.html
Disinfectants/Preservatives			
86. Health care	Biocide • Disinfectant	Biocidal product	
96.03 Funeral and related activities	Fixing agent Biocide • Embalming solution	Biocidal product	
81.2 Cleaning activities	Biocide Cleaning agents: wax blends, biocidal products, Washing and cleaning products	wax blends, biocidal products, Washing and cleaning products	
	Biocoide Cosmetics, personal care products		
75. Veterinary activities	Biocide • Disinfectant	Biocidal product	
Manufacture of plastic articles			
29.3 Manufacture of parts and accessories for motor vehicles	Binding agent Processing aid • Component of thermoplastic engineering polymer	Polymer preparations and compounds Plastic articles	http://www.icis.com/v2/chemicals/9076013/formaldehyde/uses.html http://plastics.dupont.com/plastics/pdflit/europe/delrin/DELDGe.pdf
Manufacture of chemicals			
20.3 Manufacture of paints, varnishes and similar coatings, printing ink and mastics	Biocide • Bactericide, fungicide, preservative,	Biocidal product Polymer preparations and compounds	http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=

	germicide		PREAMBLES&p_id=923
20. Manufacture of chemicals and chemical products **20.4 Manufacture of soap and detergents, cleaning and polishing preparations, perfumes and toilet preparations**	Biocide • Preservative, bactericide, germicide	Biocidal product Pharmaceuticals	http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=PREAMBLES&p_id=923
Textile finishing			
13.3 Finishing of textiles	Impregnation agent • Resin to impart wrinkle-resistance to clothing. Also used as fire retardation, increased water repellency, and stiffness	Textile dyes, finishing and impregnating products	http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=PREAMBLES&p_id=923 http://www.nclabor.com/osha/etta/indguide/ig31.pdf

Beside the uses mentioned in table 3 formaldehyde is also used in the leather industry as tanning agent, in agriculture for seed treatment, soil disinfection, and as a insecticide and fungicide, as a biocide in drilling fluids; as a stabilizer in gasoline and as film hardener. As these uses covers only a minor part of the formaldehyde consumtion, they are not subject of this case study.

2.2 Prioritising uses

As described in the previous chapter formaldehyde has four basic uses: as an intermediate in the production of **formaldehyde based resins**; as an **intermediate in the production of industrial chemicals and plastics**; as a **bactericide or fungicide**; and as a component in the **formulation of end-use consumer items** such as cosmetics, shampoos and glues. According to Globalinsight and Formacare the consumption of formaldehyde is the highest in the production of formaldehyde resins (tab. 4)

Table 4: Main downstream derivates and their consumtion of formaldehyde in EU25 + Norway in 2004

Main downstream derivate products of formaldehyde	EU25 + Norway consumption of formaldehyde in 2004
Urea-formaldehyde resins UF	55%
Melamine-formaldehyde resins MF	14%
Phenol-formaldehyde resins PF	7%
Polyacetal resins POM	6%
1.4 Butanediol BDO	4%
Pentaerythritol	3%

(Source GlobalInsight, 2007)

2.3 Exposure to formaldehyde

Humans may be exposed to formaldehyde in the environment and in the workplace. Formaldehyde concentrations in the environment generally are reported in parts per billion, but exposure levels are much higher in the workplace, occurring in the range of parts per million (National Toxicology Program, 2011)

Afsset published a report in 2009 dealing with the exposure of workers to formaldehyde (Afsset, 2009). According to this report about 105 different occupations were exposed to formaldehyde. Most occupations belongs to the healthcare sector, manufacture of furniture, manufacture of resins, and agriculture. Examples of occupations exposed to formaldehyde are listed in table 5. According to the report, which analysed the SUMER data, about 193,000 workers were exposed to formaldehyde in France in 2003. Most of them were working in the health care sector (including laboratory workers and workers in anatomy and pathology), followed by the manufacture of furniture, resins and plastic compounds (Afsset, 2009).

Lissner et al. (Expokoll, unpublished, 2012) analysed the EXPO Database which indicates that 80% of all workers in Norway were exposed to formaldehyde between 2007 and 2009.

Industrial workers who produce formaldehyde or formaldehyde-containing products, embalmers and workers in pathology may be exposed to higher levels of formaldehyde than other workers (National Cancer Institute, 2011).

Table 5: Occupations exposed to formaldehyde

Occupations exposed to formaldehyde	
Agriculture workers	Laboratory researchers/workers
Botanists	Lacquer producers and users
Carpet manufacturers/installers	Medical professionals
Disinfectant producers/users	Oil field workers
Dressmakers	Paint and varnish manufacturers
Drug makers	Paper manufacturers
Dye manufacturers	Plastics manufacturers
Embalming fluid producers	Plywood and particle board manufacturers
Fabric store personnel	Poultry processors
Fertilizer manufacturers and blenders	Rubber workers
Formaldehyde producers	Sanitation workers
Formaldehyde resin producers	Science instructors/teachers
Foundry workers	Taxidermists
Furniture makers and finishers	Textile workers: finishers, printers, cutters
Glue and adhesive makers	Veterinarians
Hazardous waste handlers	Wood preservers
Ink makers	
Insulators	

(source: N.C. Department of Labor, 2009)

The Michigan Department of Licensing and Regulatory Affairs grouped workers according to their formaldehyde exposure level: the highest exposure is among workers producing hardwood plywood, particle board, fiberboard and resins as well as workers in foundries, laboratories and funeral services (exposure levels between 0.1 to above 1.0 ppm), followed by industries in textile finishing, apparel manufacturing, formaldehyde production and plastic molding (0.1 to 1.0 ppm) and workers in pulp, paper and paperboard mills , softwood plywood manufacturers, manufacturers of various cardboard and paper products, paint, pigment and dye manufacturers, photo finishing labs, hemodialysis units, biology.

Although the use of formalin as biocide (< 1%) is very low compared to the overall production of formaldehyde in Europe (FriedliPartner AG, 2007), workers are at high exposure to formaldehyde in health care, laboratory, pathology and funeral services.

Workers in health care facilities cleaning surfaces with cleaners containing formaldehyde may be exposed to formaldehyde levels far beyond stipulated occupational exposure limits (OELs), although formaldehyde is used in high dilution (0.5 to 3%) (Eickmann and Thullner, 2006).

Formaldehyde levels during embalming can be very high, up to 4 ppm, with average levels greater than 0.5 ppm (NINCAS 2007).

Textile plant workers working in plants using formaldehyde containing finishes may also be exposed to higher levels of formaldehyde. Adults, children and babys wearing textiles treated with formaldehyde are at risk of potential health effect from dermal exposure to formaldehyde e.g. contact dermatitis or other forms of eczema.

2.4. Conclusion

The exposure to formaldehyde is a big issue in sectors with a high formaldehyde consumption as well as in sector were many workers are exposed to formaldehyde or are exposed to a high amount of formaldehyde. Based on the above information, formaldehyde is most used for the production of resins (about 76%). The sector with the most workers exposed to formaldehyde is the health care sector and the occupation with the highest exposure of formaldehyde are anatomists, pathologist and tanatologists.

Formaldehyde in textile finishing is an issue especially for children and baby wear.

For this reason substitution examples in this report will focus on substitution of formaldehyde

- in wood composites,
- in disinfectant cleaners in health care and
- in funeral services, anatomy and pathology, and
- in textile finishing

3. Regulation and standards of formaldehyde

The International Agency for Research on Cancer (IARC)[1] changed its classification of formaldehyde from a group 2A substance "probably carcinogenic to humans" to group 1 "carcinogenic to humans" in 2004. The main source of formaldehyde emission general population is from breathing indoor and outdoor air. Indoor formaldehyde emmission is caused by different sources, including off-gassing from numerous construction and home-furnishing products. Concerns relating to formaldehyde exposure has therefore advanced the research for alternative resins and wood binders that do not contain formaldehyde (National Toxicology Program, 2011) (Forest and Wood products Australia, 2010).

The European Union has developed a strategic policy for protection of workers against risks from dangerous substances. It aims to prevent or limit the exposure of workers to dangerous substances at workplaces, and to protect the workers that are likely to be exposed to these substances. Setting occupational exposure limits (OELs) is an essential part of this political strategy.

The European Commission defines two different OELs: indicative OELs and binding OELs which are published in the directives listed in table 6.

Table 6: EU Directives setting occupational exposure limits (OELs)

Indicative OELs	Binding OELs
– First list of indicative occupational exposure limit values (Directive 2000/39/EC) – Second list of indicative occupational exposure limit values (Directive 2006/15/EC) – Third list of indicative occupational exposure limit values (Directive 2009/161/EU)	– Chemical Agents Directive (Directive 98/24/EC) – Cancer Directive (Directive 2004/37/EC) – Asbestos Directive (Directive 2009/148/EC)

For Formaldehyde they have not yet defined any OEL. But the European Union Scientific Committee on Occupational Exposure Limit Values (SCOEL) proposed in 2008 an eight hour exposure limit of 0.2 ppm and short term exposure limit (STEL) of 0.4 ppm. They regard formaldehyde as a genotoxic carcinogen. SCOEL is mandated to advise the European Commission on occupational exposure limits for chemicals in the workplace. Other recommendations are listed in table 7.

[1] IARC: http://www.iarc.fr/

Table 7: OEL recommendations for formaldehyde (Bolt, 2012)

	TWA -8h (ppm) - 8 hour time-weighted average	STEL (ppm) - short-term exposure limit
ACGIH[2] (USA, 2006)	-	0.3
DECOS[3] (NL) + Nordic (2003)	0.12	0.42
DFG[4]/MAK (D, 2006)	0.3	0.6
SCOEL[5] (EU, 2006)	0.2	0.4

OELs in the EU Member States are set by competent national authorities or other relevant national institutions as limits for concentrations of hazardous compounds in workplace air (EU OSHA, 2012). These OELs are published as a legal text by an authority. The OELs differ between EU Member States. The reasons for this include divergence in assessment methods and differing assessments on the actual risks of the chemicals themselves. It is often not possible to compare exposure limits between countries because of the differing approaches (EU OSHA, 2012).

Table 8 shows the current exposure limits for formaldehyde in some EU Member States. As limits frequently change, it is necessary to consult the relevant national authorities for latest information.

Table 8: Current occupational exposure limits for formmaldehyde in some EU Member States

	TWA -8h (ppm) - 8 hour time-weighted average	STEL (ppm) - short-term exposure limit
Denmark		0.3
Finland	0.3	1
France	0.5 (VME = Valeur limite de moyenne d'exposition 8-h)	1 (VLE= Valeur limite d'exposition – 15 min)
Germany	0.3 (MAK/TWA 8- h)	0.6
Ireland*	2 (maximum exposure limit (MEL) for both TWA -8h and STEL)	2
Poland	0.5	1
Spain		0.3
Sweden	0.5	1
The Netherlands	1	1.5
UK**	2 (maximum exposure limit (MEL) for both 8 hour TWA -8h STEL)	2

*will be revised in 2013 to 0.3 ppm (TWA -8h); ** currently under review and subject to possible change

3.1 Regulation and standards for formaldehyde for composite wood products

Acceptable levels of formaldehyde emission from composite wood products have been continously reduced over the last years. In 1980 some European countries started to regulate formaldehyde emissions and developped an obligatory emission class E1 (0.1 ppm boards) for wood-based panels 1985. 2004, Europe established the emission classes E1 and E2 (European Standard EN 13986) regarding wood products used in construction, in 2006 emission class E1 became obligatory for panel production. Also North America and Japan established emission standards and occupational

[2] ACGIH = American Conference of Governmental Industrial Hygienists: http://www.acgih.org/
[3] DECOS = Dutch Expert Committee on Occupational Standards
[4] DFG = Deutsche Forschungsgemeinschaft: http://www.dfg.de/
[5] SCOEL = European Union Scientific Committee on Occupational Exposure Limit Values: http://ec.europa.eu/social/main.jsp?catId=148&langId=en&intPageId=684

exposure levels for formaldehyde (Regulation and standards: ASTM (North America), CEN (Europe), GB (China), JIS/JAS (Japan), JANZ (Australia) and ISO (international). This lead to a change in formulation of fomaldehyde resins. (Athanassiadou, 2009).

The German guideline (ETB-Richtlinie, 1980[6]) classifies particleboard according to their formaldehyde release into three different emmission classes: E1, E2, E3 (table 9)

Table 9: Formaldehyde emission class for particleboard in Germany

Emission class	Equilibrium concentration in a 40 m³ test chamber	Perforator value (mg/100g dry board)
E1	≤ 0.1 ppm	6.5 mg/100 g dry board
E2	0.1 – 1.0 ppm	10 – 30 mg/100 g dry board
E3	1.0 – 2.3 ppm	30 – 60 mg/100 g dry board

European formaldehyde limits for wood based panels are summarised in the harmonised standard EN 13986. This standard includes two emmission classes E1 and E2 (E1 ≤ 8mg/100g dry board; E2 >8 - ≤ 30 mg/100g dry board. Germany, Austria, Denmark and Sweden require compliance with emission limits of 6.5mg/100g dry board.

The Blue Angel certification for environmental friendly products require a formaldehyde emission limit of 0.05 ppm. The European panel federation (EPF[7]) decided to draw up its own standard, the EPF-S: for PB 4mg/100g and for MDF (with > 8 mm thickness) 5 mg/100g. In 2011, EPF agreed on a reduction in formaldehyde emissions for CE labeled, uncoated wood panels for construction (EN 13986). The new limit value should be determined using the chamber test method described in EN 717-1 and should not exceed 0.065ppm. IKEA also set an own emission limit that is half E1 (0.05 ppm)(IOS-MAT-003)[8].

Japanese guideline

Japan Agricultural Standards (JAS) were first established in 1953 and has been revisyed several times since. In 2003,the standards for plywoods were unified. Japanese JIS/JAS[9] emission standards are broken down into four levels labeled as F*, F**, F***, and F****. The emission standards are measured in mg/L and are therefore difficult to compare with European standards, which are measured in ppm (parts per million) (table 10). All composite wood products should be marked with a formaldehyde emission grade that determines the use of the product: e.g. F**** plywood can be used interior without limitations . F**, F***, plywood can be used interior with some limitations. F* plywood is not allowed to be used interior .
All products must be approved by the Japanese Ministry through an extensive application process that includes providing of desiccator data (JIS 1460) at minimum (Franklin Adhesive and Polymers, 2013).

[6] ETB-Richtlinie über die Verwendung von Spanplatten hinsichtlich der Vermeidung unzumutbarer Formaldehydkonzentrationen in der Raumluft (1980), http://www.beuth.de/de/verwaltungsvorschrift/spanplatterlrderl-nw/3531270

[7] http://www.europanels.org/
[8] The natural step, IKEA, a natural step case study, http://www.naturalstep.org/it/usa/ikea
[9] Japan Agricultural Standard JAS; Japan Industrial Standard JIS

Table 10: Formaldehyde emission class for particleboard in Japan

Emission class	Limit value (Desiccator test JIS A 1460)	Perforator value (EN 120)	
F**	≤ 1.5 mg/L	6.5 mg/100 g dry board	
F* "E0"**	≤ 0.5 mg/L	2.5 mg/100 g dry board	
F** "SE0" (Super E0)**	≤ 0.3 mg/L	1.5 mg/100 g dry board	Closed to the emission of solid untreated wood

North American guidelines
The National voluntary standard ANSI A208.1 & 2 ; The standard has been revised in 2011 by the American National Standards Institute (ANSI). It includes new grades and product categories as well as harmonisation with the formaldehyde emission ceilings and other requirements recently enacted by the California Air Resources Board (CARB) (Surface and Panel, 2011).

According to the Healthy building network (2012) "The California Air Resources Board established new regulations in April 2007 to regulate formaldehyde emissions from composite wood products, including particle board, MDF (medium density fiberboard), and interior plywood. The two step process set limits on emissions for products manufactured after January 1 (table 11), 2009 that will be roughly equivalent to the majority of the European and Japanese standards and will exceed them with stricter limits in 2010 (and 2012 for some products)." (Composite Panel Association, 2008)

Table 11: Phases for formaldehyde emission in California

	HWPW*-VC[10]	HWPW-CC	PB	MDF	MDF Thin	
Phase 1	0.08 ppm	0.08 ppm	0.18 ppm	0.21 ppm	0.21 ppm	Effective from 2009
Phase 2	0.05 ppm	0.05 ppm	0.09 ppm	0.11 ppm	0.13 ppm	Effective from 2010 or 2011

*HWPW Hartwood/plywood

Conclusion
All standards set limit for formaldehyde emissions only for wood panels that are already produced. The emission levels protects the end users, carpenters and workers in the furniture industry by reducing users exposure to formaldehyde. But the chemicals used may put the workers at risk during the production of the binders, or of the composite wood products.

4. Preliminary identification of alternatives

4.1 Formaldehyde in wood composites

The main use of adhesives in the wood industry, includes plywood, oriented strandboard, particleboard, fiberboard, structural composite lumber, doors, windows and frames, and factory-laminated wood products. This section provides examples of alternatives for formaldehyde in wood panels and binders available on the market. The alternatives include

- Drop-in materials or chemicals
- Changes to component/product design

[10] HWPW = Hartwood/plywood

Table 12 lists the alternatives with product examples. They are listed without priority, and are not assessed by SUBSPORT in this chapter. An evaluation and prescreening of the listed alternatives can be found in chapter 5.

The alternatives summarised in table 12 are all **no-added formaldehyde (NAF) based resins.** NAF based resins are resins formulated with no added formaldehyde as part of the resin cross linking structure, and include resins made from soy, polyvinyl acetate, or methylene diphenyl diisocyanate (MDI)", (Air Resource Board, 2013). The table does not include **ultra-low-emitting formaldehyde (ULEF) resins,** because they are made with formaldehyde and still emit low amounts of it.

Substitution of formaldehyde in wood panel may be done by substituting the formaldehyde based adhesive by an alternative product or by substitution through alternative materials such as cement bonded particle boards.

Many factors have to be considered when selecting the best adhesive for a particular application. Different applications require different technical properties of the adhesives such as: Strength, durability, wetting, consistency, pressure, temperature, moisture content, color and finishing, and costs (Frihart & Hunt, 2010).

3.1.2.1 Alternative resins – short overview

A. Synthetic resins

One group of alternative wood adhesives/resins contain isocyanates. Isocyanate- based adhesives have risen the interest of the industry because they have advantages compared to formaldehyde based resins. They have a high internal bond strength, better elasticity and mode of rapture (MOR), they are more efficient and highly effective in lower doses, and cure at higher wood moisture contents and they do not emit formaldehyde (Tan, 2012).

Methylenebis(4-phenyl isocyanate) (MDI) binders are for example used in over 20 percent of the high growth OSB (oriented strand board) industry worldwide and are in routine production in MDF (medium density fiberboard) mills in Europe and North America (Papadopulus et al. 2001). But it should be noted that MDI is synthesized with formaldehyde.

The examples below describe in brief three synthetic resins based on isocyanates:

<u>Methylenebis(4-phenyl isocyanate) MDI or pMDI</u>

a. **Use**: for wood-based products such as exterior particleboard, exterior OSB, laminated strand lumber (LSL), MDF, or other specially engineered composites/ Flakeboards;particleboard, strand-wood products
b. **Properties:** High dry and wet strength; very resistant to water and damp atmosphere; adheres to metals and plastics, good wetting and penetration behavior,
c. **Compounds/composition:** pMDI is produced during the manufacturing of monomeric MDI. pMDI is produced by phosgenation of di-, tri-, and higher amines and contains a mixture of the three different isomers (Dunky, 2003)

<u>Polyurethane adhesives</u>

a. **Use:** General purpose home and shop; construction adhesive for panelised floor and wall systems; laminating plywood to metal and plastic sheet materials; specialty laminates

b. **Properties:** High dry and wet strength; resistant to water and damp atmosphere; limited resistance to prolonged and repeated wetting and drying; gap-filling
c. **Compounds/composition**: Polyurethane adhesives are formed by the reaction of various types of **isocyanates** with polyols.

Emulsion polymer isocyanate (EPI)

a. **Use:** Laminated beams for interior and exterior use; lamination of plywood to steel metals and plastics; doors and architectural materials
b. **Properties:** High dry and wet strength; moisture resistance, resistant to prolonged and repeated wetting and drying; adheres to metals and plastics
c. **Compounds/composition:** two part system based on an acrylate, polyurethane or vinyl acetate and a **isocyanate** hardener (GlobalInsight, 2005)

The following two alternative synthetic resins are water-borne adhesives widely used in the assembly of wood and paper products (Frihart, 2005). They are made by emulsion polymerisation, which uses a free radical addition mechanism to polymerise the monomere in presence of water and stabiliser (Geddes, 2003).

Polyvinyl acetate (PVA)/ Ethyl vinyl acetate (EVA)

a. **Use:** general purpose in home and shop, assembly of wood and paper products, used for wood bonding, such as furniture construction
b. **Properties:** High dry strength; low resistance to moisture and elevated temperatures; joints yield under continued stress
c. **Compounds/composition:** linear polymers with an aliphatic backbone. Polyvinyl acetate is made by the self-polymerization of vinyl acetate usually under free radical conditions.

Acrylic adhesives

a. **Use:** surface treating, paper traeting, insulation binder
b. **Properties:** bonds well to plastics, and to metals, but not to wood, expensive,

Epoxy

a. **Use:** Laminating veneer and lumber in cold-molded wood boat hulls; assembly of wood components in aircraft; lamination of architectural railings and posts; repair of laminated wood beams and architectural building components;laminating sports equipment; general purpose home and shop, not used often for wood because of their high cost.
b. **Properties:** High dry and wet strength to wood, metal, glass, and plastic; formulations for wood resist water and damp atmospheres; delaminate with repeated wetting and drying
c. **Compounds/composition:** created by polymerizing acrylic or methylacrylic acids through a reaction with a suitable catalyst. Acrylic adhesives and acrylate adhesives cure through a free radical mechanism

B. Natural resins

Natural resins can be divided in five different classes (Afsset, 2009):

Resins made from:

1. Tannins
2. Lignins
3. Carbohydrates
4. Proteins
5. Unsatturated fatty acids

Bioresins made from proteins

a. **Use:** Decorative plywood for interior use, laminated flooring, particleboard, and oriented strandboard (OSB)
b. **Properties:** acording to the producer and user of a soybased resin (Purebon, 2013), it has the same properties like formaldehyde based resins.
c. **Compounds/composition:** mainly soy-protein-based

Bioresins made from Tannins

a. **Use:** Decorative plywood for interior use, laminated flooring, particleboard, and oriented strandboard, (OSB), particle board, medium density fibreboard, Partial replacement for phenolic adhesives in composites and plywood panel products.
b. **Properties:** high viscosity, inconsistent reactivity, composition varies according to growing conditions.
c. **Compounds/composition:** polyhydroxypolyphenolic isolated from plants

C. Examples of alternative materials for interior use

Cement bonded particle boards

a. **Use:** Cement-bonded particleboard is used for making bookcases, cabinet-ends and countertops, making it a useful interior-remodeling choice. The surface of particleboard is often laminated to make it look like hardwood. Flooring with tongue and grooved boards, large size prefabricated elements for permanent shuttering of concrete walls and floors, production of complete prefabricated houses.
b. **Properties:** fire resistant, mould and insect resistant, frost resistant, sound insulation, resistant against weather conditions
c. **Compounds/composition:** cement boards are a combination of cement and reinforcing fibers. Cement boards are mainly cement bonded particle boards and cement fibre. Cement bonded particle boards have treated wood flakes as reinforcement, whereas cement fibre boards have cellulose fibre, which is a plant extract as reinforcement. Portland cement acts as binder in both the cases.

Gypsum boards

a. **Use:** . It is used to make interior walls and ceilings.
b. **Properties:** Gypsum board walls and ceilings have several advantages such as: Ease of installation, Fire resistance, Sound isolation, Durability, Economy, Versatility
c. **Compounds/composition:** Gypsum board are panels made of gypsum plaster pressed between two sheets of paper There exist other ”gypsum panel products” that contain a gypsum cor, but can be faced with a variety of different materials, including paper and fiberglass mats (Gypsum association, 2012). To produce gypsum board, the calcined gypsum is mixed with water and additives to form a slurry which is sandwiched between two pieces of paper . The paper becomes chemically and mechanically bonded to the core.

Clay building boards

a. **Use:** It is suitable for all interior areas, especially for low energy buildings.
b. **Properties:** Once coated with a clay skim finish the surface can take picture hooks, wallpaper and paints, clay surfaces absorb and diffuse water vapour, clay absorbs odours, clay surfaces are cool in summer, warm in winter, Clay is exceptionally good at reducing noise levels' Greenspec, 2012) .
c. **Compounds/composition:** Clay boards are 100% natural. Clay is one of the earliest used basic building materials.Clay building boards are made wood materials or other natural plant-fibres like reed coated with clay.

Table 12: Examples of alternatives for formaldehyde in wood panels:

Alternative	Product examples	Description (from companies' website)	Producer, Contact, information
Chemical alternatives			
Synthetic resins			
Methylenebis (4-phenyl isocyanate) MDI or PMDI	**DHF/DFF panels from EGGER (Germany)**	DHF and DFF boards are board-shaped wood-based materials made out of wood fibre according to EN 622-5 (DHF) and EN 13171 (DFF). They have a tongue and groove profile along the edges. The boards are manufactured using the so-called dry method in a hot press process and with addition of a PMD glue and paraffin wax emulsion for hydrophobising.	EGGER http://www.egger.com/downloads/bildarchiv/43000/1_43592_ZF_EPD_OSB-Platten_DE_2011.pdf)
PVA	**Three-layer panels bonded with PVAC**	"*Environmentally-friendly PVA glue is used on HAAS solid wood panels, and that is good news for persons who suffer from allergies. There are no hazardous emissions from HAAS solid wood panels. The natural ability of wood to absorb and release moisture contributes to a healthy room climate. HAAS solid wood panels enhance the feeling of well-being*" Text from HAAS website	HAAS, http://www.haas-group.com/hp2329/Solid-wood-panels.htm
PU Binder	**Medium density fibreboard (MDF), no added formaldehyde (NAF) e.g. TOPAN MDF Standard FF from Glunz (Germany)**	Binder for TOPAN MDF FF is a formaldehyde-free polyurethane (PUR) adhesives.	Glunz http://www.glunz.de/produkt_dekorativ/gruppe/221
	Orientated strand board (OSB) panels e.g. EUROSTRAND OSB 4 TOP from EGGER (Germany)	uses PU binder = formaldehyde-free gluing (E1< 0,03 ppm). Classified as OSB/4 board according EN 300. The board complies with the strict requirements of the Federal Association of German Prefabricated Construction (BDF/QDF) in terms of emissions and the requirements of the Japanese F****,standard with regard to the level of desiccation (a measurement of formaldehyde).	EGGER http://www.egger.com/downloads/bildarchiv/43000/1_43592_ZF_EPD_OSB-Platten_DE_2011.pdf)

Alternative	Product examples	Description (from companies' website)	Producer, Contact, information
Bioresins			
Bioresins (e.g. from Soybean, Linseed, Rapeseed)	**PureBond**	Soybased resins: PureBond: Soy based plywood adhesive see TURI "Five chemicals study" "Columbia's Purebond veneer core panel is made with hardwood species wood glued together with soy flour "blended with a very small amount of proprietary resin," according to Columbia's website. That resin is Hercules Inc. chemical Kymene®, 624 Wet Strength Resin, now called ChemVisionsTM CA1000, a liquid cationic amine polymer-epichlorohydrin amine called polyamide-epichlorohydrin (PAE)."	http://www.turi.org/library/turi_publications/five_chemicals_study/final_report/chapter_4_formaldehyde
Tannins	**Glyoxalized lignin/ mimosa tannin/hexamine**	The green adhesive can be considered to be produced industrial. All properties of the adhesives correspond to the needs for an industrial panel production. http://www.lepetitsitesante.fr/Documents/Dossiers/110620_formaldehyde_panneaux_verts.pdf	Project "Panneaux Verts" Contact: Sandra Tapin-Lingua sandra.tapin-lingua@fcba.fr Michel Petit-Conil@webCTP.com
Material change and design change substitutes			
Alternative Material	**Cement-bonded particleboard (Portland cement) (CBPB)** **e.g. CETRIS** **Versapanel** **Or Aquapanel cement board**	Cement-bonded particle board CETRIS: free from green asbestos, formaldehyde, isocyanates, wood preservatives and fungicides, made from chip wood particles with cement. Additives can be: Aluminum sulfate, calcium hydroxide, sodium silicate http://www.lubw.baden-wuerttemberg.de/servlet/is/31686/zementgebundene_spanplatten.pdf?command=downloadContent&filename=zementgebundene_spanplatten.pdf Cement-bonded particleboards are frost-resistant and weather-proof, flame resistant or hardly inflammable. They are resistant against mold and fungus and provide no food value to insects. Formaldehyde-free	CETRIS, http://www.cetris.cz/en/systems/walling-systems/cetris-basic-board/ Versapanel, http://www.euroform.co.uk/pdf/versapanel/VERSAPANEL%20MANUAL%20Jan%202010%20Current.pdf Knauf Perlite http://www.perlite.de/innenwand_FAQ.html

Alternative	Product examples	Description (from companies' website)	Producer, Contact, information
Claybuilding boards	**Pavaclay**	„Pavaclay", is a wood fibre and clay board designed for use in dry construction. PAVACLAY provides ideal room air quality because of its hygroscopic and capillary properties. The system stabilizes air humidity within a pleasant range. In addition, clay and wood fiber offer an ideal capacity to act as a heat reservoir, as a result of its high specific heat storage capacity. Of special interest to all those interested in healthy living is the fact that clay purifies the air, since, similar to activated charcoal, the enormous surface leads to a high absorption. Due to the great mass and the high insulating property, PAVACLAY additionally improves noise insulation in areas exposed to high noise levels. (from the website (pavatex) http://www.pavatex.de/tabid/467/language/en-GB/Default.aspx)	Product data sheet: http://pavatex.de//Portals/0/content/Dokumente/Datenblaetter_Deutschland/9_Pavaclay_Produktdatenblatt_D.pdf

Hardwood Plywood Veneer Core, Hardwood Plywood Composite Core, Particleboard, Medium Density Fiberboard, Thin Medium Density Fiberboard (max. thickness 8 mm), (TURI, 2006)

Abbreviations used:

CARB	California Air Resource Board
CBPB	cement bonded particle board
MDF	medium density fibreboard
MDI	methylene bisphenyl isocyanate
NAF	no added formaldehyde
NIH	The National Institutes of Health (NIH), a part of the U.S. Department of Health and Human Services
OS	oriented strandboard
OSB	oriented strand board
PF	phenol-formaldehyde
PMDI	polymeric diphenyl methane diisocyanate or polymer methylene bisphenyl isocyanate
PU	polyurethane
PUR	polyurethane
PVAC	polyvinylacetate
RAC	committee for Risk Assessment
UF	urea-formaldehyde

4.2 Formaldehyde in cleaning agents and disinfectant cleaners

Environmental cleaning is a key in preventing infections in various facilities. A high hygienic standard is required in several facilities such as: health care facilities, live stock farming, schools, sanitary facilities, canteens, food manufacture. Cleaning has here a dual function: surface cleanliness, and infection prevention and control. This requires intensive and frequent cleaning with a wide range of products including disinfectants. (Markkanen et al., 2009).

Formaldehyde is a broad spectrum disinfectant and is active against bacteria, fungi and many viruses and spores. It is used to disinfect surfaces in a 0.5 – 5% solution. Its mechanism of action is based on protein denaturation (Kayser et al., 2001).

Routine disinfection of health care facilities is very common. Formaldehyde is often used in surface disinfectant cleaners. However, cleaning and disinfection are two different processes and not required for all rooms and surfaces. Cleaning is the mechanical or chemical removal of dirt from an object or an area. Normally, cleaning with soap or other detergents followed by rinsing with water is sufficient to remove visible dirt and also germs.Thorough cleaning without disinfectants can remove 50 to 80% of germs (Robert Koch Institut, 2004). But it should be noticed and taken into account that cleaning water without disinfectant show a high contamination with germs, that is not found in disinfectant cleaners. So that cross-contamination may occure . Disinfection is defined as the destruction of microorganisms and can be achieved by physical (e.g. heat) or chemical methods. However, surfaces must be clean before chemical disinfectants will work. Disinfectants are products that contain biocidal active substances with antimicrobial properties. These destroy the spread of harmful organisms. Their use is particularly required in high risk areas of specific industrial and institutional areas.

Cleaning in health care and other facilities such as retirement homes or hotels is often linked with disinfectant cleaners containing biocides (e.g. formaldehyde, glutaraldehyde, ethanol, isopropanol). The function of disinfectants is to kill microorganism (cytotoxicity), but they may also be hazardous for the environment and human health. Alternatives for harmful surface cleaning are described in different reports from Health Care without harm (2013).
The WIDES Database (2013) was developpped by Vienna Ombuds Office for Environmental Protection (Austria) in cooperation with the network ÖkoKauf Wien to support the selection of effective and safe product for disinfection and cleaning in health care. It is an industry independent user-friendly information system.

The alternatives in table 13 are listet without priority, and are not assessed by SUBSPORT. A prescreening of the alternatives can be found in chapter 5.2.

Table 13: Alternatives for formaldehyde in disinfectant cleaners

Formaldehyde use	Alternatives
Surface cleaning and disinfectant agents	Chemical alternatives: - Glutaraldehyde - Hydrogen peroxid - Ortho-phthalaldehyde - Peracetic acid - Chlorine dioxide - Quaternary ammonium compounds (benzalkonium chloride) **Non chemical alternative:** - microfiber mopping - Cleaning machines that require minimal chemicals. - Substitution through organisational measures: Cleaning areas depending on the level of disinfection required from an infection prevention and control perspective. - Substitution through design: Selection of flooring material that reduces the need of cleaning with disinfectants (sorce: green cleaning program of Magee-Women's hospital)

4.3 Formaldehyde in anatomie and pathology

Formaldehyde is extensively used for preserving cadavers in anatomy or funeral services.

Embalming includes the processes intended to delay the decomposition of a cadaver and prepare it for funeral. To prevent the decomposition of the body, the embalmer injects aqueous solutions of formaldehyde the concentration of which depends on how much the body has changed.

For anatomical studies it is extremely important to fix and preserve cadavers adequately for anatomical studies. However, preservation of human bodies for anatomical preparations poses a health risk for workers and students in gross anatomy laboratories (Al-Hayani et al. 2011). Medical students has shown to be exposed to formaldehyde concentrations greater than 5 ppm during macroscopic examinations (Hammer et al. 2011). This has resulted in closure of German dissecting rooms in medical schools in order to protect students. Safer alternatives are necessary to keep up high-quality gross anatomy training and also to ensure the quality of medical staff education. Some alternatives are listed in table 14.

Anatomists, pathologists, and funeral industry workers exposed to formaldehyde for a prolonged time, were more at risk to face lymphohematopoietic cancer and brain (Graf, 2009).

Case stories about successful substitution in scientific laboratories can be found in the SUBSPORT case story database (2013)and in the CatSub database.

Table 14: **Alternatives for formaldehyde in anatomy and pathology**

Formaldehyde use	Alternatives
Anatomie	- Ethanol-glycerin fixation with thymol conservation[11] - Shellack resin in ethanol[12] - Fixall-his (Ethanol, acetic acid, propan-2-ol) see case story No 012 in the SUBSPORT database. - 1-Methyl-3-octyloxymethylimidazolium tetrafluoroborate see case story No 40 in the SUBSPORT database - Ethanedial see case story No 41 in the SUBSPORT database - Ethanol see case story No 93 in the SUBSPORT database. You will find more case stories using ethanol in the catsub database.
Tissue fixative – non chemical alternative	- Freazing - Freaze drying - Cryosubstitution
Pathology	- PROPAN-2-OL (Freedom Cave)[13]
Pathology - non chemical solution	- Refrigeration

4.4 Formaldehyde in textile finishing

The textile finishing procedure includes preparation and pretreatment, dyeing, printing and refinement of fabrics and are used to make the fabric wrinkle resistant, to prevent shrinkage, or increase its resistance to slow combustion. Formaldehyde is used in the textile industry among others to impart wrinkle-resistance to clothing. Concerns about formaldehyde emmissions from clothes and other fabrics has stimulated the development of safer alternatives releasing less or no formaldehyde. Some alternatives are listed in table 16.

Fabrics are treated with urea-formaldehyde resins to give them all sorts of easy care properties such as:

- Permanent press / durable press
- Anti-cling, anti-static, anti-wrinkle, and anti-shrink (especially shrink proof wool)
- Waterproofing and stain resistance (especially for suede and chamois)
- Perspiration proof
- Moth proof
- Mildew resistant
- Color-fast

Ecolable and Oeko-Tex set standards for formaldehyde release in textile (table 15)

Table 15: Limits for formaldhyde release by Ecolable and Oeko-Tex Standard taken from Piccinini et al. 2007

[11] http://jnci.oxfordjournals.org/content/early/2011/02/14/jnci.djr035.full
[12] http://www.medwelljournals.com/fulltext/?doi=javaa.2011.1561.1567
[13] http://www.dodge-uk.com/pdf/MSDS/German/Cavities/Freedom%20Cav%20-%20SDS10155%20-%20German.pdf

	Textiles for babies	Textiles in direct contact with skin	Textile without direct contact with skin	Decoration material
Ecolable		30 mg/kg	300 mg/kg	300 mg/kg
Oeko-Tex	< 20 mg/kg	75 mg/kg	300 mg/kg	300 mg/kg

Table 16: Alternatives for formaldehyde in textile finishing – wrinkle resistance

Formaldehyde use	Alternatives
Finishing of textiles – wrinkle resistance	- Chitosan - Dimethyl urea glyoxal - Polyvinylpyrrolidone - Polymaleic acid

5. Screening out regrettable substitutes

The purpose of this chapter is to eliminate any alternatives that would pose a high risk to the environment or human health. SUBSPORT developed a database containing substances that are not acceptable as alternative due to their hazards. The alternatives are all screened against this database (table 17-20). It can be found on the SUBSPORT database of Hazardous Substances (SDSC) by following this link: http://www.subsport.eu/case-stories-database. If a substance meets any of the SUBSPORT screening criteria, it is removed from further consideration as an appropriate alternative, unless the author (SUBSPORT) regards the alternative safer than the original substance.

5.1 Formaldehyde in wood composites

Tabel 17: Alternatives screened against SUBSPORT database of Hazardous Substances (SDSC)

Chemical alternative	comments	SDSC	source
MDI/PMDI Diphenylmethane diisocyanate/ polymeric MDI Cas No.: 4,4' MDI: 101-68-8 4,2' MDI: 2536-05-2 2,2' MDI: 5873-54-2 Mix of Isomeres 26447-40-5	Contains Isocyanates: polymeric MDI (PMDI), the primary technical/commercial form of MDI, is actually a mixture that contains 25–80% monomeric 4,4'-MDI as well as oligomers containing 3–6 rings and other minor isomers, such as the 2,2'-isomer. The exact composition of PMDI varies with the manufacturer.	MDI is included in the SDSC because of sensitising properties. H317, H334	Toxicological review by EPA: http://www.epa.gov/iris/toxreviews/0529tr.pdf Isocyanates have a strong irritant effect on the respiratory tract. Some people may become sensitised to isocyanates, even at very low levels.
PVA (polyvinyl acrylates) Cas No. : 9003-20-7 Vinylacetate Cas No. : 108-05-04	Water based latex glue, polymere of vinylacetate Acute (short-term) inhalation exposure of workers to vinyl acetate has resulted in eye irritation and upper respiratory tract irritation.	Not included in SDSC	Toxicological review by EPA http://www.epa.gov/ttnatw01/hlthef/vinylace.html

Chemical alternative	comments	SDSC	source
PU 9009-54-5 Groupe : 61789-63-7	Polyurethanes contain isocyanate: they are formed between the reaction of a di-isocyanate and a polyol to form a urethane linkage	PU is included in the SDSC because it contains isocyanate with sensitising properties. H317, H334	Toxicological review by EPA: http://www.epa.gov/iris/toxreviews/0529tr.pdf Isocyanates have a strong irritant effect on the respiratory tract. Some people may become sensitised to isocyanates, even at very low levels.
Protein based bioresin: soybean oil Cas No.: 8001-22-7		Not included in SDSC	Purebond, TURI, Purebond contains in small amounts epichlorohydrin, a carcinogen.
Tannins Cas No.: 1401-55-4		Not l included in SDSC	
Material alternative			
Cement bonded particle boards Portland cement Cas No. 65997- 15-1	Although Portland Cement is not listed in IARC as carcinogen, it may contain small amounts of naturally occurring, but potentially harmful, substances such as free crystalline silica or havy metals. Crystalline silica has been listed by IARC as a known human carcinogen (Group I) through inhalation. Exposure to wet portland cement can cause serious, potentially irreversible tissue (skin or eye) destruction in the form of chemical (caustic) burns or an allegoric reaction.	Not included in SDSC	(MSDS by Holcim, 2005) TURI (2006) hazard assessment HSE[14]
Clay boards No Cas No. for clay (Kaolin Cas No. 1332-58-7)	Natural product Clay may contain Kaolin. Kaolin is a mixture of different minerals. Its main component is kaolinite and it frequently contains quartz, mica, feldspat, illite and montmorlilonite	Not included in SDSC	TOXNET

[14] http://www.hse.gov.uk/pubns/web/portlandcement.pdf

5.2 Formaldehyde in cleaning agents and disinfectant cleaners

Tabel 18: Alternatives screened against SUBSPORT database of Hazardous Substances (SDSC)

Chemical alternative	comments	SDSC	source
Glutaraldehyde Cas No. 11-30-8	Glutaraldehyde is a skin sensitiser and very toxic to aquatic life. Glutaraldehyde does not pass SUBSPORT criteria and will be therefore **not be added** as alternative in the case story database.	Included in SDSC because of sensitizing properties.	SDSC, ESIS
Hydrogen peroxide Cas No. 7722-84-1	Hydrogen peroxide imay cause severe skin burns and eye damages.	Not included in SDSC	
Ortho-phthalaldehyde Cas No. 643-79-8	Ortho-phthalaldehyde has no harmonised classification according to Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Please check also the ECHA's Classification and Labelling Inventory.	Not included in SDSC	ESIS, SDSC
Peracetic acid Cas No. 79-21-0	Peracetic acid is very toxic to aquatic life.	Not included in SDSC	ESIS, SDSC
Chlorine dioxide	Chlorine dioxide is very toxic to aquatic life.	Not included in SDSC	ESIS, SDSC
Quaternary ammonium compounds (benzalkonium chloride) C8-18: Cas No. 63449-41-2 C12-18: Cas No. 68391-01-5	Quarternary ammonium compounds Cas No. 63449-41-2 are very toxic to aquatic life	Not included in SDSC	ESIS, SDSC
Non-chemical alternative			
microfiber mopping	Non chemical alternative	Not included in SDSC	
Cleaning machines that require minimal chemicals	Non chemical alternative	Not included in SDSC	
Cleaning areas depending on the level of disinfection required from an infection prevention and control perspective	Substitution through organisational measures	Not included in SDSC	
Selection of flooring material that reduces the need of cleaning with disinfectants	Substitution through design	Not included in SDSC	source: green cleaning program of Magee-Women's hospital,

5.3 Formaldehyde for anatomie and pathology

Tabel 19: Alternatives screened against SUBSPORT database of Hazardous Substances (SDSC)

Chemical alternative	comments	SDSC	source
Ethanol-glycerin fixation with thymol conservation	The alternative is a mixture and is therefore categorised as other type of alternative. Glycerin is not included in the SDSC. Ethanol is included in the SDSC as being carcinogen 2A/2B (IARC) Thymol is not included in SDSC, but is toxic to aquatic life according to ESIS.	Not included in SDSC	SDSC, IARC, ESIS, Hammer et al. 2011
Shellac resin in ethanol Shellac Cas No. 9000-59-3 Ethanol Cas No. 64-17-5	Shellac is a natural polymer of animal origin. It is composed of a complex mixture aliphatic and alicyclic hydroxy acids. Ethanol is included in SDSC as carcinogen 2A/2B (IARC)	Shellac is not included in SDSC	ESIS, SDSC, IARC, Al-Hayani et al. 2011
PROPAN-2-OL (Freedom Cave) Cas No. 67-63-0	Propan-2-ol is highly flammable	Propan-2-ol is not included in SDSC	ESIS, SDSC, MSDS for Freedom Cave[15]

5.4 Formaldehyde in textile finishing

Tabel 20: Alternatives screened against SUBSPORT database of Hazardous Substances (SDSC)

Chemical alternative	comments	SDSC	source
Chitosan Cas No. 9012-76-4	Chitosan is a natural polysaccharide extracted from crustacean shells	Not included in SDSC	SDSC, Anonymus, 2009
Dimethyl urea glyoxal DMeDHEU N,N-dimethyl urea Cas No. 96-31-1 Glyoxal Cas No. 107-22-2	DMeDHEU is synthesised from N,N-dimethyl urea and glyoxal N,N-dimethyl urea Is not included in SDSC. Glyoxal is included in the SDSC being skin sentisiser (H317, H334).	DMeDHEU is not included in SDSC	SDSC, ESIS, Schwarcz, 2012
Polyvinylpyrrolidone Cas No. 9003-39-8		Not included in SDSC	SDSC, ESIS, Hashem, 2009
Polymaleic acid Cas No. 26099-09-2	Maleic acid is included in SDSC because of skin sentisising properties (H317)	Polymer not included in SDSC	SDSC, ESIS, Periyasamy, 2012

[15] http://www.dodge-uk.com/pdf/MSDS/German/Cavities/Freedom%20Cav%20-%20SDS10155%20-%20German.pdf

6. Characterising alternatives for composite wood binders

Most of the identified synthetical alternative resins (MDI and PU) did not pass the SUBSPORT criteria. SUBSPORT does not only look at the end product, but also at hazards that might put workers at risk e.g. in the production line. Wood panels produced with MDI or PU resins do not emit formaldehyde and do not contribute to formaldehyde emissions in the indoor air. But as they use isocyanate - a sensitiser - to bond wood composites, they will not be included in the SUBSPORT database of case stories. Portland cement raises different problems: it might contain free silica, which is a known cancerogen and wet Portland cement can damage/burn the skin.

PVA adhesives are used to assemble wood parts in the furniture industry. Some companies use PVA to assamble three-layer solid wood panels (e.g. Haas, Germany). Commercially available PVA-based panels could not be identified by the author. PVA is not water resistant and not heat resistant. PVA can substitute urea formaldehyde resin or MDI only in a very small application range.

The bioresins are still in the stage of development. Different research groups are developing bioresins ("green products") for the wood and construction industry (panneaux verts, Neolignin[16]).

The alternative material such as clay boards can also be used only in a very small application range. Clay boards can mainly be used indoors as structural panels. Clay may also contain small amounts free crystalline silica and heavy metals.

6.1 Hazard characteristics of alternatives: formaldehyde free wood panels

A detailed documentation and hazard assessment on formaldehyde in wood panels and possible alternatives has been done by the Toxics Use Reduction Institute in Massachusetts (TURI, 2006). The hazard assessment of SUBSPORT follows the SUBSPORT methodology (table 21-23). Afsset the French Agency for Environmental and Occupational Health Safety (since 2010 the French Agency for Food, Environmental and Occupational Health and Safety ANSES) published a detailed French study about formaldehyde in its divers uses and possible alternatives (Afsset, 2009)

Table 21: Hazard characteristics of soy bean resin used for Purebond (based on soil bean oil CAS 8001-22-7 and known additives)

	Properties	Source of information
Soy bean oil CAS 8001-22-7: This substance is not classified in the Annex I of Directive 67/548/EEC		
Physical Hazards		
Explosivity	Not applicable	GHS
	Not explosive	European Comission[17]
Flammability	Not applicable	GHS
	May be combustible at high temperature	European Comission
Oxidizing	Not applicable	GHS
	Not oxidising	European Comission
Other properties of reactivity	Not applicable	

[16] http://www.lepetitsitesante.fr/Documents/Dossiers/110620_formaldehyde_panneaux_verts.pdf
[17] Review of Annex IV of the regulation No 1907/2006 (REACH), evaluation of existing entries, Appendix 2, retrieved at: http://ec.europa.eu/environment/chemicals/reach/pdf/6B%20Appendix%202.pdf

	Properties	Source of information
Human Health Hazards		
Acute toxicity		
Highly toxic	Not applicable	
Skin or eye corrosion / irritation	Not applicable	
	Slightly toxic in case of skin and eye contact	European Commisiion
Carcinogenicity	Not listed in IARC, CLP and ESIS,	CLP, List of harmonized classification and labbeleing of hazardous substances ESIS
Mutagenicity	Not listed	
Reproductive toxicity (including developmental toxicity)	Not listed	
Endocrine disruption	Not listed	OECD, EU Endocrine disruptor database, SIN list
Respiratory or skin sensitization	Not listed Not sensitising	CLP European Comission
Neurotoxicity	Not listed	Vela et al. 2003
Immune system toxicity		
Systemic Toxicity		
Toxic metabolites		
Acute/chronic aquatic toxicity	Not applicable	
	No aquatic toxicity	European Comisson
Bioaccumulation	Not applicable	
	biodegredable	European Commission
Persistence	Not applicable	
Greenhouse gas formation potential	Not listed	Kyoto Protocol, Annex A
Ozone-depletion potential	Not listed	Montreal Protocol
Monitoring – has the substance been found in human or environmental samples?		
Epichlorohydrin CAS 106-89-8		
Physical Hazards		
Explosivity	Due to the molecular structure the prediction of explosive properties is negative	ECHA registered substances, data dossier epichlorohydrin
Flammability	Flamm Liq. 3	CLP, SDSC
Oxidizing		
Other properties of reactivity		
Human Health Hazards		
Acute toxicity		
Highly toxic	Acute tox 3: H331, H311, H301	CLP, SDSC
Skin or eye corrosion / irritation	Skin Corr 1B	CLP, SDSC
Carcinogenicity	Cat 2A, Carc 1B	IARC, SDSC CLP, SDSC
Mutagenicity	No data	

	Properties	Source of information
Reproductive toxicity (including developmental toxicity)	No adverse reproductive effects in humans were reported in available studies	scorecard
Endocrine disruption	Cat 1	EU EDC DB, SDSC
Respiratory or skin sensitization	Skin sens 1	CLP, SDSC
Neurotoxicity	Not listed	SDSC, Vela et al, 2003
Immune system toxicity		
Systemic Toxicity		
Toxic metabolites		
Acute/chronic aquatic toxicity	No data	CLP
	Toxicity to aquatic organisms	PAN
	Toxicity to aquatic organisms	SIGMA Aldrich safety data sheet
Bioaccumulation	Data waving	ECHA registered substances, data dossier epichlorohydrin
	bioconcentration in aquatic organisms is low	TOXNET/HSDB
Persistence	no	Environment Canada
Greenhouse gas formation potential	Not listed	Kyoto Protocol, Annex A
Ozone-depletion potential	Not listed	Montreal Protocol
Monitoring – has the substance been found in human or environmental samples?		

Table 22: Hazard characteristics of clay boards

	Properties	Source of information
Physical Hazards: This substance is not classified in the Annex I of Directive 67/548/EEC		
Explosivity	Not applicable	
Flammability	Not applicable	
Oxidizing	Not applicable	
Other properties of reactivity	no	
Human Health Hazards		
Acute toxicity		
Highly toxic	Not applicable	
Skin or eye corrosion / irritation	Not applicable	
Carcinogenicity	Not listed in IARC, CLP and ESIS,	CLP, List of harmonized classification and labbeleing of hazardous substances ESIS, IARC
Mutagenicity	Not listed	CLP, SDSC
Reproductive toxicity (including developmental toxicity)	Not listed	CLP, SDSC
Endocrine disruption	Not listed	OECD, EU Endocrine disruptor database, SIN list (ChemSec 2013)
Respiratory or skin sensitization	Not listed	CLP

	Properties	Source of information
Neurotoxicity	Not listed	Vela et al., 2003
Immune system toxicity	Not applicable	
Systemic Toxicity	Not applicable	
Toxic metabolites	Not applicable	
Acute/chronic aquatic toxicity	Not applicable	
Bioaccumulation	Not applicable	
Persistence	Natural product	
Greenhouse gas formation potential	Not listed	Kyoto Protocol, Annex A
Ozone-depletion potential	Not listed	IPCC, Montreal protocol
Monitoring – has the substance been found in human or environmental samples?		

*Clay may contain small amounts free crystalline silica and heavy metals. Workers producing or working with clayboards (e.g. when sawing clayboards) may be at risk of dust.

Table 23: Hazard characteristics of PVA (CAS 9003-20-7)

	Properties	Source of information
Physical Hazards		
Explosivity	No	MSDS, http://www.carlroth.de/jsp/de-de/sdpdf/9154.PDF
Flammability	No	MSDS, http://www.carlroth.de/jsp/de-de/sdpdf/9154.PDF
Oxidizing	No	MSDS, http://www.carlroth.de/jsp/de-de/sdpdf/9154.PDF
Other properties of reactivity		
Human Health Hazards		
Acute toxicity		
Highly toxic	No toxic or other hazards are associated with the use of this latex adhesive	Toxnet/HSDB
Skin or eye corrosion / irritation	May cause irritation in respiratory tract and eyes	U.S. EPA
Carcinogenicity	Not listed in IARC, CLP and ESIS,	CLP, List of harmonized classification and labbeleing of hazardous substances ESIS, SDSC
Mutagenicity	Not listed	SDSC
Reproductive toxicity (including developmental toxicity)	Not listed	SDSC
Endocrine disruption	Not listed	OECD, EU Endocrine disruptor database, SIN list (ChemSec 2013)
Respiratory or skin sensitization	Not listed	CLP
Neurotoxicity	Not listed	Vela et al. 2003
Immune system toxicity		

	Properties	Source of information
Systemic Toxicity		
Toxic metabolites		
Acute/chronic aquatic toxicity	Not applicable	
Bioaccumulation	Not applicable	
Persistence	Not biodegradeble	
Greenhouse gas formation potential	Not listed	Kyoto Protocol, Annex A
Ozone-depletion potential	Not listed	Montreal Protocol
Monitoring – has the substance been found in human or environmental samples?		

6.2 Technical feasibility of alternatives for wood composite binders

The alternatives based on bioresins are mainly in the stage of research. A research group in France working on tannins as alternative, are close to develop an alternative ready for industrial use (see SUBSPORT case story No. 201).

Currently, the use spectrum of the presented alternatives is not as broad as for formaldehyde-based or isocyanate-based resins. It is necessary to improve the performance of alternative resins (e.g. bioresins) to push the substitution of formaldehyde based wood panels. Bioresins able to compete with formaldehyde- or isocyanate-based resins need additives that may be hazardous. PureBond® is one of the biobased resin that is already produced for industrial uses. It is used by Columbia Forest Products for hardwood plywood manufacturing. It reaches similar performances as formaldehyde based resins.

Alternative material like cement or clay are produced in an industrial scale. Cement bonded particle boards can be used outside and indoors, but they have a high weight. Clay boards can only be used in doors.

Poly vinyl acetate, PVA is a water-borne adhesives that is widely used for wood bonding, such as furniture construction. PVAs do not work well at high moisture levels (Frihart, 2010). PVA can be used to bond three layer panels such as solid wood panels from hardwood (e.g. from Tilly or Haas). These wood panels are not weather resistant and not suitable for outside uses.

6.3 Economical feasibility of alternatives for formaldehyde free wood panels

Taking into account, that the presented alternatives are suitable for different uses (indoors/outside/construction/ interior works/furniture construction) it is difficult to compare the costs.
Purebond is currently available at a similar cost to formaldehyde-based plywood (TURI, 2006, Purebond, 2013).

Clayboards are currently more expensive than traditional formaldehyde-based structural panels (Naturbauhof, 2013).

The author has no information for the PVA bonded three layer panels.

7. Comparing alternatives for wood composite binders

	Bioresins/PureBond	Clay boards	PVA
Health aspects	PROS: no hazardous substances (tannins, lignins) CONS: PureBond contains Epichlorohydrin (Classified by IARC group 2A). According to US EPA (1984) it is completely consumed in the batch manufacturing process used to make the resin. Other bioresins intended for industrial production contains also small amounts of dangerous substances (e.g.)	PROS: natural product, not suspected to contain dangerous substances	PROS: CONS: some PVA glues include an isocyanate catalyst (isocyanates are sensitisers and can cause asthma and dermatitis
Environmental aspect	PROS: readily biodegradable; natural product	PROS: not biodegradable, but natural component of the soil	PROS: CONS: No information
Performance aspects	PROS: Purebond: performance aspects similar to formaldehyde-based plywood CONS: most of the bioresins are still in the stage of development	PROS: very good properties regarding the indoor air and moisture CONS: can substitute Formaldehyde only in a small range.	PROS: excellent performance characteristics for interior (TURI, 2006) CONS : PVA is not waterresistant and can substitute Formaldehyde only in a small range (cabinetry)
Cost aspects	PROS: PureBond: currently available at a similar cost to formaldehyde-based plywood (TURI, 2006, Purebond	CONS: currently more expensive than traditional formaldehyde-based structural panels (Naturbauhof, 2013)	No information

Examples of related case stories:
009-EN 'Five Chemicals Alternatives Assessment Study'
096-EN 'Substitution of formaldehyde by starch in adhesives used in the manufacture of wood particle boards'
122-EN 'Green Glue - alternative for methanol releasing silane based parquet adhesives'
201-EN 'Glues from renewable resources for panelboard manufacture'

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