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Chapter

FORMALDEHYDE EMISSIONS FROM WOOD-BASED PANELS - TESTING METHODS AND INDUSTRIAL PERSPECTIVES

Luisa H. Carvalho*

DEMad - Departamento de Engenharia de Madeiras,
Instituto Politécnico de Viseu, Campus Politécnico de Repeses,
Viseu, Portugal

Fernão D. Magalhães[†]

LEPAE - Departamento de Engenharia Química,
Faculdade de Engenharia da Universidade do Porto, Porto, Portugal

João M. Ferra[‡]

Euroresinas – Industrias Químicas, S. A., Sines, Portugal

ABSTRACT

Formaldehyde is an important chemical feedstock for the production of phenoplast and aminoplast thermosetting resins, by reaction with other monomers (mostly urea, but also melamine, phenol and resorcinol). These adhesives are mainly used in the manufacture of wood-based panels: plywood, particleboard, hardboard, medium density fiberboard

* E-mail: lhcarvalho@demad.estv.ipv.pt.

[†] E-mail: fdmagalh@fe.up.pt.

[‡] E-mail: joao.ferra@sonaeindustria.com.

(MDF) and oriented strand board (OSB). These products have a wide range of applications, from non-structural to structural, outdoor or indoor, mostly in construction and furniture, but also in decoration and packaging. The WBP industry plays an important role in the global economy and contributes for forest sustainability and carbon sequestration. In 2009, FAO (Food and Agriculture Organization) reported that a total of 260 million m³ WBPs were produced in the world (Europe 29.7%, Asia 43.9%, North America 18.3% and others 2.5%).

Being economically competitive and highly performing, a major drawback of formaldehyde-based resins, mostly urea-formaldehyde, is the formaldehyde emission during panel manufacturing and service life. There are two sources of emission: release of unreacted monomer, during or after panel production, and long-term resin degradation (hydrolysis). The formaldehyde content and chemical stability of the resin will therefore affect emission levels. In addition, external factors like temperature, humidity or air renewal rate will also play a role. It must be noted that wood itself contributes to formaldehyde emission, since it is a product of metabolism and decomposition processes. The actual emission level depends strongly on the type(s) of wood used in panel production.

Due to information considering formaldehyde as potentially carcinogenic to humans, the implementation of international regulations and requirements for emissions from WBPs has led to establishment of standard testing methods. Two main groups are considered: chamber methods (emulating indoor living environments, mentioned in ASTM, ISO and European standards), and small scale methods, also called derived tests, oriented to industrial quality control and development. This second group includes commonly used methods, mentioned in different international standards, like the so-called: perforator (actually a test of potential formaldehyde emission), flask, desiccator, and gas analysis methods. Correlation between results from different methods has been a matter of debate, not yet completely elucidated.

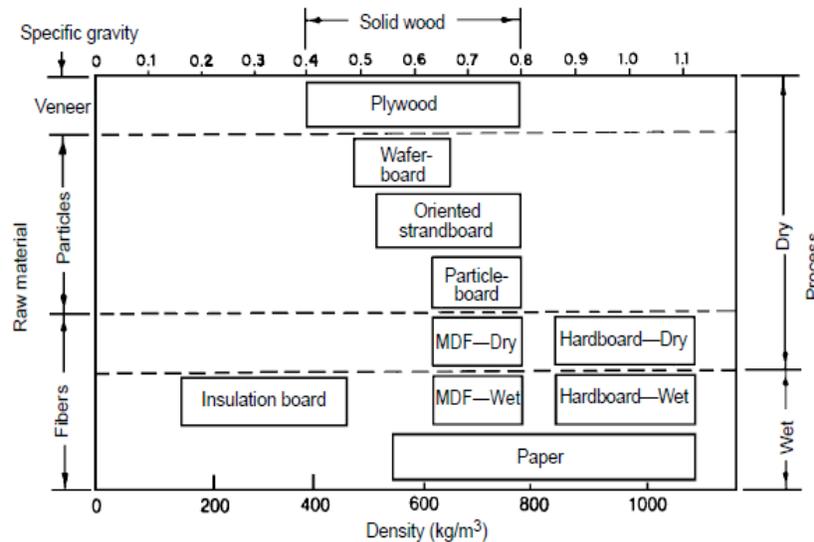
Based on different test methods, emission limit standards for WBPs have been issued by several governmental organizations in Europe, Japan and United States, allowing for product classification according to emission level. Additionally, limits drawn by major industrial consumers, like IKEA, have been a defining guideline for WBP producers.

In order to comply with increasingly stringent requirements, the industry has been developing strategies to minimize formaldehyde emissions from WBPs. Four major approaches can be found: 1) reduction of formaldehyde content in resin formulation, while attempting to maintain adhesive performance, 2) addition of formaldehyde scavengers to resin or wood particles, having the negative effect of consuming formaldehyde prior to resin cure, 3) implementation of surface treatments after board production, and 4) use of alternative adhesive systems with

reduced or no emissions, with an impact on product cost and/or performance.

1. INDUSTRIAL PRODUCTION OF WOOD-BASED PANELS

Wood-based panels (WBPs) are manufactured from wood materials having various geometries (e.g., fibers, particles, strands, flakes, veneers, and lumber), combined with an adhesive, and bonded in a press. The press applies heat (if needed) and pressure to activate (chemically cross-link) the adhesive resin and bond the wood material into a solid panel having good mechanical and physical properties (strength, stiffness, form, dimensional stability, etc.).



Source: (Suchsland and Woodson, 1987).

Figure 2.1. Classification of wood-based panels by particle size, density, and process type.

The most used wood-based panels are plywood, particleboard (PB), medium density fiberboard (MDF) and oriented strand board (OSB). Other examples of wood-based panels are hardboard, LVL-laminated veneer lumber, SWP-solid wood panels and cement-bonded particleboard. Modern plywood, made by gluing together several hardwood veneers or plies, was the first type of wood-based panel produced in 1935 in Portland, USA (APA). Only 60

years later particleboard panels were manufactured. Figure 2.1 summarizes the classification of wood-based panels according to particle size, density, and process type (Suchsland and Woodson, 1987).

1.1. Manufacture of Particleboard

Particleboard is manufactured from wood chips, sawdust, waste materials and recycled woodchips (Youngquist, 1999). Typically, it is made in three layers. The two external layers consist of finer particles and sawdust, while the core layer is made of coarser material.

The manufacture of particleboard has five main steps: (1) furnish preparation, (2) resin application, (3) mat formation, (4) hot pressing, and (5) finishing. The furnish is prepared by refining the raw materials into small particles and drying them to achieve a desired moisture content, about 2 to 7 % (Youngquist, 1999). The type of resin used in particleboard depends of the characteristics desired, but normally urea-formaldehyde (UF) resin is used. The resin/wood ratio, based on resin dry solids content, and particle dry weight, is usually 6 to 9 % (Youngquist, 1999; Dunky, 2003). Additives to enhance characteristics like fire retardancy or moisture resistance can be applied at this stage. After mechanically mixing the particles and the adhesive system, the material goes through a continuous mat-forming system and is then hot-pressed under pressures between two and three MPa and temperatures between 140 °C and 220 °C (Youngquist, 1999; Dunky, 2003). After the press cycle is complete, the panel is transported to a board cooler, and then hot-stacked to wait sawing into finished panel sizes and sanding.

1.2. Manufacture of OSB

OSB (oriented strand board) is a structural building material used for residential and commercial construction. It is a multi-layered board mainly made from strands of wood together with a binder. The strands in the external layer are aligned and parallel to the board length or width. The strands in the internal layer or layers can be randomly orientated or aligned, generally at right angles to the strands in the external layers (EN 300). The manufacture process of OSB is very similar to particleboard. The main differences are the type of particles, resination process and mat formation (Marra, 1992).

Typically OSB is made from freshly harvested aspen poplar, pine or other mixed hardwood and softwood logs, recovered wood are not use. Phenol-formaldehyde (PF) resin and pMDI are the most commonly adhesives used in OSB industries, although melamine urea formaldehyde (MUF) resins and melamine and/or urea modified PF resins are also used to decrease the price of adhesive (Dunky, 2003, Marra, 1992). Irle and Barbu (2010) reported that the current trend in Europe is the use of pMDI adhesive on face (3-6 %) and core (4-10 %) due to the low formaldehyde emission and short pressing time.

1.3. Manufacture of MDF

MDF (medium density fiber) panels consist of ligno-cellulosic fibres manufactured by the “dry process”, i.e. having a fiber moisture content less than 20 % at the forming stage and being essentially produced under heat and pressure, after mixing with adhesive and wax. Fibers are usually obtained from a thermo mechanical pulping process, which consists in the combination of heat and mechanical energy to break the bonds between wood cells (Irle and Barbu, 2010). UF and fortified UF resins are the most used adhesives to manufacture MDF. In specific products, requiring moisture resistance and fire retardancy, MUF resins and pMDI are used. The resins are sprayed onto wood fibers passing in a blowline. Understanding and optimizing this step is the most challenging task in the MDF process (Waters, 1990). According to Chapman (Chapman, 2011) the optimization of the blowline and the resin injection nozzles permits to reduce significantly resin consumption.

1.4. Manufacture of Plywood

Plywood is a composite panel made from thin layers of wood veneer. The layers are glued together under heat and pressure, each with its grain at right angles to adjacent layers to improve strength (Sellers, 1985). Usually UF resins are used to produce interior boards without special requirements concerning water resistance. PF and MUF or MUPF resins are used for making exterior plywood (Dunky, 2003). The plywood manufacturing process has three main stages: 1) log preparation, 2) veneer plain slicing or rotary cutting, drying and grading, and 3) board lay-up, pressing and finishing (Irle and Barbu, 2010). Resin grammage typically ranges from 140 to 240 g/m² per

face that depend of the type of wood veneer and the operation conditions, temperature and pressing times (Irle and Barbu, 2010).

Plywood is considered a material of choice in the building industry because of outstanding structural performance, as defined by a high strength-to-weight ratio, excellent dimensional stability, and durability compared to other building material. Due to the high price, plywood has been substituted by OSB in specific applications.

1.5. Market

The increase of the world demand for wood-based composites and the awareness of the tree role in the global ecosystem are driving the use of recycled wood and wood from different sources/species in the formulation of wood composites (Carvalho, 1999). The variability of available wood creates difficulties concerning the compatibility/adequacy of the resin (binding agent) with the wood (Sigvartsen and Dunky, 2005).

Food and Agriculture Organization of the United Nations (FAO, 2011) reported that in 2010 approximately 100 million m³ of particleboard (EUA, Germany, Canada and China manufacture 20 %, 10 %, 9 % and 8 % respectively), 70 million m³ of MDF (China, Germany and EUA manufacture 45 %, 8 % and 6 % respectively) and 84 million m³ of plywood (EUA, Germany, Canada and China manufacture 20 %, 10 %, 9 % and 8 % respectively) were manufactured in the world (see Figure 2.2) (FAO, 2011).

European Panel Federation (EPF) reported that the wood-based panels industry was affected by the economic crisis in 2008 (Wijnendaele, 2009), in particular the production of particleboard and MDF, which decreased in 2008 by 8.7 % and 8 % respectively (Wijnendaele, 2009).

1.6. Environmental Impact

The European woodworking industry stands for about 100,000 companies, two million employees and an annual turnover of 150 billion € (EPF, 2011). Furthermore, forests and forest-based industries provide direct employment to three million people throughout the EU, especially in remote areas (EPF, 2011). They represent 10 % of the total production value of the EU manufacturing industry (EPF, 2011). According to European woodworking industry, these businesses invest continuously in sustainable forest

management, deforestation and reforestation activities to ensure reliable wood availability.

Wood is formed by photosynthesis of CO₂ and water, thereby blocking carbon in a durable way. During growth a tree absorbs, through photosynthesis, approximately the equivalent of 1 ton of CO₂ for every m³ growth, while producing the equivalent of 0.7 ton of oxygen (CEI-Bois, 2007). Wood therefore plays a major role in fighting climate changes. Rational use of wood sources stimulates forest expansion and reduces greenhouse gas emissions.

Wood products require less energy for manufacturing (up to 6000 MJ/m³) than alternative raw materials, hence contributing even more to the reduction of fossil fuel consumption. By using the full potential of wood (sink and substitution effects) in buildings, Europe could reduce emissions of CO₂ with 300 million ton or 15 to 20% (EPF, 2011).

The recycling process has a great paper in future of wood-based panels industry. In 2004 the proportion of recycled wood used in manufacturing of particleboard was 23 % (EPF, 2005). Roffael et al. (2009) studied the use of recycled fiberboards with raw material to making MDF. They concluded that the use of waste fiberboards up to 33 % does not have effect on the mechanical properties of the panels.

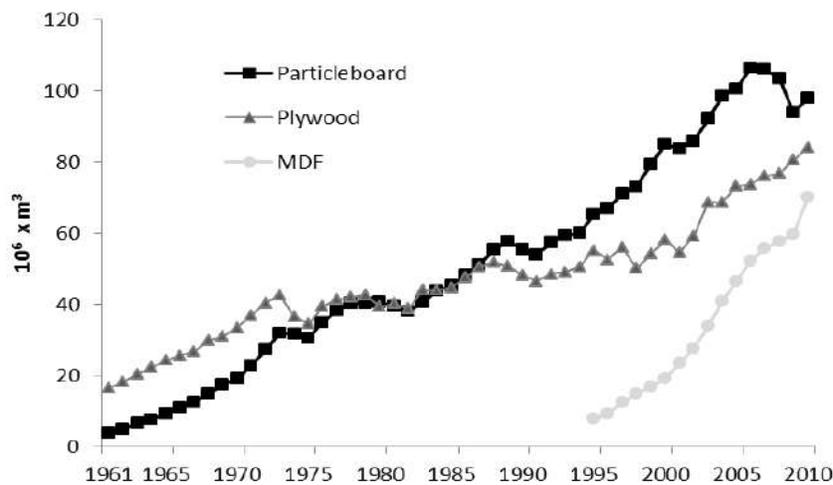


Figure 2.2. Evolution of the global production of wood-based panels. Source: (FAO, 2011).

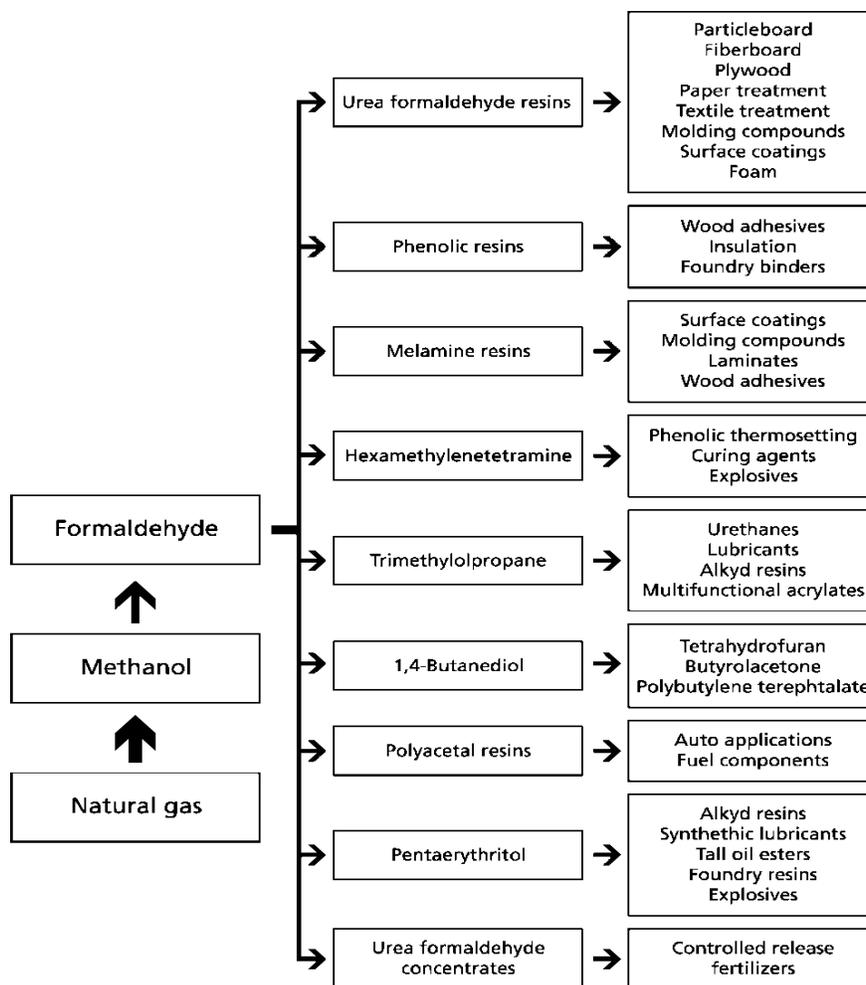


Figure 3.1. Product Tree for Formaldehyde. Reprinted with permission from: Salthammer, T., Mentese, S., Marutzky, R., “Formaldehyde in the indoor environment” *Chemical reviews*, 110, 2536-72, 2010. Copyright 2010 American Chemical Society.

In 2003 the European Woodworking Industries, Pulp and Paper Industries and the European Commission created a work group for discuss the use of the wood sources with energy and wood products (CEI-Bois, 2007). The main recommendation was to consider “wood-based products as carbon sinks under the Kyoto Protocol, thereby acknowledging the contribution of wood-based products to climate change mitigation and the carbon cycle, and recognize

their superior eco-efficiency versus other materials, as well as their outstanding properties in recycling with minimal energy use” (CEI-Bois, 2007).

2. CURRENT USE OF FORMALDEHYDE-BASED RESINS

Formaldehyde is an important chemical for the global economy, widely used in the production of thermosetting resins, as an intermediate raw material in the synthesis of several chemicals, and for preservation and disinfection (Global Insight Inc., 2006; Tang et al., 2009). The annual world production is about 21 million ton. Figure 3.1 summarizes the industrial uses of formaldehyde and related products. Production of urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde resins accounts for about 50 % of global formaldehyde consumption (Global Insight Inc., 2006). In 2003, the value of sales of formaldehyde and derivative products in United States and Canada reached approximately USD\$ 145 billion. The number of workers involved in related activities was reportedly 4.2 million, which represents nearly 3.4 % of employment in private, nonfarm establishments in North America (Global Insight Inc., 2006).

2.1. Urea-formaldehyde Resins

Urea-formaldehyde (UF) polymers have been for decades the most widely used adhesives in the manufacture of wood-based panels, such as particleboard (PB), medium density fiberboard (MDF) (both consuming 68 % of the world’s UF resins production) and plywood (consuming 23 %) (SRI, 2009).

According to SRI Consulting (SRI, 2009) the global production of UF resins in 2008 was approximately 14 million ton. Their consumption increased 2.8 % in 2008, and is expected to grow an average 3.2 % per year from 2008 to 2013, and just under 2 % per year from 2013 to 2018. Table 3.1 describes the main uses of UF resins (Dunky, 1998; Dunky and Pizzi, 2002; Dunky, 2003).

The main reasons for the wide use of UF resin in wood based panels are high reactivity, low cost and excellent adhesion to wood. On the other hand, the most important drawbacks are low moisture resistance and formaldehyde emission during panel manufacture and service life (Pizzi, 2003; Dunky, 1996). Although free formaldehyde content on these resins has been decreased

during the last decades, the recent reclassification of formaldehyde by International Agency for Research on Cancer (IARC) as “carcinogenic to humans”, is forcing resin producers to develop systems that lead to a decrease in its emissions to levels as low as the present in natural wood (Athanassiadou, 2009; Athanassiadou, 2007). This imposition has been a driving force for considerable research effort, not only in the engineering of UF resins, but also in the development of all sort of alternative resins. In 2007, Dynea AS Company started commercializing AsWood™ resin (formaldehyde based resin), which presented formaldehyde emissions in WBPs similar to the level found in solid wood. However, the price of this product is too high for production of standard particleboard and MDF (Durkic, 2009).

Table 3.1. Main applications of urea-formaldehyde resins

Application	%
Wood Composites: adhesives for non-structural panels, particleboard and MDF, for structural panels, plywood and OSB.	95
Cork Composites: adhesive for interior application of cork panels	5
Decorative e protective laminates: countertops, cabinets, furniture, flooring, wall covering, sheathing, automobile interiors	
Paper treating and coating: wet-strength resins added to sanitary paper products such as facial tissue, table napkins, and roll towels.	
Surface coatings: crosslinkers in stove paint systems in combination with other polymeric materials including alkyds, acrylics, epoxies and saturated polyesters.	
Textile treatment: printing inks, dyes and textile finishing products (crease-resistant textile products e.g. products that does not wrinkle easily).	
Foundry materials and binders (adhesives in molds to produce castings): sand binder to coat sand, which is then used in core making for casting operations in the foundry industry.	
Fiberglass and rock wool insulation: specific applications include low-density insulation, high-density industrial insulation, and other specialty insulation.	
Molded plastic products: electrical switches, circuit breakers, stove hardware, buttons and housings.	
Abrasive materials: coated and bonded abrasives.	

Until now, the decrease on free formaldehyde emissions has been obtained by decreasing the molar ratio F/U and/or by the addition of formaldehyde scavengers. Both lead to a decrease on reactivity and degree of curing, harming the formation of adhesive bonds. Moreover, currently used hardeners are adapted to high F/U molar ratios and high levels of free formaldehyde in solution. Therefore, the decrease in F/U molar ratio can result in panels with low mechanical performance. The experience of WBP producers is that resins with lower molar ratio F/U are less adaptable to different panel production process conditions and raw materials. This is an important factor, since WBP production nowadays uses mixtures incorporating recycled wood and wood from different origins.

2.2. Melamine-formaldehyde Resins

Melamine-formaldehyde (MF) resins are used mainly as paper impregnating polymers for surfacing of wood-based panels (particleboard and MDF) and decorative laminate. These resins are also used as adhesives to produce particleboard, MDF and plywood when moisture resistance is a desired property. The reduced number of applications, shown in Table 3.2, has to do its high cost (Dunky and Pizzi, 2002 ; Dunky, 2003).

Melamine-formaldehyde resins are also used in specially formulated (i.e. alkylated, methylated, butylated, or isobutylated) resin systems to produce highly durable surface coatings. The coating can be either water based or solvent based. During the coating process these resins form efficient cross-linking systems as they react with polyester, acrylics and epoxies. The benefits of melamine cross-linked coatings include better color retention, wear resistance and scratch resistance. The automobile market accounts for about 40% of MF resin consumption in the surface coating market. (Global Insight Inc., 2007).

2.3. Phenol-formaldehyde Resins

In 1909, Leo Bakeland invented the first synthetic thermosetting resin, a phenol-formaldehyde (PF) resin sold commercially as Bakelite. Even though they found very diverse applications in the past, current use is more restricted, mainly due to high cost (Gardziella et al., 2000; Detlefsen, 2002). Table 3.3 lists the main current applications (Gardziella et al., 2000; Dunky and Pizzi,

2002; Detlefsen, 2002; Dunky, 2003). The high thermal stability and fire resistant properties of these resins allows a wide spectrum of uses in automotive and construction industries (Gardziella et al., 2000). The main use is in the manufacture of fiberglass and rock wool insulation. They are also used as adhesives in structural wood-based panels and as binders in fiberglass and mineral wool insulation.

Table 3.2. Main applications of melamine-formaldehyde resins

Application	%
Wood Composites: adhesives for moisture resistant composite panels (PB and MDF) and for structural panels (e.g. plywood).	3
Decorative and protective laminates: high-pressure decorative laminates and electrical and mechanical grade industrial laminates: countertops, cabinets, furniture, flooring, wall covering, sheathing, automobile interiors	65
Surface coatings: crosslinkers in stoved paint systems in combination with other polymeric materials including alkyds, acrylics, epoxies and saturated polyesters (automobile, metal containers and furniture, coil coating).	31
Others: Textile treatment	1

Table 3.3. Main applications of phenol-formaldehyde resins

Application	%
Wood Composites: adhesives for composite panels (PB and MDF) and for structural panels (e.g plywood, OSB, LVL).	20
Decorative and protective Laminates: Resins for high-pressure decorative laminates (countertops, cabinets, furniture, flooring, wall covering, sheathing, automobile interiors) and electrical and mechanical grade industrial laminates.	10
Fiberglass and mineral wool insulation: bind fibreglass, mineral wool or shredded waste products for structural and acoustical insulation, specific applications include low-density insulation, high-density industrial insulation, and other specialty insulation.	30
Abrasive materials: bonded and coated abrasives.	6
Foundry materials: sand binder to coat sand which is then used in core making for casting operations in the foundry industry.	5
Others: Molded plastic products, saturating applications, protective surface coatings, fiber reinforced plastic applications, foam insulation, etc	29

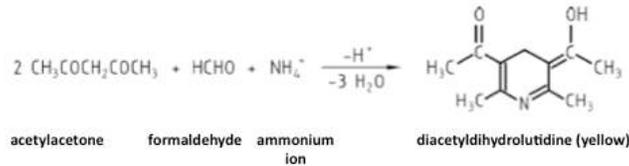


Figure 4.1. Reaction of acetylacetone with formaldehyde (adapted from EN 717-1).

Another major end use of PF resins is high pressure lamination (HPL), either for decorative or industrial laminates. HPL are composed by a sheet of MF-impregnated decorative paper and several sheets of PF-impregnated kraft paper. The laminated paper is then adhered to a substrate material, usually particleboard or plywood, and is used for countertops, furniture tops, cabinet and drawer faces, wall cladding, automobile interiors, laminated flooring, and wall coverings.

Phenol-formaldehyde resins are also widely used to produce softwood plywood for severe service conditions, oriented strand board (OSB), and particleboard and MDF with high moisture resistance and low formaldehyde emission (Gardziella et al. 2000; Dunky and Pizzi, 2002; Detlefsen, 2002; Dunky, 2003).

3. FORMALDEHYDE EMISSIONS

3.1. Causes of Emissions

Oxidation of biogenic and anthropogenic hydrocarbons is a source of outdoors formaldehyde emissions. However, exposure to formaldehyde is higher indoors than outdoors due to low air exchange rates (Salthammer et al., 2010). Possible sources of formaldehyde in indoor environments are wood-based materials, insulation materials, coatings, textiles, flooring materials, etc.

Formaldehyde is one of the main components in aminoplastic and phenoplastic resins used in the manufacture of wood-based panels. In board production, formaldehyde can be emitted from the wood raw materials during drying. In the subsequent hot-pressing process, formaldehyde is released from the glue resin and evaporated together with steam (Dunky, 2004). After panel manufacture, formaldehyde emissions during service life are originated not

only in residual gas trapped in the substrate structure, but also in formaldehyde dissolved in water present within the board (moisture), and in the hydrolysis of weakly bound formaldehyde from N-methylol groups, acetals and hemiacetals and methylene ether bridges (Dunky, 1998). After panel manufacture, formaldehyde emissions during service life are originated not only in residual gas trapped in the substrate structure, but also in formaldehyde dissolved in water present within the board (moisture), and in the hydrolysis of weakly bound formaldehyde from N-methylol groups, acetals and hemiacetals and methylene ether bridges (Dunky, 1998).

Formaldehyde release from finished panels depends on internal and external factors. The first include the type of wood and resin used, parameters and operating conditions during panel production, and panel age. External factors are temperature, humidity, air exchange rate, and the total exposed panel area in relation to the total volume of the space in which the panels are placed (Athanasidou and Ohlmeyer 2009). Test methods for the determination of formaldehyde emission should take into account the factors listed above, in order to be reliable and reproducible.

3.2. Formaldehyde Analysis

Salthammer et al. (2010) present an overview of sampling methods and analytical techniques for the determination of formaldehyde in air. Three main types of methods can be identified: in-situ analysis, derivatization methods and sensor-based methods. For in-situ analysis in outdoor environments, the determination of the concentration of formaldehyde in air is usually made using spectroscopic techniques. The most popular are Fourier Transform Infrared Spectroscopy (FTIR), but other monitoring techniques can be used as differential optical absorption spectroscopy (DOAS), laser induced fluorescence spectroscopy (LIFS) and tuneable diode laser spectroscopy (TDLS). It is important to take into account the detection limits for these methods (Finlaynon-Pitts and Pitts, 2000). Some of them require long optical paths, which makes the procedure unsuitable for routine applications. Photoacoustics spectroscopy (PAS) can also be used in indoor air.

For indoor applications, derivatization methods are more convenient. Sampling is carried out in batch mode, and formaldehyde from an air stream is trapped in an absorber (generally water, taking advantage of the compound's high solubility) or adsorbed in filters or cartridges. The derivatization reaction results in a chromophore that can be analysed by chromatography and/or

spectroscopy. Some of these photometric methods are not formaldehyde-specific, and by-products may interfere in the analysis. The most popular derivatization procedures for formaldehyde analysis are: the chromotropic acid method, the acetylacetone method and the DNPH method, which are briefly summarized below.

In the chromotropic method, formaldehyde reacts with concentrated sulphuric acid (catalyst) and chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) resulting in a red-violet hydroxydiphenylmethane derivative. Then, it reacts with the atmospheric oxygen and gives a violet quinoid. This compound has a maximum absorption at 580 nm and can be detected using a UV/VIS spectrometer (Altshuller et al., 1961). One of the main disadvantages is the low stability of chromotropic acid in solution (Salthammer et al., 2010). An adaptation of the National Institute for Occupational Safety and Health (NIOSH) 3500 chromotropic acid test procedure is used in the large chamber ASTM 1333, small chamber ASTM D 6007 and desiccator ASTM D 5582.

The acetylacetone method (Nash, 1953) is the method recommended by European and Japanese Standards for the determination of formaldehyde content and emission from wood-based panels. Determination is based on the Hantzsch reaction in which formaldehyde reacts with ammonium ions and acetylacetone to yield diacetyldihydrolutidine (DDL) (see Figure 4.1). The determination can be performed by quantitative UV/Vis spectroscopy at 412 nm (DDL has an absorption maximum at 412 nm). The reaction is specific to formaldehyde (EN 717-1).

In European standards EN 717-1, 717-2 and EN 120, the formaldehyde solution is mixed with ammonium acetate and acetylacetone solutions and let to react in stoppered flasks during 15 min in a water bath at (40 ± 1) °C. In the desiccator method JIS 1460, the quantities of the reactants are not the same, and the reaction is carried out at (65 ± 2) °C during 10 min. The calibration curve is established from a standard formaldehyde solution. The concentration of formaldehyde is determined by iodometric titration. As DDL also exhibits fluorescence, it can be determined using a fluorimetric spectrophotometer at a wavelength of excitation $\lambda_{\text{ex}} = 410$ nm and a wavelength of emission $\lambda_{\text{em}} = 510$ nm. An alternative to acetylacetone has been introduced for derivatization, using acetoacetalide, which reacts with formaldehyde at room temperature (Li et al, 2007).

The DNPH (2,4-dinitrophenylhydrazine) method is used for the simultaneous analysis of formaldehyde, other aldehydes and ketones (Andrade et al., 1992). In this method, DNPH reacts in acidic solution to give

hydrazones, by nucleophilic addition, with liberation of water. The air stream passes through cartridges containing silica gel coated with an acid solution of DNPH. After sampling, the cartridges are eluted with acetonitrile and analysed by HPLC. The separated hydrazones are detected with UV detector (max absorption ranging from 340-427 nm (US EPA Method). It is also accepted by ISO 16000-3. This method can also be used to determine free formaldehyde in phenolic resins (Oliva-Teles, 2002).

It is important to study the sensitivity (analysis threshold) and specificity of formaldehyde detection for the various methods. Hak et al. (2005) presented an interesting state of the art about the comparison of these methods. They presented an intercomparison of measurement techniques currently used for the detection of atmospheric formaldehyde, as Differential Optical Absorption Spectroscopy (DOAS), Fourier Transform Infra Red (FTIR) interferometry, the fluorimetric Hantzsch reaction technique (five instruments) and a chromatographic technique employing C18-DNPH-cartridges (2,4-dinitrophenylhydrazine).

Other methods for the monitoring of formaldehyde in air are based on sensors. Different kinds of systems have been developed, namely biosensors. However, available sensors have a high detection limit, which makes the technique more suitable for workplace environments (Salthammer et al., 2010). An example of an on-line monitoring system available commercially is the AL4021 by Aerolaser.

3.3. Standard Methods for Emission Testing

The existing methods can be divided in two main categories: measurable emission methods, which determine the actual amount of formaldehyde emitted under the test conditions, and emittable potential methods, which determine the amount of free formaldehyde present in the panel, without considering whether that quantity may actually be released or not, or in how much time (Dunky, 2004). Table 4.1 summarizes the most important test methods and related standards for the determination of formaldehyde from wood-based panels. The methods are described below.

Table 4.1. Standards and test methods for the determination of formaldehyde from wood-based panels (Athanasidou, 2000, Marutzy, 2008)

Test method	Standard, standard draft or method name
Chamber	ASTM E 1333, ASTM D 6007, EN 717-1, JIS A 1901, JIS A 1911, ISO 12460-1, ISO 12460-2
Gas analysis	EN 717-2, ISO 12460-3
Flask method	EN 717-3, método AWPA
Desiccator	ASTM D 5582, ISO 12460-4, JIS A 1460, JAS MAFF 235, JAS 233, AS/NZS 4266.16
Perforator	EN 120, ISO 12460-5
Other	Field and Laboratory Emission Cell “FLEC”, Dynamic Microchamber “DMC”

3.3.1. Chamber Method

The evaluation of the real emission of formaldehyde from a product under typical indoor conditions in real-life, and over defined time scales requires the use of a climate-controlled chamber. The formaldehyde concentration in the air inside the chamber is measured along time. The American standard ASTM E 1333 presents a large test chamber that aims to imitate the conditions of a living room with 22 m². This test method determines the average formaldehyde concentration in air and emission rate from a number of large size samples under controlled conditions: temperature of (25 ± 1) °C, (50 ± 4) % of relative humidity and air exchange of 0.5/hr. The large test chamber methods, due to their perceived accuracy can be regarded as “standard meter” in formaldehyde testing (Salthammer et al., 2010). However, they are very expensive and time consuming (7 days of conditioning prior testing. The analysis is made at the end of at least a 16 to 20 h period, which could be extended until the formaldehyde concentrations from simultaneous air samples taken from at least two lines do not vary by more than 0.03 ppm. The standard ASTM D 6007 presents a smaller chamber (0.02 a 1 m³) where the specimens remain until a steady state formaldehyde concentration is reached. The time may be estimated using an equation, which gives a time of analysis around 2.5 hours under the same conditions of ASTM E 1333. Test results in several laboratories indicate a precision of within 0.03 ppm on the same samples in case of ASTM E 1333 and ranging from 0.01 to 0.02 in case of ASTM D 6007. The Californian Air Resources Board (CARB) approved recently

regulations that require the use of these chambers for the qualifying tests, which increased the importance of these methods. The International Organization for Standardization (ISO) presents as reference method the standard ISO/FDIS 12460-1 (1 m^3) and a derived method (ISO/DIS 12460-2). The European standard EN 717-1 (chamber method) presents three volume options: $> 12 \text{ m}^3$, 1 m^3 and 225 L . The operating conditions are slightly different from the American standard: temperature of $(23 \pm 0,5) \text{ }^\circ\text{C}$ and relative humidity of $(45 \pm 3) \%$. The air exchange rate is the double of the American standard, i.e $1/\text{hr}$. The analysis time is at least ten days and the result expressed in $\text{mg}\cdot\text{m}^{-3}$.



Figure 4.2. Images of small chamber method implementation. Left: 1 m^3 chamber according to EN 717-1 and air cleaning and conditioning system. Right: gas sampling system.

The main advantages of the chamber method are the more accurate simulation of the indoor environment and the use of a large volume of sample, which minimizes the influence of material variability. Small chambers, in particular, are currently widely used in Europe and North America and can be very accurate, relatively easy to adapt at both laboratory and plant and correlate well with the large chambers. The formaldehyde concentration is determined by drawing air from the outlet of the chamber through gas washing bottles containing water, which absorbs formaldehyde (Figure 4.2). The concentration of formaldehyde in the chamber atmosphere is calculated from the concentration in water (determined photometrically using the acetylacetone method) and the volume of sampled air. Each of the standards specifies a different procedure for determining when a steady-state condition is achieved. All, however, accept a change in formaldehyde emission of less than 5% over a given period as representing a quasi steady-state condition. In addition, all the standards propose that the test is stopped after 28 days, even if the steady-state condition is not reached (Irle, 2011).

3.3.2. Gas Analysis Method

The gas analysis (EN 717-2) is a derived test that determines formaldehyde release under accelerated conditions: a temperature of 60°C and within a period of 4 hours. In this method, a test piece with dimensions of 400 mm x 50 mm x board thickness and edges sealed is placed in a closed chamber at (60 ± 0.5) °C with a relative humidity lower than 3 %, an airflow of (60 ± 3) L/h and under an overpressure of 1000 to 1200 Pa. Formaldehyde released from test piece is continually drawn from the chamber and passes through gas wash bottles containing water (Figure 4.3). The formaldehyde is determined at hourly intervals, up to 4 hours. Every hour, the air is automatically led into one of a series of pairs of wash bottles. At the end of the test, formaldehyde release is calculated from the formaldehyde concentration, the sampling time and exposed area of the test piece expressed in mg/m²h. Even though the time of analysis is short, this test involves a high investment in equipment. The standard EN13986 indicates this method for faced, coated, overlaid or veneered wood-based panels.

In this method, as well as for the other European methods, the concentration of formaldehyde is determined photometrically (UV/Vis spectrometer) using the acetylacetone method, described above.



Figure 4.3. Gas analysis method implementation.

3.3.3 Desiccator Method

The more relevant desiccator method is defined in the Japanese standard JIS A 1460. It is one of the most economical methods, but it has a drawback. The test pieces shall be conditioned under standard conditions at temperature of $(20 \pm 2) ^\circ\text{C}$ and a relative humidity of $(65 \pm 5) \%$ until they have attained constant mass, which can take up to one week. Test-pieces are cut into rectangles of 150 mm by 50 mm. A number of test-pieces, corresponding as close as possible to 1800 cm^2 total surface area (ends, sides and faces), are attached to a supporting metal frame and placed on a stainless steel wire net above a crystallizing dish containing water, inside a desiccator with a nominal dimension of 240 mm (Figure 4.4). The lid is placed on the desiccator and the samples are maintained inside for 24 hours at $(20 \pm 1) ^\circ\text{C}$. The emitted formaldehyde is absorbed by the water in the crystallizing dish. The concentration of dissolved formaldehyde is then determined photometrically using the acetylacetone method, but the reaction conditions and reagent quantities are different from European standards EN 717-1 and EN 120. The emission of formaldehyde is expressed in mg.L^{-1} .

There are several variations of the desiccator method as defined in ASTM D 5582, with some differences: the desiccator diameter (250 mm), and the procedure duration, which is 2 hours. Other standards that are based on the same principle are JAS 233 and JAS 235. A recent harmonized standard was

adopted by the International Standardization Organization, as ISO/CD 12460-4.



Figure 4.4. Implementation of desiccator method.

3.3.4. Flask Method

The flask method was developed in the Fraunhofer Institute for Wood Research WKI by Roffael in 1975. A slight modified version of this method was published as EN 717-3. It is a quick method that is suitable for internal quality control in production lines of wood-based panels. This is a static method that consists in suspending test pieces with a total mass of 20 g in a closed container (flask), containing water (50 mL) and maintained at a $(40 \pm 1)^\circ\text{C}$ during 3 hours. The formaldehyde content in water is determined photometrically by the acetylacetone method and expressed in (mg/kg dry board). The AWWA (American Wood Protection Association) presents a similar method, with the same principle but with different dimensions of the flask. This method does not have great acceptance by the market, nor is significantly used at industrial or academic level.

3.3.5. Perforator Method (Potential Emission)

The perforator method (EN 120) measures the formaldehyde content of wood-based panels and not the actual emission level. While a chamber method test may take several days until the samples attain the equilibrium stage, the perforator method is quicker and expeditious, being indicated for daily factory

production control. This is the most popular procedure for measuring formaldehyde content in particleboard and MDF in Europe. EN 13986 indicates this method for unfaced particleboard, OSB, MDF and flaxboards. It is also employed worldwide, except in North America. Formaldehyde is extracted from test pieces (110 g of 25×25 mm specimens) by means of boiling in toluene (600 ml), in a round bottom flask connected to a perforator apparatus containing 1000 ml of distilled water. The extraction is carried out during 2 hours, starting at the moment that the first bubbles pass through the filter insert. The water contained in the perforator is, after cooling to room temperature, transferred into a volumetric flask (Figure 4.5). The formaldehyde content of this aqueous solution is determined photometrically by the acetylacetone method. The disadvantage of this method is the environmental impact of the toluene emission and residues. The results are expressed in (mg/100 g oven dry board). The perforator values for particleboards, OSB and MDF shall be applied to wood-based panels conditioned to a reference moisture content (6.5 %). For different moisture contents, correction factors, calculated by an equation stated in the specifications standards for each type of wood-based panel, are used. This correction factor is contestable as it depends on other factors rather than the moisture content of boards (Roffael and Johnsson, 2011). The accuracy of this method has been very discussed for values below 4 mg/100 g oven dry board. A similar method was established by ISO 12460-5.





Figure 4.5. Implementation of perforator method.

3.3.6. Other Methods

There are other methods, used mostly in universities, research laboratories or testing laboratories. One example is the DMC (Dynamic Micro Chamber) used in the United States in factory control quality, but it has not yet been accepted as standard. This method utilizes a combination of a small chamber and electrochemical sensor. It has the advantage of being a short duration test. Another example is the FLEC (Field and Laboratory Emission Cell) implemented for the first time in Scandinavia. In this device, a controlled purified air flow enters the cell and passes through the testing material. The outlet air passes through adsorption tubes, which are connected to a thermal desorption system and analysed in GC/MS or GC/FID system. The great advantage lies in being a transportable emission cell for mobile application (Salthammer et al., 2010). However, a standardized method has not yet been established.

3.3.7. Formaldehyde Methods Survey

Considering the different existing methods, and taking into account that it is difficult to find worldwide agreement on establishing a reference method, it is important to understand the main features of the main methods in use. Table

4.2 summarizes the testing parameters for each method. Table 4.3 surveys the pros and cons for each one.

Table 4.2. Testing parameters for the main formaldehyde emission methods

	Methods			
	Chamber EN 717-1	Gas analysis EN 717-2	Desiccator JIS 1460	Perforator EN 120
Pre-conditioning	no	no	7 days	no
Volume	1 m ³	4 L	6 L	-
Temperature	(23 ± 0.5) °C	(60 ± 0.5) °C	(20 ± 0.5) °C	-
Relative humidity	(45 ± 3) %	< 3 %	-	-
Air exchange rate	1 h ⁻¹	-	-	-
Loading ratio	1 m ² /m ³	10 m ² /m ³	≈ 30 m ² /m ³	-
Total surface area	1 m ² (2 boards)	0.040 m ² (2 boards)	≈ 0.18 m ²	110 g
Unsealed Edges	1.5 m/m ²	no	yes	yes
Testing time	10 to 28 days	4 hours	24 hours	3 hours
Analysis method	acetylacetone	acetylacetone	acetylacetone	acetylacetone
Units	mg.m ⁻³ (air)	mg.m ⁻² h ⁻¹	mg.L ⁻¹	mg/100 g oven dry board

In reality, no method clearly stands out, all presenting advantages and drawbacks. Implementation costs have been estimated to rate at 0.5:8:100 for perforator, gas analysis and large chamber, respectively (Athanasidou and Ohlmeyer, 2009). Formaldehyde testing by chamber methods is usually the most time consuming and uses the most sophisticated equipment.

Due to the need of wood-based panel producers to operate in the global market, they have to certificate their products according to the different country or region regulations, which consider different reference methods, like Japan (desiccator), U.S.A. (chamber method) and Europe (perforator method). A new approach for a closer co-operation between different world regions

with regard to formaldehyde release test methods was taken between CEN/TC 112 and ISO/TC 89. A resolution was taken in Sydney, 2011-2: "ISO/TC 89 unanimously supports a further development of the standards series ISO 12460 "Determination of formaldehyde release" under the Vienna Agreement in cooperation with CEN/TC 112 to become EN ISO standards".

Table 4.3. Survey of formaldehyde test methods

	Methods			
	Chamber	Gas analysis	Desiccator	Perforator
Pros	- Testing conditions similar to real life - Uses large sample dimensions, which reduces the influence of sample variability	- Short analysis time - Easy to implement	- Low cost equipment	- Short analysis time - Low cost equipment
Cons	- Long analysis time - High cost equipment	- High cost equipment	- Pre-conditioning of samples takes approximately one week	- Toxic waste (toluene) - Low accuracy for very low formaldehyde content

3.4. INTERNATIONAL REGULATIONS AND REQUIREMENTS

3.4.1. Formaldehyde Classification

Adverse health effects from exposure to formaldehyde in pre-fabricated houses, especially irritation involving eyes and upper airways, were the first reported in the mid-1960's (Salthammer et al., 2010). In 2004, the International Agency for Research on Cancer (IARC), from World Health Organization, recommended the reclassification of formaldehyde as "carcinogenic to humans (group 1)". In 2006 this recommendation was finally published (IARC, 2006). As a consequence, various authorities and institutions have been concerned about formaldehyde as an indoor pollutant and new regulations have emerged involving increasingly lower exposure limits. Within the European Union, formaldehyde is currently classified as a 3-R40 substance ("limited evidence of carcinogenic effect"), but the classification is being reviewed under the new regulation for chemicals "Registration,

evaluation, authorization and restrictions of Chemicals” (REACH). For this purpose, FormaCare (formaldehyde sector group of the European Chemical Industry Council) established a REACH taskforce to facilitate the creation of a consortium allowing European formaldehyde manufacturers to work together as a unified group for their REACH compliance activities.

3.4.2. Occupational Exposure Limits

In the last decades, governments and industry have made considerable efforts to reduce exposure to formaldehyde. The limit levels are separated into two groups: workplace environments (i.e. occupational), and non-occupational environments (i.e. residential) (Salthamer et al., 2010). The occupational exposure limits (OELs) for formaldehyde are separated into three categories: time-weighted average (TWA), short-term exposure limit (STEL) and ceiling limit (exposure limit which should not be exceeded at any time). These limits are different for each country, as seen in Table 4.4. For working place thresholds, there are various limits in different European countries, as can be observed in this table. For living room thresholds, recommendation of the German Federal Health Agency in 1977 was 0.1 ppm. Countries with higher limits were compelled to follow the recommendations of IARC (Dunky, 2001). In 1987, the US Occupational Safety and Health Administration (OSHA) established a federal standard that reduced the amount of formaldehyde to which workers can be exposed over an 8-hour work day from 3 ppm to 1 ppm. In 1992, the formaldehyde exposure limit was further reduced to 0.75 ppm. For indoor domestic exposure, the World Health Organisation (WHO) still recommends a limit for formaldehyde air concentration of 0.1 mg/m³ (for short and long-term exposure) from all sources combined (at this level or below, transient sensory effects should be avoided) (EPF, 2010). The use of the short-term (30 minute) guideline of 0.1 mg/m³ (0.08 ppm) also prevents long-term health effects, including cancer (WHO, 2010). The short term exposure levels are associated with acute health effects on individuals, while long-term exposure is related to chronic health effects (Salthamer et al., 2010; Blair, 1986).

An EC funded project involving EPF (European Panel Federation) and CEIBois launched a European formaldehyde-in-air monitoring campaign within the wood-based panel manufacturing industry (EPF, 2010). Five small to medium sized manufacturing companies of considerably different ages, located in France, Germany, Poland, Spain and the UK, were selected. Site

work was conducted over the 3-week period Wednesday 30th September to Saturday 17th October 2009. In this study, TWA exposure values for a press operator ranged from 0.017 to 0.176 mg/m³, for a press cleaner TWA ranged from 0.311 to 0.766 and STEL from 0.130 to 1.667, and for a press inspector STEL ranged from 0.183 to 1.187.

3.4.3. Emission Limits for Wood-based Products

In recent years, national regulations for formaldehyde were established and/or reformulated in some countries, limiting formaldehyde emission levels from wood-based panels. The standards for formaldehyde test methods do not refer to a classification of wood-based panels according to the results of formaldehyde emission or release. This classification is established in the specification standards of each product. Table 4.5 lists the current specifications.

The harmonized European standard EN 13986 (“Wood-based panels for use in construction”) classifies formaldehyde emission into two classes: E1 and E2. Internal discussions within the European wood-based panel associations, lead EPF (European Panel Federation) to launch its own formaldehyde standard, EPF-S, that corresponds to a perforator value below 4 mg/100 g oven dry wood for PB and 5 mg/100 g oven dry wood for MDF (thickness > 8 mm). Driven by IKEA (IOSMAT 0003), an equivalent class with half E1 formaldehyde emission limits has been introduced: the so-called E0 (or E0.5) (not yet recognized officially by CEN - European Committee for Standardization). Recently, the members of EPF agreed to only produce E1 class, abandoning production of E2 class panels.

In Japan, more strict limits are defined in standards JIS A 5908 e 5905 as, by descending order of emission level, F^{**}, F^{***} e F^{****}. The F^{**} is more or less equivalent to European E1 class, while the F^{***} and F^{****} are much lower. F^{****} is close to the emission of solid untreated wood, between 0.5 - 2 mg/100 g (Athanasiadou and Ohlmeyer, 2009).

Limits for formaldehyde emission in the United States are described by ANSI A208.1 & 2. More recently, CARB (California Air Resources Board) established more stringent formaldehyde limits for wood-based panels, being nowadays as reference for the wood-based panels market. Phase 1 limits are roughly equivalent to E1 (and F^{**}) class, while Phase 2 limits are similar to F^{***}. These regulations state that, beyond the compliance of those emission limits, wood-based panels and finishing goods for sale or used in California

must also be certified by a CARB approved third party certification laboratory, unless they are approved Ultra Low Emission Formaldehyde (ULEF) or No Added Formaldehyde (NAF) products. NAF and ULEF products must demonstrate a 90% or better compliance with a 0.04 ppm (ASTM E1333) limit.

Table 4.4. Occupational Exposure Limits (OELs) for formaldehyde (IARC, 2006, FormaCare 2007, Q&A on formaldehyde, * Decreto Lei 79/2006), adapted from (Athanassiadou and Ohlmeyer, 2009)

Country	Concentration (ppm)	Type
Australia	1.0	TWA
Austria	0.3	TWA
Belgium	0.3	Ceiling
Brazil	1.6	Ceiling
Canada - Alberta	2.0	Ceiling
Canada- Ontário	0.3	Ceiling
Canada - Quebec	2.0	Ceiling
Denmark	0.3	TWA and STEL
Finland	0.3	TWA
France	0.5	TWA
Germany	0.3	TWA
Greece	2.0	TWA
Hong Kong	0.3	Ceiling
Ireland	2.0	TWA
Italy	0.3	Ceiling
Japan	0.5	TWA
Mexico	2.0	Ceiling
Netherlands	1.0	TWA
New Zealand	0.5	Ceiling
Norway	0.5	TWA
Portugal*	0.08	Ceiling
South Africa	2.0	TWA
Spain	0.3	STEL
Sweden	0.5	TWA
Switzerland	0.3	TWA
United Kingdom	2.0	TWA
USA - ACGIH	0.3	Ceiling
USA - NIOSH	0.016	TWA
USA - OSHA	0.75	TWA

TWA –time weight average, STEL – short term exposure limit.

Table 4.5. Overview on current upper limits of formaldehyde emission (PB – Particleboard, MDF – Medium Density Fibreboard, PW – Plywood, OSB – Oriented Strand Board, LVL – Laminated Veneer Lumber). Adapted from Athanassiadou et al. (2007)

Region	Standard	Test method	Board class	Board type	Limit value	
Europa	EN 13986	EN 717-1	E2	PB, OSB and MDF (unfaced)	$> 0.124 \text{ mg/m}^3$ air	
		EN 120			$8 < \text{mg}/100 \text{ g}$ oven dry board ≤ 30	
		EN 717-1			PW, SWP and LVL (unfaced)	$> 0.124 \text{ mg/m}^3$ air
		EN 717-2			PW, PB, OSB, MDF, LVL (and others) overlaid	$3.5 < \text{mg/m}^2 \cdot \text{h} \leq 8$
		EN 717-1	E1	PB, OSB and MDF (unfaced)	$\leq 0.124 \text{ mg/m}^3$ air	
		EN 120			$\leq 8 \text{ mg}/100 \text{ g}$ oven dry board	
		EN 717-1			PW, SWP e LVL (unfaced)	$\leq 0.124 \text{ mg/m}^3$ ar
		EN 717-2			PW, PB, OSB, MDF, LVL (and others) overlaid	$\leq 3.5 \text{ mg/m}^2 \cdot \text{h}$
Japão	JIS A 5908 & 5905	JIS A 1460	F**		$\leq 1.5 \text{ mg/L}$	
			F***		$\leq 0.5 \text{ mg/L}$	
			F****		$\leq 0.3 \text{ mg/L}$	
USA	ANSI A208.1 & 2	ASTM E1333 (large chamber)		PB, MDF	$\leq 0.3 \text{ ppm}$	
				PW	$\leq 0.2 \text{ ppm}$	
	CARB	ASTM E1333	Phase 1	PB	0.18 ppm	
				MDF	0.21 ppm	
			Phase 2	PB	0.09 ppm	
		MDF	0.11 ppm			

**Table 4.6. Relationship between different methods and standard limits
(^aValues obtained by correlation) Adapted from Harmon (2008))**

Method	Japan		Europe	IKEA	USA	
	F ^{***}	F ^{****}	E1	E0.5	CARB F1	CARB F2
EN 120 (mg / 100 g odb)	≤ 4.5 ^a	≤ 2.7 ^a	≤ 8.0	≤ 4.0	≤ 11.3 ^a	≤ 5.6 ^a
EN 717-1 (mg / m ³ air)	≤ 0.054 ^a	≤ 0.034 ^a	≤ 0.124	≤ 0.050	≤ 0.176 ^a	≤ 0.088 ^a
ASTM E1333 (ppm)	≤ 0.055 ^a	≤ 0.035 ^a	≤ 0.127 ^a	≤ 0.051 ^a	≤ 0.180	≤ 0.090
JIS A 1460 (mg / L)	≤ 0.5	≤ 0.3	≤ 0.9 ^a	≤ 0.4 ^a	≤ 1.3 ^a	≤ 0.6 ^a

Recently, a new important challenge has been recently imposed by LEED (Leadership in Energy and Environmental Design®) certification, implying the absence of adhesives with urea-formaldehyde chemical bonds in “Green Building” construction (LEED, 2011). Minimizing indoor air contamination associated to substances that are odorous, irritating and/or harmful to the comfort and well-being of installers and occupants is one of the objectives of this organization.

3.5. Correlation between Different Testing Methods

Different authors have attempted to establish correlations between formaldehyde testing methods (desiccator, perforator and chamber). Due to the different operating conditions used in each method, it is not possible to obtain a direct relation, although approximate correlations can be found in literature (Risholm-Sundman et al. 2006; Que and Furuno 2007; Park et al. 2010). In the very low emission range, correlation between corrected perforator values and the real emission of boards is poor (Roffael and Johnsson, 2011). According to these authors, since the mass transfer coefficient is not considered in the perforator method, boards with the same emission value but with different densities may have different real emission characteristics. Table 4.6 presents the transposition of standard limit values to different test methods.

4. INDUSTRIAL APPROACHES FOR REDUCTION OF FORMALDEHYDE EMISSIONS

4.1. Low Formaldehyde Content Resins

Formaldehyde-based resins are still the preferred type of adhesive for industrial production of wood based panels. The most widely used are urea-formaldehyde (UF) resins, followed by phenol-formaldehyde (PF) and melamine-formaldehyde (MF). The industrial success of UF resins is due to the combination of low cost with high reactivity and good physic-mechanical performance.

During service life, formaldehyde emissions (FE) from panels bonded with UF resins can have two origins, besides wood itself: release of unreacted formaldehyde monomer (adsorbed within wood, dissolved in entrapped moisture, or retained in interparticular void space), and long-term resin degradation due to hydrolysis of weak or covalent bonds (Dunky, 2003). Aminomethylene bonds in UF resins are particularly susceptible to hydrolytic attack under humidity conditions. PF resins, on the other hand, are highly resistant to hydrolysis and present much lower formaldehyde emissions after cure. However, the higher cost and lower reactivity imply that PF resins are used mainly in applications implying exterior weather exposure.

In face of increasingly restrict regulations, the initial approaches to reduce formaldehyde emissions in UF resins focused on decreasing the formaldehyde/urea molar ratio (F/U) in synthesis formulations (Myers, 1989). In the last decades, F/U values in resins for WBP production have decreased from about 1.6 to a range between 0.9 and 1.1. The effects of this strategy are well documented (Myers, 1984; Park et al., 2006; Que et al., 2007). In parallel with significant FE decrease, several WBP properties are penalized: internal bond strength, thickness swelling, and water absorption. This lower performance can be compensated by increasing resin dosage, affecting panel cost. In addition to F/U ratio, the synthesis process has a relevant role in the final resin properties, including formaldehyde emissions. Identification of the most favorable reaction conditions and pathways is therefore essential for optimizing the overall performance of the resin (Ferra et al., 2012; Costa et al., 2012; Ferra et al., 2010).

One strategy to counteract the negative effects of decreasing F/U ratio is resin modification with co-monomers, like melamine or phenol. UF resins fortified with relatively small melamine content are a common approach

nowadays (Sun et al., 2010; Paiva et al., 2011). These present good mechanical properties and higher resistance to hydrolysis, and hence lower formaldehyde emissions, due to the stability of the bond between methylene and amide group from melamine ring. Due to the much higher cost of melamine in relation to the other monomers, incorporation levels are kept below 5 %. Other co-monomers can be used to attempt a good balance between mechanical properties and formaldehyde emission, like resorcinol, diisocyanates and succinaldehyde (Basta et al., 2006).

Formaldehyde-free urea resins have been reported (Despres et al., 2010), based on dimethoxyethanal, a non-volatile and non-toxic. However, reactivity is much lower than for conventional formaldehyde-urea resins. Combination with about 20 % isocyanate (pMDI) is necessary in order to reduce pressing time and obtain good panel properties.

Concomitantly with decreasing F/U ratio, some key variables related to the WBP production process must be taken into consideration in order to minimize formaldehyde emission during the subsequent panel's usable life. Some key variables are (Dunky et al., 2001):

- Moisture content of wood particles or fibers. Higher moisture content usually implies higher FE, either due to retention of dissolved formaldehyde, less effective cure or higher hydrolysis rate.
- Press temperature and press time. Higher cure temperatures and/or times imply higher reaction extension, therefore residual free formaldehyde is decreased and FE will be lower.
- Resin content (gluing factor). Even though higher emissions may be expected from higher resin content in the panel, if higher panel density is obtained then FE tends to decrease. The more tightly packed structure decreases the rate of emission.

4.2. Formaldehyde Scavenger Additives

Formaldehyde scavengers, capable of capturing formaldehyde either physically or chemically and forming stable products, are added to UF resins or to wood particles before pressing. These additives should provide long-term FE reduction, in principle along the panel's service life. Examples used in industry include addition of urea in aqueous solution or powder form, organic amines, scavenger resins (like UF resins with F/U well below 1.0), sulfites, and functionalized paraffin waxes.

The fact that the scavenger inevitably reacts with formaldehyde during pressing, and not only after panel manufacture, has usually a negative effect on bond strength and other properties, since less formaldehyde will be available for the cure reaction. The performance of the panels produced has therefore to be taken into consideration when a scavenger is used. Interestingly, on the other hand, a recent work (Hematabadi et al., 2012) reported that pre-treatment of wheat straw particles with urea solution at 95 °C yielded panels with better mechanical and physical properties, in addition to FE reduction. This was attributed to reaction of free formaldehyde with penetrated urea, resulting in improved bonding performance.

In addition to the cases mentioned above, other formaldehyde scavengers have been reported in the literature, with varying effectiveness. Porous adsorbers like pozzolan and charcoal have been shown to possess some scavenging capability (Kim et al., 2009; Kim et al., 2006). Proteins present in pulp and paper sludge were associated to FE reduction but WBP performance was penalized (Migneault et al., 2011). Addition of tannin solution of UF resin lead to significant FE decrease, due to the reactivity of the hydroxyl groups towards formaldehyde, but caused some reduction in internal bond strength and increased water absorption (Boran et al., 2011a). Very good FE reduction is obtainable by adding sodium metabissulfite to the resin, with no negative impact on other panel properties, but safe handling of this material implies encapsulation (Sene, 2009). Positive results have been reported with several amine solutions besides urea (propylamine, methylamine, ethylamine, and cyclopentylamine), with improvement in physical-mechanical properties in addition to reduction in FE (Boran et al., 2011b). Good results have also been reported for use of different starch derivatives as scavengers (Basta et al., 2006). A recently published work (Zhang et al., 2011) presented significant improvements in bond strength and FE emission in panels prepared with UF resin containing nano-crystalline cellulose previously amino-functionalized with an alkoxy silane.

4.3. Post-treatments

Post-treatments for FE reduction are applied after pressing. Currently used methods include panel impregnation with formaldehyde scavenging species, like aqueous solutions of ammonia, ammonium salts, or urea (Sene, 2009; Dunky et al., 2001). Use of ammonia, however, tends to be abandoned due to toxicity concerns.

Another strategy is the creation of diffusional barriers in the panel surfaces that keep formaldehyde confined. This approach takes advantage of the fact that WPB finishing usually implies application of a laminate, overlay or coating in order to obtain the final decorative appearance. This includes the use of paints, varnishes, veneers, laminates, or resin-impregnated papers. A few works in the literature compare the effectiveness of different barrier materials on FE reduction (Lee et al., 2011; Barry et al., 2006; Composite Panel Association, 2003; Myers, 1986). Epoxy powder coatings and laminate finishes usually imply the highest reduction levels, above 90 %. Combination of liquid coatings with formaldehyde scavenging additives can significantly improve FE reduction. It must be noted, that emissions of other volatile organics (VOCs), in addition to formaldehyde, must also be considered when using coatings.

4.4. Alternative Adhesives

4.4.1. Polyisocyanates

Isocyanate-based adhesives can be used instead of formaldehyde-based resins in production of WBPs. The most common material is pMDI, a complex mixture of the three isomers of methylene diphenyl diisocyanate (MDI), triisocyanates and higher polymeric species. pMDI is used either in solvent free form or as emulsion in water (EMDI) (Papadopoulos et al., 2002). Isocyanates react with hydroxyl groups in lignocellulosic wood fibers and with entrapped water (moisture), creating a strong and water-resistant cross-linked structure. Advantages of pMDI for WBP production include: excellent hydrolysis resistance, no volatile emissions after cross-linking, good substrate wettability and penetration, good reactivity (may be increased by addition of catalysts), and excellent mechanical properties at low adhesive contents. On the other hand, several limitations can be identified: high cost in relation to UF resins, need for efficient gas extraction in industrial use, and demoulding difficulties due to adhesion to metal surfaces (Stöckel et al., 2011; Sene, 2009; Dunky, 2003).

Isocyanate-only adhesives are used industrially for production of particleboards, MDF and OSB, but consumption is still much lower in relation to formaldehyde-based resins, mainly due to economic reasons. Hybrid UF-isocyanate adhesives are also used in industrial WBP production. These are obtained by mixing UF resins with lower amounts of pMDI, yielding a copolymerized structure upon cure, with improvements in physical-mechanical

properties and formaldehyde emissions (Wang et al., 2004; Simon et al., 2002). The applicability of this type of approach is determined mainly by economic factors.

4.4.2. Natural Adhesives

Industrial use of adhesives obtainable from natural resources (also called bioadhesives or bioresins) has been researched since the 70's, but industrial implementation is still restricted. Production costs, limited availability and consistency of raw materials, and land use issues have been the limiting factors. Advantages of natural adhesives include lower toxicity, biodegradability and production from renewable resources (Dennis, 2007; Dunky, 2003). Three materials have found some success in industrial applications: tannins, lignins and vegetable proteins.

Tannins are polyphenolic compounds obtainable by extraction from wood, bark, leaves, and fruits. Tannin industrial extraction and use is performed almost solely in the Southern hemisphere, using mostly bark from *Mimosa*, *Quebracho* and *Radiata Pine* (Kim, 2009; Dunky, 2003). Use as adhesives implies addition of a hardener, usually formaldehyde. Low FE tannin adhesives are commercially available, but in face of pressure to reduce use of formaldehyde-based adhesives, non-aldehyde hardeners (like hexamine) and autocondensation processes have been investigated, with apparent success (Dennis, 2007; Pizzi, 2006). Addition of tannins to UF and PF resins was reported to reduce FE without impairing mechanical performance (Moubarik et al., 2010). Combination of tannin-formaldehyde adhesives from different origins with poly(vinyl acetate) (PVAc) resins was found to improve bond strength and reduce FE (Kim, 2009; Kim, 2010).

Lignins are abundant phenolic natural polymers that confer mechanical stability to plants, by crosslinking cellulosic components of cell walls. They are obtainable as byproducts of wood pulping. Unlike tannins, there is not a fixed molecular structure attributable to lignins. Composition varies widely depending on the source. Low reactivity is a major disadvantage of its use as an adhesive in pure form (Pizzi, 2006; Dunky, 2003). The most interesting potential application is partial substitution of phenol in PF resins, but does not have relevant industrial impact (Sene, 2009; Dennis, 2007; Dunky, 2003).

Soy protein is obtained from soybean, and has been used for centuries as a wood adhesive. In the context of WBP production, soy protein has been added to PF resins to lower FE, but lower water resistance is an important limitation (Sene, 2009). Formaldehyde-free WBPs have been obtained using an adhesive based on soy flour and glyoxal – a non-toxic, but less reactive, aldehyde

(Amaral-Labat, et al. 2008). Use of soy protein combined with polyamidoamine-epichlorohydrin (PAE) resins yields a strong and water resistant product that is commercially available for wood composites (Sene, 2009; Li et al., 2004). Another interesting formaldehyde-free adhesive system, successfully tested in production of plywood and OSB panels, is based on a combination of soy flour, polyethylenimine, maleic anhydride, and sodium hydroxide (Schwarzkopf et al., 2010).

5. FUTURE PERSPECTIVES

The issue of formaldehyde emissions has just recently stirred the WBP industry, in view of the mandatory VOC emission labeling system imposed by French regulations in 2012. This affects all construction products, flooring and wall surfaces, paints and lacquers used indoors. Formaldehyde emissions are seriously restricted: upgrading the rating from C (lowest) to A+ (highest) implies reducing formaldehyde emission from 120 $\mu\text{g}/\text{m}^3$ (or greater) to 10 $\mu\text{g}/\text{m}^3$ (or lower), measured in a ventilated test chamber after 28 days of storage. The measurement procedure is based on ISO 16000 testing method. In the short term, this will imply definition of a new class for formaldehyde emission levels from WBPs within Europe, corresponding to emission levels very similar to the ones already established in Japan and USA, namely classes F**** and Carb II, respectively. One other class must be clearly defined, corresponding to emission levels within the range of natural wood (Schafer and Roffael, 2000; Martins et al., 2007). This must take into account that the wood species, and the amount and type of recycled wood, used in panel production can affect “natural” formaldehyde emission significantly (Durkic, 2009;).

Also recently, the California Environmental Protection Agency adopted two new classifications for WBPs produced with two particular kinds of adhesives: no-added formaldehyde resins (NAF), and ultra-low-emitting formaldehyde resins (ULEF). Additionally, the U.S. Green Building Council has defined the Leadership in Energy and Environmental (LEED) rating system for green building construction, which specifies that wood composite materials must contain no added urea-formaldehyde resins.

In this context of more stringent regulations, classes E1 and E2, which are currently still allowed in Europe, China, Australia, and Africa, will be reviewed and probably extinct in 2013-2015. It will also be necessary to

clarify the relation between the different methods for emission measurement, in order to uniformize the existing classification systems throughout the world (Japan, Europe, USA, and China, among others).

Table 6.1. Possible future WBP classes concerning formaldehyde emission levels

WBP classes	Formaldehyde emission level	Complying adhesive systems
E0 /Carb II/EPF-S	4-5 mg/100 g oven dry board	UF resin modified with 1 -5 % melamine; molar ratio F/(NH ₂) ₂ between 1.00 to 0.90.
F**** ULEF (Ultra Low Emitting Formaldehyde Resins)	0.3 mg/mL	MUF resin with 5 -10 % melamine; molar ratio F/(NH ₂) ₂ between 0.90 to 0.80.
Natural Wood	0.007-0.0125 ppm	MUF resin with 10 - 16 % melamine; molar ratio F/(NH ₂) ₂ between 0.85 to 0.70.
LEED (Leadership in Energy and Environmental Design)	not specified	MF and PF resins (composite materials must contain no added urea-formaldehyde resins)
NAF (No Added Formaldehyde Resins)	not specified	p-MDI; Soy based Adhesive Technology; Bio-adhesives; acrylic resins

Table 6.1 presents the WBP classes, concerning formaldehyde emission, that will probably prevail in the near future, as well as the complying adhesives (Roschmann and Käsmayr, 2010; Durkic, 2009, Georgia-Pacific, 2009).

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P. K.