FORMALDEHYDE FREE AMINOPLASTIC BONDED COMPOSITES

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ABSTRACT

Formaldehyde, a major indoor pollutant, originates mainly from the urea formaldehyde aminoplastic resins, which are used in the production of composite wood panels (e.g. particleboard, fibreboard, plywood) employed in furniture, flooring, wall partitions and ceilings. The acceptable levels of formaldehyde emission from composite panel products have been continuously reduced over the last two decades. The driving forces have been the increased public awareness and consumer demand for non-hazardous products as well as governmental regulations. Maximum emission values of only 2 mg/100g of dry board (perforator method, EN 120), i.e. as low as natural wood itself are currently being aimed for.

In this work, the formaldehyde emission property of wood-based panels and its evolution during the past two decades are presented in connection with the research effort devoted to its limitation. The evolution of related international standards and regulations is presented in parallel. The development of F-zero class products with emissions of the level of natural wood or even less, is addressed in terms of aminoplastic resin systems, whose performance has been questioned as compared to polymeric isocyanates or phenol-formaldehyde binders.

Keywords: Indoor pollution, formaldehyde emission, formaldehyde-based resins, wood panels.

INTRODUCTION

Aminoplastic glue resins are the most important types of adhesives in the wood based panels industry, especially for the production of particleboards (PB), medium density fibreboards (MDF), oriented strand boards (OSB), plywood, blockboards and some other types of panels [1]. They are used in the furniture industry and in carpenter's shop too. They comprise thermosetting polymers based on three different monomers:

1. Formaldehyde
2. Urea and
3. Melamine

from which various resin types can be formulated. Urea formaldehyde resins (UF) represent the most important aminoplastic resin type conventionally employed in the manufacture of composite panels due to their high reactivity, outstanding production performance and appreciably low cost. Currently, approximately 6 billion tons are produced per annum worldwide, based on a usual solids content of 66% w/w [2]. Their susceptibility to hydrolysis renders them more effective in interior grade panels and together with the presence of free non-reacted formaldehyde contributes to the problem of formaldehyde emission from the products both during manufacture and service.

Composite wood panels (mainly particleboard, MDF and plywood) are used in furniture, shelves, cabinets, wall partitions, drawers, flooring underlayment, ceilings and other wooden constructions [3]. Large quantities of them are used in mobile and prefabricated houses [4, 5]. Indoor air quality and formaldehyde emissions from composite wood products first became subject to broad public and governmental concern in the late 1970s, when the energy crisis encouraged heat conservation through tight sealing of homes [6]. This reduced the rate of outdoor air infiltration and overall ventilation rates leading to the entrapment of gaseous pollutants inside home air atmosphere. With Europe and North America as pioneers, test methods to accurately measure formaldehyde emissions from panels were developed and product emission guidelines were established. A total change in the formulation of UF resins was made to meet these guidelines.

FORMALDEHYDE HEALTH EFFECTS

Formaldehyde (chemical formula: HCHO) is an important industrial chemical used to make other chemicals, building materials, and household products. It is one of the large family of chemical compounds called volatile organic compounds (VOCs). Formaldehyde serves many purposes in products being a part of:

1. the glue or adhesive in pressed wood products (composite wood panels);
2. preservatives in some paints, coatings, and cosmetics;
3. the coating that provides permanent press quality to fabrics and draperies;
4. the finish used to coat paper products; and
5. certain insulation materials (urea-formaldehyde foam).

Formaldehyde is released into the air by burning wood, kerosene or natural gas, by automobiles, and by cigarettes. Formaldehyde can off-gas from materials made of it. It is also a naturally occurring substance.

Formaldehyde is a colourless, strong-smelling gas. When present in the air at levels above 0.1 ppm, it can cause watery eyes, burning sensations in the eyes, nose and throat, nausea, coughing, chest tightness, wheezing, skin rashes, and allergic reactions [3]. It can affect people differently; some people are very sensitive to formaldehyde while others may not have any noticeable reaction to the same level. The health effects of short-term exposure to formaldehyde are presented in Table 1, as reported in an official publication of the European

Commission. Furthermore, the contribution of various atmospheric compartments to the average exposure to formaldehyde is given in Table 2.

Table 1. Effects of formaldehyde in humans after short-term exposure [7].

Effect	Estimated Median (mg/m^3)	Reported Range (mg/m^3)
Odour detection	0.1	0.06-1.2
Eye irritation threshold	0.5	0.01-1.9
Throat irritation threshold	0.6	0.1-3.1
Biting sensation in nose, eye	3.1	2.5-3.7
Tolerable for 30 minutes (lachrymation)	5.6	5.0-8.2
Strong lachrymation	17.8	12.0-25
Danger to life, oedema, pneumonia	37.5	37-60
Death	125	60-125

Scientific studies in the early 1980s have demonstrated that formaldehyde is a strong nasal carcinogen in rodents and this has led to concerns about the potential for carcinogenic risk to humans. Since then, various groups have conducted carcinogenic risk assessments for formaldehyde as additional toxicological, mechanistic and dosimetric data on formaldehyde have accumulated, in which they classified formaldehyde as probable/suspected human carcinogen (U.S. Environmental Protection Agency, American Conference of Governmental Industrial Hygienists, and International Agency for Research on Cancer) [8].

Table 2. Contributions to formaldehyde exposures [7].

Atmospheric Compartment	Formaldehyde	
	Estimated Concentration (mg/m^3)	Daily Intake (mg)
Air		
1. Ambient Air (10% of the time)	0.01	0.02
2. Indoor Air		
•Home (65% of the time) -prefabricated particleboard	0.08-0.80	1.0-10
•Workplace (25% of the time) -without occupational exposure	0.04-0.16	0.2-0.8
-with 1mg/m^3 occupational exposure	1	5
3. Environmental tobacco smoke (ETS)	0.02-0.20	0.1-1
Smoking (20 cigarettes per day)		1

A recent evaluation prepared by researchers at the U.S. Chemical Industry Institute of Toxicology, predicts a cancer risk in humans exposed to low levels of formaldehyde lower by many orders of magnitude than the previous assessments [9]. At a level of 0.1 ppm occupational exposure, the new assessment estimates an increased lifetime risk of cancer of 1 in 10,000,000 (ten million) for smokers and 4.1 in 1,000,000,000 (one billion) for non-smokers. The increased risk of developing cancer from a lifetime of exposure to 0.1 ppm (environmental exposure) is estimated at 6.7 in 10,000,000 (ten million) for smokers and 2.7 in 100,000,000 (one hundred million) for non-smokers (see also Table 3).

DETERMINATION OF FORMALDEHYDE EMISSIONS FROM WOOD-BASED PANELS

Key element for the efforts to evaluate or control the contribution of wood products on the quality of indoor air is the means of measuring the actual formaldehyde emissions of a product. Measurement of a product's potential to emit formaldehyde is the basis for determining indoor air quality through modelling (Figure 1). A variety of test methods for measuring product emission levels are applied worldwide, producing a corresponding variety of test results. Each method measures a slightly different emission characteristic and frequently produces results in different and non-interchangeable units. This proliferation of test methods and incomparable results often creates confusion among government regulators, consumers and industry personnel. One of the most common misunderstandings is that citing a formaldehyde level of a wood product is meaningless unless the test method and conditions are also cited. Over the past several years there has been an increasing effort to bridge these differences in testing methods between Europe and North America mainly.

Table 3. **Predicted human additional risk of respiratory tract cancer due to environmental and occupational exposures to formaldehyde [9].**

Formaldehyde Exposure Concentration(ppm)	Exposure scenarios					
	Environmental[a]	Occupational[b]				
	Non-smoking	Mixed	Smoking	Non-smoking	Mixed	Smoking
0.001	$2.3X10^{-10}$	$3.9X10^{-9}$	$4.9X10^{-9}$	---c	---	---
0.02	$4.8X10^{-9}$	$1.0X10^{-7}$	$1.2X10^{-7}$	---	---	---
0.04	$1.0X10^{-8}$	$2.1X10^{-7}$	$2.5X10^{-7}$	---	---	---
0.06	$1.5X10^{-8}$	$3.3X10^{-7}$	$3.8X10^{-7}$	---	---	---
0.08	$2.1X10^{-8}$	$4.5X10^{-7}$	$5.3X10^{-7}$	---	---	---
0.10	$2.7X10^{-8}$	$5.8X10^{-7}$	$6.7X10^{-7}$	$4.1X10^{-9}$	$7.6X10^{-8}$	$1.0X10^{-7}$

0.30	---[c]	---	---	$1.3X10^{-8}$	$2.6X10^{-7}$	$3.8X10^{-7}$
0.50	---	---	---	$2.5X10^{-8}$	$5.0X10^{-7}$	$7.2X10^{-7}$
0.70	---	---	---	$3.4X10^{-7}$	$8.0X10^{-6}$	$6.6X10^{-6}$
1.00	---	---	---	$8.8X10^{-6}$	$2.1X10^{-4}$	$1.5X10^{-4}$

[a] 80 year lifetime continuous exposure at indicated ppm.

[b] 80 year lifetime continuous exposure at 0.004 ppm with 40 years occupational exposure (8hr/day, 5 days/week) at indicated ppm beginning at age 18 years. ICRP66 (1994) "light working" breathing pattern.

[c] simulations not done.

Formaldehyde emissions from pressed wood products come from two sources within the product: free formaldehyde (formaldehyde molecules left non-reacted) and the long-term relatively steady-state breakdown of the urea-formaldehyde bond (resin hydrolysis). Furthermore, there are two types of factors influencing the level of formaldehyde emissions from panel products: internal and external factors [10]. Internal factors comprise of the type of wood and resin employed, the parameters and conditions of panel production, and the panel age as well. External factors represent the temperature, relative humidity, air exchange rate, and total panel area in relation to the total volume of the space in which the panels are placed. All these factors are taken into consideration when measuring formaldehyde emission.

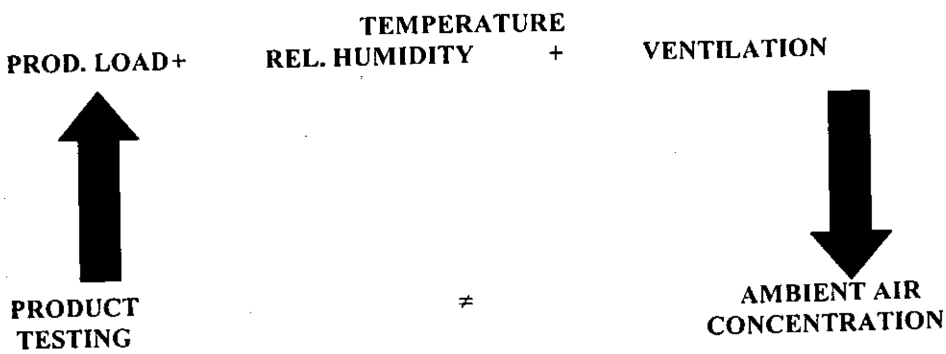

Figure 1. Prediction of formaldehyde ambient concentration through modelling.

Formaldehyde test methods were developed along two tracks: large test chambers designed to imitate a room in a home, and smaller, quicker tests suitable for lab bench and plant quality control. The large chambers, due to their perceived accuracy with which they simulate human environments, became known as "reference" tests and were frequently cited in government regulations and standards. The smaller tests, while not actually developed directly from the large chamber tests, became known in Europe as "derived" test methods [6]. An overview of the test methods and related standards is presented in Table 4 [6, 10-22].

In industrial practice, the perforator method is the most widespread test procedure for measuring formaldehyde content from particleboards and MDF in Europe, and is also employed worldwide with the exception of North America. It is accurate, reproducible, and its application cost as compared to the gas analysis and large chamber methods has been calculated to rate at 0.5:8:100 respectively. Small chambers are also widely utilised in Europe and North America and can be very accurate, relatively easy to adapt at both laboratory and plant environments, and correlate well to large chambers. The North American Dynamic Microchamber (DMC) test method is currently being examined by the European Panel Federation [20].

Table 4. Formaldehyde test methods [6, 10-22].

Method	Country	Standard	HCHO units	Suitability
Reference tests				
Large Chamber (~30 m^3)	N. America	ASTM E 1333-96 ($\geq$22 m^3)	ppm	wood panels
Large Chamber (12-52 m^3)	Europe	prEN 717-1-96 ($\geq$12 m^3)	ppm	wood panels
Derived tests				
Perforator	Europe	EN 120-92	mg/100gr dry board	PB, MDF
Desiccator	USA	FTM 1-1983	μg/ml	wood panels
Desiccator	Japan	JIS R 3503	mg/ml	wood panels
Gas analysis	Europe	EN 717-2-95	mg/h * m^2	wood panels
Flask method	Europe	EN 717-3-96	mg/100gr dry board	PB, MDF
Small Chamber (75 ml-1 m^3)	Europe	SS 270236 prEN 717-1-96 (1 & 0.225 m^3)	ppm	wood panels
Small Chamber (0.02-1 m^3)	USA	FTM 3-1996 (DMC)	ppm	wood panels

FORMALDEHYDE EMISSION REGULATIONS

Ever since formaldehyde emission was identified as a potential contributor to low indoor air quality, efforts were made by both the government and industry to reduce exposure to it. One of the measures taken was the establishment of both occupational and residential exposure limits for formaldehyde. Table 5 presents the formaldehyde maximum exposure limits (MEL) in the workplace environment, in several countries and in three different calendar years [23]. The data given indicate that the formaldehyde concentration limits in most of the industrialized countries have been dramatically reduced over the last 20 years, in order to protect human health. Furthermore in Table 6, the formaldehyde maximum exposure limits in the living space are presented in parallel to those in the workplace environment, for several countries and for the previous calendar year (1999).

Table 5: Formaldehyde maximum exposure limits (MEL) in the workplace environment in various countries (as in year 1976, 1985 and 1999) [23, 24].

Country	1976 HCHO MEL (ppm)	1985 HCHO MEL (ppm)	1999 HCHO MEL (ppm)
USA	5.0	3.0	0,75
Denmark	5.0	1.0	0.30
Finland	5.0	1.0	0.50
Norway	-	1.0	0.50
Sweden	-	1.0	0.50
Austria	-	-	0.50
Germany	5.0	1.0	0.50
Switzerland	-	1.0	0.50
United Kingdom	10.0	2.0	2.00
Belgium	-	2.0	1.00
France	-	-	2.00
Greece	-	-	2.00
Australia	-	-	1.00
Canada	-	-	0,3-2.0

In Table 6, it is shown that for workplace exposures, the allowable formaldehyde concentration (occupational exposure limit) for 14 countries ranges from 0.3 ppm to 2.0 ppm, with the majority of them to range between 0.5 and 1.0 ppm. Also, the lowest exposure limit in the living space in most countries is around 0.1 ppm. It is obvious that the acceptable exposure levels in the ambient air are usually 5-10 times lower than the exposure limits in the workplace, except for three countries. Four of the countries mentioned have no limits for the living space.

Apart from regulations governing formaldehyde concentration in workplace and living environments, guidelines for panel formaldehyde emission levels have been established. Germany pioneered in this field as well as in reducing panel formaldehyde emissions in actual industrial practice. In 1980, the world's first formaldehyde regulation for wood products was published in Germany (ETB-

Richtlinie). That guideline combined the formaldehyde steady state concentration, determined by a large chamber test, and the formaldehyde content, determined by the perforator method, classifying particleboards according to their formaldehyde release into three different emission classes, E1, E2 and E3, Table 7.

Table 6: Formaldehyde maximum exposure limits (MEL) in the living space and the workplace environment in various countries (as in 1999) [23, 24].

Country	HCHO MEL, living space (ppm)	HCHO MEL, workplace (ppm)
USA	0.10	0,75
Denmark	0.12	0.30
Finland	0.12	0.50
Norway	0.10	0.50
Sweden	0.20	0.50
Austria	0.10	0.50
Germany	0.10	0.50
Switzerland	0.10	0.50
UK	--	2.00
Belgium	--	1.00
France	--	2.00
Greece	--	2.00
Australia	0.10	1.00
Canada	0.10	0,3-2.0

Table 7: Classification of particleboards according to their formaldehyde emission (ETB-Richtlinie) [25].

Emission class	Equilibrium concentration in a 40 m^3 test chamber (ppm)	Iodometric Perforator value (mg/100g dry board)
E1	≤0.1	≤10
E2	0.1-1.0	10-30
E3	1.0-2.3	30-60

In 1989, there was a new regulation determining a more stringent E1 level (photometric average perforator value= 6.5 mg/100g dry board). This E1 level is valid till today and has been adopted, more by trade than by regulation, by a lot of other European countries. Nowadays, nearly all companies in Germany are producing almost exclusively particleboards of this E1 emission class. Table 8 summarizes the current regulations with regard to formaldehyde emission from wood-based panels in Germany, which are also valid in Denmark. These two countries together with Austria and Sweden have different and more stringent allowable emission classes than the rest of the members of CEN (European Committee for Standardization), forming the so-called A-deviations of the European standards (EN 312-1-96 for particleboards and EN 622-1-97 for fibreboards), which are considered as trade barriers by the European Commission. Today, a harmonised formaldehyde regulation within the European Union is a matter of high importance.

Table 8: Current regulations concerning the subsequent formaldehyde emission from wood-based panels in Germany (Regulation of Prohibition of Chemicals) [26, 27].

a) maximum steady state concentration in a test chamber: 0.1 ppm (prEN 717-1)	
b) laboratory test methods[a]	
PB:	6.5 mg/100g dry board photometric perforator value (EN 120)[b]
MDF:	7.0 mg/100g dry board photometric perforator value (EN 120)[b]
Plywood:	2.5 mg/h * m^2 with gas analysis method (EN 717-2)

[a] 6 month average values for uncoated boards.

[b] Correction of the perforator value to 6.5% board moisture content.

Despite the fact that the enforcement of the above regulations has essentially solved the formaldehyde emission problem, there have been new discussions over the last few years proposing even more stringent limitations (see Table 9). The latest proposal refers to a formaldehyde emission similar to dried natural wood, called “F-zero” (or “E-zero”). Formaldehyde emission is not practically zero, due to formaldehyde traces emitted from the wood material itself during the thermal processing steps of board manufacture [1, 26]. The adhesives industry has placed considerable effort in meeting these new demands with the use of aminoplastic resin systems as compared to formaldehyde-free advertised adhesives like polymeric isocyanates (PMDI) and phenol-formaldehyde resins.

The panel industry in the United States and Canada conforms to existing national voluntary standards such as the American National Standards ANSI A208.1-1999 for particleboard, and ANSI A208.2-1994 for MDF. These standards limit all board emissions to 0.3 ppm (ASTM E 1333), while restricting particleboard flooring products emissions to 0.2 ppm [28, 29].

Table 9: Proposed regulations concerning the subsequent formaldehyde emission from raw panels (without coating) in Germany [26].

a) UZ 38: 4.5 mg/100g dry board (EN 120) or 0.1 ppm[a]
b) UZ 76 (“Blue Angel”): 3.0-3.2 mg/100g dry board (EN 120) or 0.05 ppm[a]
c) “F-zero”: <2 or <2.5 mg/100g dry board (EN 120); <0.025 or <0.03 ppm[a]

[a] Steady state concentration (chamber test).

For the protection of consumer safety, both in Europe and North America, the composite panels are labelled or stamped to be in conformance with the related standards/emission classes.

REDUCTION OF FORMALDEHYDE EMISSIONS FROM COMPOSITE PANELS

The problem of the subsequent formaldehyde emission from UF-bonded wood products can be considered as solved when following the stringent regulations valid nowadays. The E1 emission class describes a formaldehyde emission, which is sufficiently low to avoid any danger, irritation or inflammation of the mucous membranes in the eyes, nose and mouth, as it had been sometimes the case in former times with higher levels of emission, and even any molestation. However, it is important that not only the boards themselves, but also veneering and carpenter's glue resins, laquers and varnishes and other sources of formaldehyde are under control. Additionally it should be kept in mind that the most severe source of formaldehyde in an "E1"–dwelling room is tobacco smoke [1].

For the production of boards of the E1 quality, the following means are employed:

1. aminoplastic resins with low molar ratios F/U or $F/(NH_2)_2$, respectively;
2. introduction of substances containing NH_2 groups (formaldehyde catchers), which decrease the molar ratio $F/(NH_2)_2$ of the resin mix;
3. addition of formaldehyde catchers or scavengers during the production of the boards, e.g. to the wet or to the dried chips;
4. post manufacture treatment of the boards;
5. application of a diffusion barrier by coating or laminating or veneering of the board.

The major approach to achieve lower formaldehyde emissions over the last 20 years has been to lower the F/U molar ratio of UF resins, thus decreasing the amount of free formaldehyde in the resin, while maintaining the required resin performance. In Europe, most of the resins currently used for E1 particleboard production have a F/U molar ratio between 1.02-1.08 [1, 26], while in E1 MDF the F/U ratio is even smaller, ranging within 0.90-1.00 [23]. Given the fact that at the end of the '70s the majority of the resins used in the wood industry had a molar ratio as high as 1.4-1.7 [1, 5, 23, 26, 30], the above reductions of the F/U ratio are important. Noteworthy is that a decrease in the resin molar ratio of from 1.5 to 1.1 can reduce the formaldehyde emission of a board up to 10 times.

The reduction of the molar ratio was initially achieved by introducing in the resin production process one or two extra steps of urea addition. The urea reacted with the residual formaldehyde and the free formaldehyde emitted from the board was drastically reduced. The resin performance was affected negatively, however. The addition of small quantities of melamine helped to achieve altogether the formaldehyde emission, mechanical strength and water resistance board quality requirements. This generation of melamine-fortified UF resins (UMF) with a melamine content usually in the range of 1-4% on a liquid basis, although it results at an increased resin cost, appears to be the only way to produce either particleboard or MDF of the German E1 class valid today, without the use of any additives [5, 30].

In the meantime, the resin industry has managed to optimize the synthetic route of low molar ratio straight UF resins and together with improved board preparation conditions and the sophisticated equipment employed in board manufacturing plants, it claims that they can be used in the production of low formaldehyde emission boards without any loss in performance as compared to the high molar ratio resins used twenty years ago. However, in order to meet the stringent German E1 specification, the addition of formaldehyde catchers (or scavengers) is needed [5, 30].

By employing formaldehyde, urea and melamine at higher levels than 8% on a liquid basis (MUF resins), it is possible to produce resins with an extremely low molar ratio $F/(NH_2)_2$ in the range of 0.75-0.90. These values are distinctly outside the range of the mole ratios which had been used until now. Fortification with melamine is necessary to improve the hydrolytic stability of the cured resins. It is also necessary to enhance the reactivity of these resins by special types of cooking procedures. These procedures are no longer a two- or three-step process as described in the chemical literature from the last decades, but multi-step processes requiring careful control of temperature, pH, and time parameters. In this case, the cost increase is higher than in the fortified UF resins and much higher than in straight UF resins, due to the cost of melamine employed [26].

In addition to resins with a very low formaldehyde content (expressed by a very low molar ratio F/U or formaldehyde to amido groups (NH_2)), it is possible to achieve such a low overall molar ratio by adding so-called formaldehyde scavengers at one of the several stages of the board production process. One of the easiest and cheapest, but not always most desirable, scavenger is urea itself. In most cases, however, is preferable to add special scavengers like some condensation products with high deficiency of formaldehyde, directly to the liquid resin. This gives the additional advantage that this scavenger might replace part of the resin itself. The formaldehyde catchers can be in most cases tailor-made to meet the needs of the particular plant. They are used up to a maximum level of 25% of the resin used and can achieve reductions in formaldehyde emission of up to 60% [5, 30].

It is important to point out that it is not possible anymore to use the conventional catalysts (resin hardeners) in combination with the low molar ratio UF resins used nowadays. Ammonium salts commonly employed as resin hardeners react with the free formaldehyde in the resin and liberate acids, promoting the resin polymerization reaction by lowering the pH value. The low free formaldehyde present in modern UF systems renders these types of catalysts ineffective and special hardener systems, which do not rely on the available formaldehyde in order to generate acidity, should be employed [5, 26, 30].

Finally, it should be considered that neither the content of free formaldehyde itself nor the molar ratio should eventually be taken as the decisive and only criterion for the classification of a resin regarding the subsequent formaldehyde emission from the boards produced with it. This is because the composition of the adhesive mix as well as the various process parameters during board production, determine the extent of formaldehyde emission. Depending on the type of board and process, sometimes it is recommended to use a UF resin with an already low F/U molar ratio, e.g. 1.03, and hence, a low content of free formaldehyde. On the other hand, sometimes the use of a resin with a higher molar ratio, e.g. F/U=1.10, combined with the addition of a formaldehyde catcher will give better results. Which of these possible ways will be the best in practice can only be decided separately in each case by trial and error.

THE A.C.M. WOOD CHEMICALS SOLUTION TO F-ZERO DEMAND

The new and more stringent regulations for formaldehyde emission now under discussion (see Table 9), have forced the wood adhesives industry to develop new highly sophisticated aminoplastic resin systems which allow the production of wood–based panels with formaldehyde emission rates as low as natural wood itself.

It has been believed and advertised that so low emission levels can only be achieved by the means of other types of binders, like phenol-formaldehyde (PF) and tannin resins, and polymeric isocyanates (PMDI). These binders have often been addressed as "formaldehyde free" or with "no added formaldehyde" [8]. They are, however, related with problems of low reactivity, difficulty in applicability and handling and considerably increased cost. Questionable is furthermore, the level to which the use of these systems does not incur toxicity problems.

A.C.M. Wood Chemicals plc has proved that solving the formaldehyde emission problem is not a matter of changing the resin alone, but rather changing the resin system itself. It has developed a unique cost effective F-zero system based on an aminoplastic resin. This system relies on a combination of a melamine-urea-formaldehyde (MUF) resin, a formaldehyde catcher and a special hardener. The application of this system in the industrial production of particleboards, provided formaldehyde emission values below 2.0 mg/100g dry board (photometric perforator value, EN 120) and its successful performance is due to the synergistic action of its properly formulated components. Representative results of this industrial trial are given in Table 10, whereby the figures reported in column I have been derived from the boards produced without any formaldehyde catcher and without any special hardener, while the figures of column II correspond to the boards produced with both a formaldehyde catcher and a special hardener. These figures represent averages values over a running period of 12h.

The data of Table 10 prove that it is possible to attain the more stringent F-zero limits for formaldehyde emission proposed nowadays, photometric perforator value of 1.9 mg/100g dry board, without any deterioration in the board properties and without increasing either the pressing times (reducing productivity) or the amount of resin required for bonding. So low formaldehyde emission values may be obtained from the wood itself and thus the boards are considered to be formaldehyde free

CONCLUSION

Recent developments have shown that it is possible to meet the new demands for F-zero formaldehyde emission from composite panels products with the use of properly formulated aminoplastic resins systems, without any deterioration in panel performance or significant modification of plant operating conditions or need to employ other types of binders. The formaldehyde emission values obtained were so low as those from the wood itself and thus the panels are considered to be formaldehyde free.

Table 10. Industrial trial for the production of particleboards with extremely low formaldehyde emission [5, 29].

Parameter/property	I	II
% dry resin/dry wood (core)	8.0	8.0
% dry resin/dry wood (face)	9.5	9.5
% dry hardener/dry resin	2.5	2.5
% formaldehyde catcher on liquid resin	-	25.0
% special hardener on normal hardener	-	25.0
Pressing time (s/mm)	7.0	7.0
Pressing temperature (°C)	200	200
Thickness (mm)	16.1	16.1
Density (Kg/m^3)	651	658.0
Internal Bond Strength (N/mm^2)	0.5	0.48
Bending Strength (MOR, N/mm^2)	17.2	17.3
2h thickness swelling (%)	5.1	5.5

24h thickness swelling (%)	13.9	13.7
Formaldehyde (mg/100g dry board)	7.6	1.9
Moisture content (%)	6.7	6.5

REFERENCES

1. Dunky M. Aminoplastic glue resins: State of the art to meet the challenges of the wood based panels industry. Proceedings of the 3rd ICFWST. 385-392. 1997.
2. Dunky M. Urea-formaldehyde (UF) adhesive resins for wood. International Journal of Adhesion & Adhesives. 18, 95-107, 1998.
3. An update on formaldehyde: 1997 revision. U.S. Consumer Product Safety Commission Document 725. http://www.cpsc.gov. 1997.
4. Markessini E. Indoor pollution by formaldehyde – A review. Monument & Environment. Scientific-technical revue for the architectural heritage and the environment. Thessaloniki, Greece. 1, 73-77,1993 (in Greek).
5. Markessini E. Formaldehyde emissions from wood based panels and ways to reduce them. Monument & Environment. Scientific-technical revue for the architectural heritage and the environment. Thessaloniki, Greece. 2, 57-74, 1994.
6. Marutzky R., Margosian R. Measuring formaldehyde emissions from pressed wood products: an international perspective. Measuring and Controlling Volatile Organic Compound and Particulate Emissions from Wood Processing Operations and Wood-Based Products. Forest Products Society. Proceedings 7301, 62-73, 1995.
7. Commission of the European Communities. EUR 13216-European concerted action "Indoor Air Pollution and its impact on Man." Cost Project 613: Report No. 7: "Indoor Air Pollution by Formaldehyde in European Countries." Office for Official Publications of the European Communities. Luxembourg. 1990.
8. Wolf F. Wood–based panels produced with amino resins with formaldehyde release "like natural wood". Proceedings of the first European panel products symposium. 243-249, 1997.
9. Formaldehyde: Hazard Characterization and Dose-Response Assessment for Carcinogenicity by the Route of Inhalation. Revised Edition. U.S. Chemical Industry Institute of Toxicology. 1999.
10. Grigoriou A. Technology of wood-based products. Department of Forestry and Natural Environment. Aristotle University of Thessaloniki. 1996.
11. ASTM. Standard Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Using a Large Chamber. E1333, 1996.
12. CEN. Wood-based panels. Determination of formaldehyde release. Part 1: Formaldehyde emission by the chamber method.PrEN 717-1, 1996.
13. CEN. Wood-based panels. Determination of formaldehyde content; Extraction method called the perforator method. EN 120, 1992.
14. U.S. Small scale test method for determining formaldehyde emissions from wood products, two hours desiccator test. FTM 1, 1983.
15. Japanese Industrial Standard for particleboards. Collection of Formaldehyde. JIS R3503.
16. CEN. Wood-based panels. Determination of formaldehyde release-Part 2: Formaldehyde release by the gas analysis method. EN 717-2, 1994.
17. CEN. Wood-based panels. Determination of formaldehyde release-Part 3: Formaldehyde release by the flask method. EN 717-3, 1996.

18. Swedish standard. SS 270236, 1991.
19. U.S. Standard test method for determining formaldehyde concentrations in air from wood products using a small–scale chamber; small chamber method. FTM 3, 1996.
20. European Panel Federation. Annual Report. 1998-1999.
21. Lehmann F.W., Roffael E. International guidelines and regulations for formaldehyde emissions. Proceedings of 26th International Particleboard/Composite materials symposium. W.S.U. 124-150, 1992.
22. Marutzky R. Topical Ecological Challenges of the Wood-based Panel Industry. Proceedings of 2nd European Wood-Based Panel Symposium. 1999.
23. Alexandropoulos D., Nakos P. and Mantanis G. European Approach to Particleboard and MDF adhesives. Proceedings of 1998 Resin & Blending Seminar. Bradfield J., CPA. 137-146, 1998.
24. Hellenic Ministry of Employment. Hellenic Government Official Newsletter 94. 1704-1717, 1999 (in Greek).
25. Roffael E. Formaldehyde release from particleboard and other wood based panels. Khoo K.C., Koh M.P. and Ong C.L. Forest Research Institute Malaysia. p263-264, 1993.
26. Dunky M. Formaldehyde Based Glue resins: European State of the Art in the 1990s. Wood Adhesives 1995. Forest Products Society. Proceedings No 7296, 77-80, 1995.
27. Dunky M. Adhesives for New Types and Applications of Wood-based Panels. Proceedings of 2nd European Wood-Based Panel Symposium. 1999.
28. American National Standard for Particleboard. ANSI A208.1. 1999.
29. American national Standard for MDF. ANSI A208.2. 1994.
30. Markessini C.A. Formaldehyde Emission a novel approach–standards and limitations in Europe. Proceedings of 27th International Particleboard/Composite materials symposium. W.S.U. 207-219. 1993.
31. Meyer B., Boehme C. Formaldehyde Emission from solid wood. Forest Products Journal. 47 (5), 45-48, 1997.
32. Markessini E., Mantanis G. Formaldehyde Emission from wood-based panels: Current status. Wood-Furniture. 169, 63-69, 1998 (in Greek).