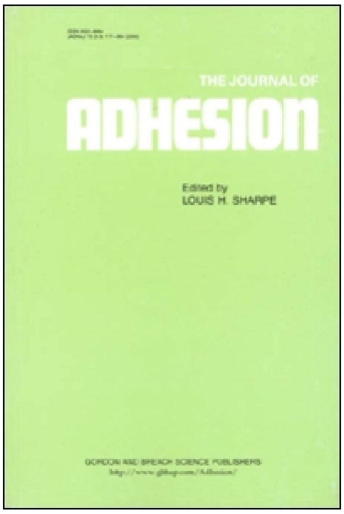

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Formaldehyde Release From Urea-Formaldehyde Bonded Wood Products

B. Meyer[a]; K. Hermanns[a]; D. C. Smith[bc]
[a] Chemistry Department, University of Washington, Seattle, WA, U.S.A. [b] Washington Iron Works, Seattle, WA, U.S.A. [c] Plum Creek Lumber Co;, Columbia Falls, MT, U.S.A.

To cite this Article Meyer, B. , Hermanns, K. and Smith, D. C.(1985) 'Formaldehyde Release From Urea-Formaldehyde Bonded Wood Products', The Journal of Adhesion, 17: 4, 297 — 308

To link to this Article: DOI: 10.1080/00218468508081166

URL: http://dx.doi.org/10.1080/00218468508081166

J. Adhesion, 1985, Vol. 17, pp. 297–308
0021–8464/85/1704–0297 $18.50/0

Printed in te United Kingdom

Formaldehyde Release From Urea-Formaldehyde Bonded Wood Products

B. MEYER,[1] K. HERMANNS

Chemistry Department, University of Washington, Seattle, WA 98195, U.S.A.

and

D. C. SMITH†

Washington Iron Works, Seattle, WA 98134, U.S.A.

(*Received September 27, 1983; in final form June 4, 1984*)

During the past decade significant progress has been made in reducing formaldehyde release from UF-bonded wood products. The purpose of this work was to test formaldehyde release from medium density fibreboard (MDF) manufactured in a commercial pilot plant using seven different UF resins with molar ratios between 1.85 and 1.05 that were available in spring 1983. Formaldehyde release measured with the 2 hr. U.S. desiccator test ranged from 8.6 mg/l to 0.3 mg/l after 6 weeks. European perforator standard values ranged from 80 mg/100 g to 9 mg/100 g. Low molar ratio resin produced MDF with good mechanical properties while yielding formaldehyde release rates that were sufficiently low to meet the requirement of the German wood product class E-1 and the 0.1 ppm requirement of ASHRAE 62-1981 or similar standards for minimum acceptable indoor air quality at reasonable product loading ratios.

INTRODUCTION

The purpose of this work was to compare the formaldehyde release

---

Presented at the Third Annual International Symposium on Adhesion and Adhesives for Structural Materials, Washington State University, Pullman, WA 99164, U.S.A., September 27–29, 1983.

[1] To whom correspondence should be addressed.

†Current address: Plum Creek Lumber Co; Columbia Falls, MT 59912, U.S.A.

potential of UF-bonded wood products made with six different commercial adhesive resins that were available in the Spring of 1983.

Urea-formaldehyde adhesives are used to manufacture plywood, particleboard, medium density fibreboard (MDF), and other wood products that are present in almost every office and residence throughout the entire world. In the U.S. alone, some 500 kilotons (kt) of urea-formaldehyde resins (UFR) were manufactured for this purpose last year. The art of making and using these resins commenced more than fifty years ago and is still developing.[1] The only disadvantage of UF-bonded wood products is that they are not weather resistant and that they have a tendency to release some formaldehyde vapor if they are improperly manufactured or used. The nature and source of the formaldehyde release mechanism is complex, as it involves every parameter in the manufacture of the resin and the product, as well as its use. The problem can lead to indoor air complaints, especially in poorly ventilated rooms,[2] in extreme climates, and if large quantities of new products are installed in a small space. Thus, reoccuring problems have been observed in manufactured housing, because a standard, single-wide mobile home contains about 170 kg UFR in the form of 250 m^2 of 5/32″ hardwood paneling, 140 m^2 of 5/8″ particleboard flooring as well as furniture and cabinet work, all in an air-space of less than 250 m^3.

The formaldehyde release problem has been recognized for more than twenty years, and there has been steady progress in reducing formaldehyde release. During the last ten years great progress has been made in modifying the manufacturing process of wood products. Thus, wood chips are now widely pre-treated with urea,[3-5] ammonium salts,[6] lignosulfonates,[7] tanning agents, or various natural products containing proteins.[8] Good results have also been obtained by after-treatment of finished products with chemical scavengers.[9,10] Further improvements involve variation of process parameters such as wood moisture before and after resinating and pressing, press temperature, and press duration.[11] However, most of these actions involve extra manufacturing steps and thus extra costs. Thus, at the same time, efforts have been made to find new adhesives, or to modify traditional adhesives by mixing resins with different characteristics,[12] or addition of various salts,[13,14] or to modify traditional resin manufacturing so as to optimize the formation of desirable functions, such as methylene linkage.[15] Thus, during the last two decades, the concentration of free formaldehyde in adhesive resins has dropped from 1–6 wt% in 1964[16] to values as small as 0.2 ppm.[17] At the same time the over-all molar ratio of formaldehyde to urea (F:U) in commercial resins has been gradually reduced from F:U = 2 to F:U = 1.65 and even lower.[18] Commercial resins with F:U = 1.26 have been used in Scandinavia since 1974. However, below a molar ratio of about 1.2 several problems crop up. For example, the resin gellation time increases, and the finished wood products exhibit rapidly decreasing internal bond strength and swelling that has to be compensated for with secondary measures,[19] such as modified wax solutions, or by increasing[3] the adhesive content of the finished products by 20–60%. Another drawback is that low molar ratio resins tend to have a reduced storage life and that their solubility and viscosity are highly concentration dependent. Thus, until recently, it was believed that a F:U ratio of 1.20 was a practical limit. However, recently several companies have started to market resins with a molar ratio of F:U = 1.25 and even F:U = 1.05, and the patent literature reveals increased efforts to produce resins with ratios as low as 0.5. Such resins can apparently be made via several different paths, for example, by third or forth addition of urea to traditional resins,[17] by pH buffered high temperature and pressure condensation,[20] by addition of polyfunctional alcohols,[20,21] by co-condensation of small quantities, as little as 0.1 mole%, melamine and/or phenol,[21–23] and by reacting precondensates of resins with different molecular weights.[24]

The goal of this work was to test the performance of resins without any additives or scavengers, in order to establish how these resins perform under traditional process conditions, such as commonly employed before formaldehyde scavengers were introduced in the wood product manufacturing process.

EXPERIMENTAL

Adhesive formulation

Six commercial resins and a laboratory product with F:U ratios between 1.84 and 1.05 were tested as supplied to us (Table I). All resins were between six and eight weeks old and had been stored at ambient temperatures between 18 and 22°C. Resins A and C were commercial MDF resins for blender application. Resin B was made in the laboratory from UF concentrate by addition of urea; resin D was a dry resin for particleboard, and resins E,F and G were particleboard resins. All resins exhibited C-13 NMR spectra typical for basic UF resins,[25] indicating the presence of methylol ureas, methylene bridges and ether bridges, with only little or no noticeable free methylene glycol. All resins contained some unreacted urea.

As it was impractical for us to optimize application conditions for each individual resin, all resins were mixed according to one standardized procedure regardless of the supplier's instructions or guidelines. Thus, no buffers or additives were used. All resins were diluted to yield 50 wt% solid resin content. Ammonium chloride hardener was added in an amount of 1.5 to 3 wt%, depending on the gellation time of the resin, and 1 wt% of a commercial wax dispersion was added, together with additional water, as necessary to bring the moisture content of the resinated wood fibre to 8 wt%.

Manufacture of boards

For each adhesive three single-layer medium density fibreboard panels, 3 ft × 3 ft × 5/8″, were manufactured in a pilot plant that is commonly used to predict full size plant performance. Ponderosa pine medium density fiber manufactured with a commercial defibrator was used in all experiments. Fibres were dried in an oil-heated air dryer to reduce moisture content to 2–3 wt%; glue was applied in a paddle blender with a spray system with separate control for liquid and air pressure; the resinated fibers were passed through an attrition mill to break up fiber balls, and then blown through a cyclone into a vacuum former. The resulting mat was scalped to yield the desired weight and pre-pressed at 28 atm (400 psi). The mats were pressed without cauls with a platen surface temperature of 300°F (150°C) at a pressure of 300 psi (20 atm) until the core temperature of the board reached 222°F (105.5°C). The over all press time was between 16 and 20 seconds per millimeter. Hot boards were individually trimmed, cooled and sanded on a commercial sander to 5/8″ thickness, and then stored under ambient plant conditions at 20 ± 2°C and 50 ± 10%RH.

Sample testing:

Standard ASTM and NPA[26] test methods were used for measuring the modulus of rupture (MOR), modulus of elasticity (MOE), internal bond strength (IB), density, linear soak expansion and screw holding properties of samples selected from a predetermined pattern from one board for each adhesive resin. Formaldehyde release was measured with the 1982 version of the NPA-HPMA 2 hr desiccator test FTM-1, without coating the edge of the samples.[27] In this test eight wood samples, 70 × 127 × 16 mm, are placed in a circle, inside a 10 liter desiccator flask, around a glass dish containing 25 ml water. The formaldehyde release rate is determined after 2 hrs by photometric analysis of the formaldehyde content of the water. The FESYP perforator tests[28,37] were measured at AB Casco. In this test 100 g of the wood sample in form of cubes measuring 25 × 25 × 16 mm is refluxed with 600 ml toluene (b.p. 110°C) for two hours. The formaldehyde vapor is collected in 1 liter water and titrated with iodine. In both tests the moisture content of the sample must be accurately known.

RESULTS AND DISCUSSION

All resins were about six to eight weeks old and could be handled without any problems. The gellation time of all resins, including those with molar ratios of 1.05, remained unchanged for at least a month beyond the conclusion of our experiments.

Due to limited resources, the results of the mechanical tests on finished boards are limited in quantity, and thus not statistically significant, but data from one board of each resin show no strong correlations between F:U in the resin and the MOR, MOE, linear soak expansion and face screw holding properties of the finished boards. Thus, the highest MOR was measured in a board made with resin G, and the lowest in one made with resin A. Likewise, there was no significant trend in IB and edge screw holding, except for boards made with resin G for which values for both properties were between 10 and 20% below those of the other resins. This observation is not surprising, because the manufacturer recommends the use of 10 wt% resin rather than the 8.5 wt% which we used. Furthermore, we omitted the recommended buffer. However, the linear soak expansion of resin G boards was only 0.14%, *i.e.* among the lowest, and only about a third of the allowed standard value.[26] This shows that resin G, with a molar ratio of 1.05, has higher internal bond strength than traditional UF resins have at this ratio. While we do not know how this has been achieved in resin G, the patent literature reveals claims that this can be achieved by addition of 20 wt% of several proteins to the resin,[6] by addition of cellulose,[7] by co-condensation of melamine,[22,23] by co-condensation of melamine and phenol, and by reaction of precondensates containing different molecular weight ranges.[24] An increase in mechanical strength can apparently also be achieved by addition of ethyl cellulose or other thickeners.[29-31]

While the mechanical performance of all boards was comparable, the formaldehyde release rate differed significantly and showed a strong correlation to the over-all F:U molar ratio. Table I shows the results of three measurements of each sample from three boards of each adhesive after three days, six weeks, and five months storage under ambient laboratory conditions of 20 ± 2°C and 50 ± 10%RH. Formaldehyde release after 6 weeks differs by a factor of 25 between resin A and resin G boards. Similarly great contrasts in emission rates were noticed in the pilot plant during hot pressing and when boards were removed from the press. In fact, boards made with resin G had only a faint formaldehyde odor when leaving the hot press. Figure 1 shows the correlation between the desiccator tests and the perforator tests for all observed boards, yielding an almost linear correlation over the entire observed range. However, the slope for our MDF boards is not

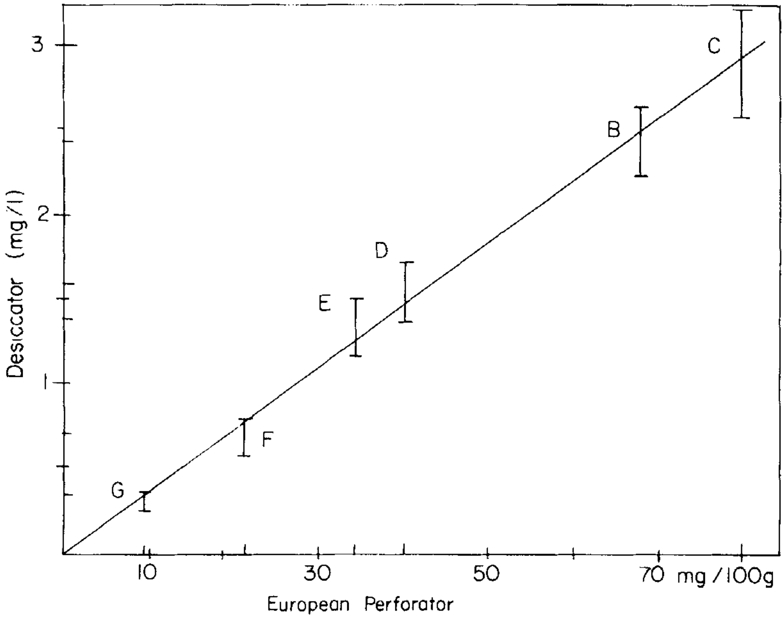

FIGURE 1 Observed desiccator values and observed perforator values for six urea-formaldehyde adhesives. Products were six weeks old.

TABLE I
Formaldehyde release from MDF

Adhesive	Name	F:U Molar ratio	3 days	Desiccator value (mg/l) 6 wks	5 mos[a]	core[b]	Perforator value (mg/100 g) 6 weeks
A	Commercial MDF	1.85	—	8.4	—	—	—
B	UF-Concentrate + Urea Reflux	1.65	4.8	2.3	2.0	3.5	68
C	Commercial MDF	1.65	5.6	3.0	2.3	3.3	80
D	Dynorit L-530 S	1.65	2.6	1.6	0.86	—	—
E	Dynobel 1142	1.26	2.5	1.4	0.85	1.8	34
F	Dynobel 1143	1.20	1.4	0.72	0.62	1.4	23
G	Dynobel 1150	1.05	0.54	0.36	0.38	0.7	9.3

[a] Samples cut one day before testing from center of 1 m^2 boards.
[b] 5 months after manufacture.

exactly the same as that observed for particleboard made with higher F:U ratio resins by earlier authors.[32–34]

Obviously, the seven adhesives yield such different emissions that the field performance of the MDF board will be noticeably different: Boards made with resin A, yielding desiccator values of about 8.6 milligrams per liter, represent adhesive products widely used in the past. If used indoors, this product would likely initially exude a noticeable odor and would continue to emit measurable quantities of formaldehyde for more than a year. MDF boards made with resins B and C, yielding desiccator values between 2.5 and 4 milligrams per liter, represent a significant fraction of current commercial production. This type of material initially exudes noticeable quantities of formaldehyde,[35] but this is rarely objectionable, because most of the production is used in furniture and other products that are used in comparatively modest quantities, yielding low surface-to-air volume ratios. However, this material would not be acceptable in countries such as East Germany and Denmark where furniture falls under the same regulations as paneling and flooring. MDF boards made with resins D and E represent commercial products currently used widely in the particleboard industry. In Europe,[36] products made with this type of resin belong to emission class E-2 and are now commonly treated during the manufacturing process to reduce formaldehyde emission to class E-1 and to eliminate the risk of complaints in homes.[11] In the U.S. some companies treat boards similarly, especially if they are used for mobile homes.

MDF boards made with resin F reflect recent state of the art. With careful quality control and production optimization, products made with this resin cause few consumer complaints, except under severe climatic conditions or high loading when the installed product to indoor air volume ratio exceeds $1 m^2/m^3$. However, these resins must be used in conjunction with special wax solutions containing scavengers and wood sealants that are applied before the wood chips are resinated, if products with perforator values below 10 mg/100 g, *i.e.* class E-1 properties, are required.

MDF boards manufactured with resin G consistently yielded desiccator values below 0.4 milligrams per liter and perforator values of 9 or even lower. This places resin G in an entirely different emission class from all other resins used in our tests, in that these boards, used under appropriate conditions, would not contribute measurably to ambient indoor formaldehyde concentrations. This is evident from

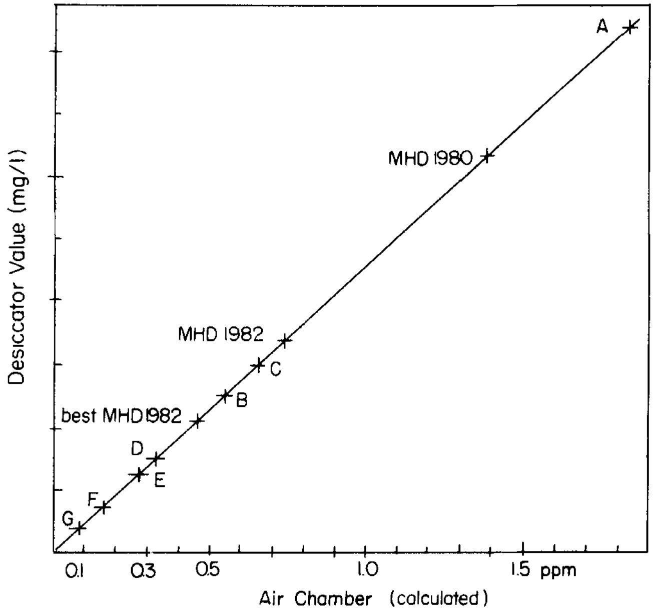

FIGURE 2. Observed desiccator values and calculated large air chamber values (refs. 32–34). Products A to G were 6 weeks old. Mobile home decking (MHD) values are average values of six or more random samples measured when the products were 6–12 months old.

Figure 2 which shows that our pilot plant MDF board would be able to meet, for example, the German class E-1 requirements[36] that are aimed at securing an indoor formaldehyde concentration of less than 0.1 ppm at 23°C, 45% RH, a loading factor of 1 m^2/m^3 and 1 air change per hour.[36] Until a year ago, most experts believed that such low emission could not be reached with UFR, except by addition of scavengers or by special manufacturing precautions.[11] In fact, the FESYP perforator values of pilot plant MDF boards made with resin G lie below the useful sensitivity range of this test which was introduced as an official European standard only two years ago.[37]

The belief that such low formaldehyde emission rates were unachievable has several reasons: One is that UF bonded products are formed in presses that expose the mat to large temperature and humidity gradients. This is necessary to impart to the finished product the desired surface strength, but the adhesive is not evenly cured and the finished board is left with high moisture in the core, causing the accumulation of low molecular weight resin residues and formaldehyde. Another problem is that resins can only adequately cure if the adhesive contains excess formaldehyde for cross-linking low molecular weight resin chains. A third problem is that formaldehyde functions in the resin, such as N-methylol or N-methyl ethers, can readily equilibrate during the resin storage or during curing[38,39] and thus yield methylene glycol that later vaporizes as formaldehyde.

Table I lists formaldehyde release of the seven board types as a function of age. Specimens were stored at 20 ± 2°C and 50 ± 10% RH between measurement. As is well known,[1] the formaldehyde release of traditional UF bonded board decreases with time. The decrease is dependent on the original emission rate. This trend is reflected in Table I for all high emitting boards. Thus, for boards A to F the formaldehyde release rate decreases in the first six weeks to 48–62% of the value measured three days after manufacture, and drops to 33–44% after five months. It is generally accepted[40,41] that this effect is due to gradual diffusion of labile formaldehyde from the core where it accumulates during manufacture due to high moisture gradients. Table I shows the difference between formaldehyde release from the face and the core of our boards after 5 months.

MDF boards G differ from all others in that the formaldehyde release rate does not drop after six weeks. Instead, careful measurements show that it increases about 5% from the lowest value and then remains virtually constant. This behavior indicates that this type of adhesive, which does not release much labile formaldehyde during manufacture, by itself acts as a scavenger for the residual formaldehyde that is necessary to cure the resin in the press. The patent literature indicates that several paths may be followed to achieve the observed effect.[17–24]

In summary, we observe distinct differences between commercial adhesives sold in spring 1983. Thus, the large range of formaldehyde emissions[42] from currently marketed UF-bonded wood products is not random, but is at least partly due to intrinsic differences in the adhesives. Our pilot plant tests show that resins with low F:U ratios reliably yield low formaldehyde emission, and that commercial UFRs are now available that yield very low formaldehyde emission while maintaining good mechanical properties. Furthermore, resins of the type G, that are available from several manufacturers, can be processed in the traditional manner, using the accumulated art for UFR without any modification of the wood manufacturing process and without any use of scavengers. In fact, our experiments indicate that formaldehyde emission from wood products made with resin type G is so low that any further treatment with scavengers is unnecessary and ineffective, because these products add little to the ambient formaldehyde level in most offices and residences.

Acknowledgments

All boards were manufactured at Washington Iron Works, Inc. Standard MDF resins were made available by Washington Iron Works. Resin D (Dynorit L-530 S) was made available by Mr. P. E. Funnemark of Dynobel in Oslo. Resins E (Dynobel 1142), F (Dynobel 1143), and G (Dynobel 1150) were provided by Mr. B. Sundin of AB Casco in Stockholm. Dynobel and AB Casco provided valuable technical support and partial financial support for manufacturing the test boards, and measured the perforator values of the samples reported in Figure 1.

References

1. B. Meyer, *Urea-Formaldehyde Resins* (Addison-Wesley, Reading, MA, 1979).
2. H. J. Einbrodt and D. Prajsnar, in *Organische Verunreinigungen in der Umwelt* (Schmidt Verlag, Berlin, 1978), p. 428–433.
3. H. Petersen, W. Reuther, W. Eisele and O. Wittmann, *Holz als Roh- und Werkstoff* **32**, 402 (1974).
4. B. Gøte-Helgesson, B. Mannson and N.-H. Wallin, British Patent Application 2,019,854 (1979).
5. M. Graser and E. W. Hann, European Patent 1237 (1981).
6. C. Newmann, European Patent 23,002 (1983).
7. H. W. Holmquist, U.S. Patent 4,186,242 (1980).
8. A. Tinkelenberg, H. W. L. Vaessen, K. W. Suen and A. J. Van Doorn, U.S. Patent 4,282,119 (1981).
9. J. B. Verbestel, European Patent 27,487 (1979).
10. E. Roffael, German Patent Application 2,829,021 (1980).
11. K. Ernst, *Holz als Roh- und Werkstoff* **40**, 249 (1982).
12. E. Roffael, European Patent Application 12,169 (1979).
13. Sadepar Chimia, European Patent 21,745 (1980).
14. R. Bruguera, German Patent Application 2,914,009 (1978).
15. J. Barse, *et al.*, European Patent 38,408 (1981), and J. Barse, H. Drechsel and G. Esser, European Patent Application 48,877 (1981).
16. K. Starsynska, *Klebetechnik in der Holzindustrie, Holztechnologie*, **5**, 86–89 (1964).
17. H. N. Spurlock, U.S. Patent 4,381,368 (1983).
18. J. Mayer, *Particleboard, Future and Present*, FESYP Symp. (DRW Publishers, Stuttgart, 1979), pp. 102–110.

19. (a) B. Sundin, *Proc. Washington State Univ. Int. Symp. on Particleboard* **16,** 3 (1982).
(b) B. Sundin, *Swedish Pulp and Paper, and Cellulose Institute* (SPCI) Conference, Stockholm, April 9–13, 1984.
20. C. Dudeck, E. Weber H. Diem and O. Wittmann, German Patent Application 3,115,208 (1982).
21. H. Schittek, German Patent 3,027,203 (1982).
22. H. Diem, *et al.*, German Patent Application 3,145,328 (1983).
23. H. Diem, *et al.*, German Patent Application 3,125,874 (1983).
24. F. Brunnmueller, *et al.*, German Patent Application 2,747,830 (1979).
25. B. Meyer, K. Hermanns and D. C. Smith, Applied Polymer Symp., in press.
26. American National Standards Institute—National Particleboard Association, *Medium Density Fiberboard for Interior Use,* ANSI-AHA-NAP Standard A-208.2 (1980).
27. (a) National Particleboard Association—Hardwood Plywood Manufacturers' Association, *Test Methods for the Emission of Formaldehyde from Wood Products; Desiccator Method,* Silversprings, MD, December 1982.
(b) J. Rybicky, K. Horst and S. M. Kambanis, *Forest Products Journal* **33,** (9), 50 (1983).
28. European Federation of Associations of Particleboard Manufacturers (FESYP), *Formaldehyd Bestimmung bei Spanplatten* (FESYP, Giessen, 1975).
29. H. Mayerhoffer, European Patent 10,537 and European Patent Application 18,355 (1982).
30. H. Diem, *et al.*, German Patent Application 2,553,459 (1975).
31. W. F. Lehmann, U.S. Patent 4,397,756 (1983).
32. W. F. Lehmann, *Proc. Wash. State Univ. Int. Symp. Particleboard* **16,** 35 (1982).
33. D. T. McVey, *ibid.* **16,** 45 (1982).
34. L. R. Newton, *ibid.* **16,** 21 (1982).
35. B. Meyer, *Indoor Air Quality* (Addison-Wesley, Reading, MA, 1983).
36. ETB-Baurichtlinie, *Richtlinie ueber die Verwendung von Spanplatten hinsichtlich der Vermeidung unzumutbarer Formaldehydkonzentrationen,* German Committee for Uniform Technical Regulations (Beuth Publishers, Berlin, 1980).
37. European Committee for Standardization (CEN), *Particleboard; Determination of Formaldehyde Content; Extraction Method Called Perforator Method;* Standard EN-120, rev. March 1982, CEN, Brussels (1982).
38. M. Cherubim, *Holz als Roh- und Werkstoff* **34,** 449 (1976).
39. J. I. de Jong and J. de Jonge, *Recueil* **71,** 643 and 661 (1952).
40. P. Hanetho, *Wash. State Univ. Int. Symp. Particleboard* **12,** 275 (1978).
41. E. Roffael, *Formaldehyd Abgabe von Spanplatten und anderen Werkstoffen* (DRW Publishers, Stuttgart, 1982).
42. G. Myers, *Forest Products Journal* **33,** (5), 27 (1983).