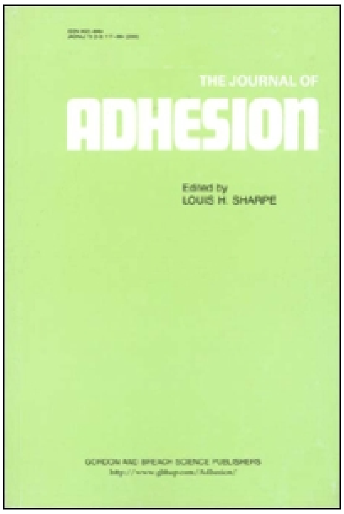

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Tinkelenberg, A. , Vaessen, H. W. , Suen, K. W. and Leusink, P. G. J.(1982) 'Combinations of Low Formaldehyde-Aminoplast Glues and PMDI', The Journal of Adhesion, 14: 3, 219 — 231
To link to this Article: DOI: 10.1080/00218468208073205
URL: http://dx.doi.org/10.1080/00218468208073205

J. Adhesion, 1982, Vol. 14, pp. 219–231
0021-8464/82/1404–0219 $06.50/0

Combinations of Low Formaldehyde-Aminoplast Glues and PMDI

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(*Received October 26, 1981; in final form April 12, 1982*)

Basic research on the formaldehyde emission from aminoplast-bonded particleboard has led to the conclusion that F-emission is essentially governed by the gross molar ratio of formaldehyde to NH_2 equivalents in the material.

From this starting point a new approach was chosen in the development of a glue for low-F-emission boards: such a level of the effective F/NH_2 molar ratio is chosen for the UF or UMF glue that F-emission standards can be met, following which methods or additives are developed to bring mechanical quality back to an acceptable level.

It is shown that addition of approx. 10% of polymeric isocyanate (PMDI) to UMF glue can meet our purpose on a commercially acceptable basis. The performance of the system, using different UMF/PMDI compositions over a range of F-emission levels, is described. An indication is given of possibilities and limitations of the system in commercial practice.

1. INTRODUCTION

In recent years the growing concern about F-emission has set the stage for a multitude of new developments in the particleboard field. Apart from an interesting competition between the F-emitting aminoplasts and the phenolics

Presented at the First Annual International Symposium on Adhesion and Adhesives for Structural Materials, Washington State University, Pullman, WA 99164, U.S.A., September 29–October 1, 1981.

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and isocyanates which emit little or no F, the range of aminoplasts themselves has been enriched by numerous modifications, additions and other methods to meet the limits set by environmental considerations. A problem in this development is formed by the state of confusion and constant movement characterizing the international picture of proposed and approved limits for F-concentrations in living areas and F-emission from various materials. For practical purposes we developed our own measuring methods for evaluating F-emission; details of these methods, showing a good correlation with "climate-chamber practice", are reported elsewhere.

In our research on aminoplast glues, one line along which we advanced followed paths also taken by others, which means that we looked for modification of recipes and application of additives, with the main objective of diminishing F-emission without impairing mechanical strength properties and reactivity. Although some results were obtained along this line, we have not been more successful than others. Our general impression is that the application of F-binding additives† can only give acceptable results at the expense of a cost level, higher than that of "classical" board. The same is true, although to a lesser degree, of, *e.g.*, treatment with ammonia. Some uncertainty exists here about the persistence of the—undoubtedly large—initial effect.

Basic research on F-emission, using different types of measuring methods, led us to a new approach: F-emission appeared to be essentially governed by the gross molar ratio of formaldehyde to NH_2 equivalents in the end product. Variations in resin recipe, raw materials (*e.g.* urea, melamine, NH_2-containing additives, NH_3) and in methods of glue application and board production have only a secondary influence in this respect. In general, the effective F/NH_2 molar ratio, calculated on the basis of all glue components in the board, will give a good prediction of F-emission, apart from the effect of surface porosity. The main problem is the fact that reducing the F/NH_2 ratio generally results in an unacceptable deterioration of mechanical strength and swelling properties under humid conditions. An effective approach seemed to be the following: choose such an F/NH_2 molar ratio for the glue that F-emission limits can be met, even if this results in a decrease of board strength properties to almost zero. Then look for methods which restore mechanical properties to an acceptable level.

A first indication that this approach offers real possibilities came from the application of blood albumin as an additive to UMF glue: addition of approx. 10% of blood albumin (based on glue solids)—which has only a minor influence in "classical" UMF—results in an appreciable improvement of mechanical properties (especially the V-100 tensile strength), if it is used

† Normally urea in some form is used.

together with a UMF glue of reduced formaldehyde content.[1] A comparable, but much more pronounced effect is reached by using isocyanate (PMDI)[2] as the additive; details are given below. Although more or less comparable results have been reached with standard (UF) and weatherproof (UMF) particleboard grades, we will give a survey of system performance here for UMF-bonded board only, because the very critical wet strength (V-100) presents the clearest picture in this case.

2. ISOCYANATES

In the combined systems based on aminoplast resin and isocyanate, the isocyanate component is of great importance. Without going into detail, some background information is given here.

Isocyanates have been used for wood bonding in two ways for many years: in their original form, as glues in the particleboard industry; after reaction with polyols to form urethane prepolymers, as laminating adhesives. The basic type of diisocyanate normally used for most applications is 4-4′ diphenylmethane diisocyanate (MDI). Most activities are concentrated on polymeric MDI (PMDI), because of its well-accepted advantages, such as low vapour pressure (diminishing toxicity problems), acceptable viscosity and relatively low price.

PMDI is undoubtedly an excellent bonding agent for wood. We can refer in this connection to the work of Deppe, Ernst, Sachs, Wittmann, Ball, Redman, Wilson, Johns and many others. The NCO group is capable of reacting with active hydrogen in almost any form under either acid or alkaline conditions. The reactions most likely to be involved in the manufacture of particleboard result in the formation of urethane-type bonds with wood hydroxyls and the formation of polyureas.

In view of the well-known advantages and disadvantages of aminoplasts and PMDI in wood bonding, and of the potentialities of PMDI in particleboard production in particular, the introduction of aminoplast/PMDI combinations seems a normal step in development. In fact, this possibility has been mentioned by various authors.[3] New, however, is the discovery of the spectacular specific effect of PMDI in combination with aminoplast resins extremely poor in formaldehyde. This effect is detailed below.

3. EXPERIMENTAL

3.1. Manufacture of particleboard

The special UMF resins with very low F-content were produced on a semi-technical scale.

The glue solutions were mixed with an accelerator system (1.5% by weight of NH_4Cl and, depending on the F/NH_2 molar ratio, up to 0.5% aqueous ammonia (25%) or up to 2% HCl (10 N solution)) and diluted with water to the viscosity required for spraying. As moisture-repellant Mobilcer ED 80-53 paraffin emulsion was used (0.6%, based on dry wood particles), introduced as a mixture with the UMF glue.

The isocyanate component Bayer Desmodur PU 1520 A was used in most cases. Other types of PMDI used in the investigations are: Desmodur PU 1520 E†, Suprasec DRW (ICI), PBA 1042† (ICI).

In various experimental series the PMDI component was introduced in the form of a mixture with the UMF glue, in others it was separately sprayed onto the wood particles, both as first and as second component.

In most series, a wood mixture consisting of approx. 70% coniferous wood and 30% hardwood was used.

Particleboards were manufactured on a semi-technical scale by spraying wood particles with the adhesive components in a suitable mixer (Lödige system), followed by pressing at 180°C with a maximum compression force of 3.4 N/mm^2; pressing time 12–15 sec/mm board thickness. As a standard, boards measuring 40 × 40 cm were produced, with 16 mm thickness and a density of approx. 700 kg/m^3.

3.2. Testing procedure

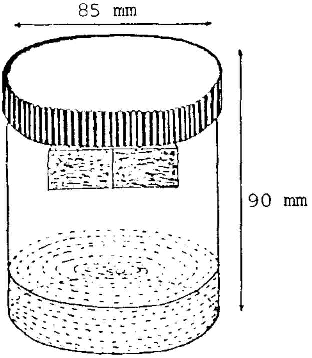
The mechanical properties of the particleboards were measured in accordance with DIN 68763. Emphasis was put on the swelling properties and especially the tensile strength (IB) after 2 h of submersion in boiling water (V-100).

The F-emission of the boards was determined using the modified DSM/Roffael method. In this method, a board sample (4 × 5 cm) is suspended over a saturated NaCl solution in a well-sealed bottle (Figure 1) at a temperature of 40°C.

The salt solution has a double function: it maintains a relative humidity of 75% in the system and it absorbs the formaldehyde emitted by the board sample almost quantitatively.

At subsequent intervals of 24, 24, 120, 24 and 24 h the salt solution is renewed, followed by determination of the quantity of formaldehyde absorbed (an iodometric titration method or, at low F-level, a spectrophotometric method (MBTH) is used). An analytical result is given in terms of mg F per m^2 of particleboard absorbed over the full period of 216 hours.

† Emulsifiable PMDI-types.



Standard conditions

- Specimen 5 x 4 cm.
- Saturated NaCl solution as absorption liquid, giving 75% rel. humidity.
- Temperature: 40 °C.

Standard procedure

5 cycles of 24-24-120-24-24 hours.

Short procedure

2 cycles of 96-72 hours.

FIGURE 1 DSM/Roffael method for F-emission measurement.

4. F-EMISSION AS A FUNCTION OF MOLAR RATIO

The measurement of F-emission from particleboard deserves a critical evaluation in itself. Apart from the FESYP-Perforator method, in which the free-formaldehyde content of board samples is determined *via* extraction with boiling toluene, no method for measuring F-emission on a small scale sample has so far gained general acceptance. Although a fairly good correlation has been shown to exist between Perforator data and climate-chamber experiments[4] for "normal" quality UF boards, the validity of Perforator data for discriminating between boards with really low F-emission is questionable.

For our glue research, we developed a modified version of the WKI-flask method (Roffael),[5] as described in the preceding section. Background research on this method, which will be reported elsewhere, has given strong indications for a good translatability of the results to practice. Testing of some samples taken at random with a modified version of a ventilated interstice[6] method as first described by Mohl[7] showed a good correlation. This comparative background work has led us to the conclusion that a DSM/Roffael value of 500–600 mg $F/m^2/216$ h is required for meeting the demands of the German E-1 class, which is the best-defined standard so far.

The general picture emerging from our F-emission research is shown in Figure 2, in which the F-emission is represented in correlation with the effective $F/(NH_2)_2$ molar ratio of the glue† for boards of otherwise identical composition.

We must conclude that $F/(NH_2)_2$ molar ratio is by far the most important

† For UF: $F/(NH_2)_2 = F/U$
For MF: $F/(NH_2)_2 = 2/3.F/M$.

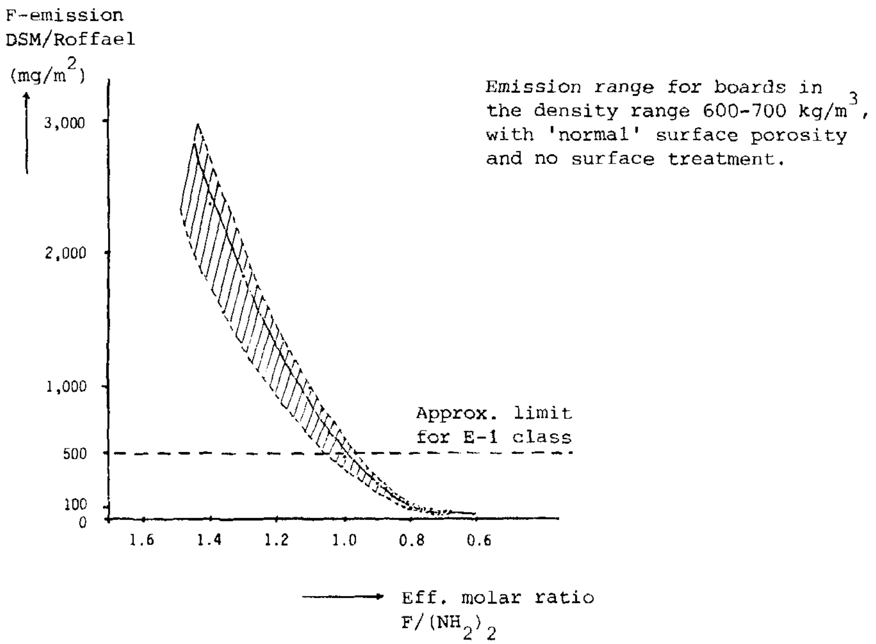


FIGURE 2 F-emission of aminoplast-bonded particleboard in relation to F/NH_2 molar ratio. (DSM/Roffael method)

governing factor in F-emission. Included in this picture are UF and UMF resins of different compositions, where extra urea or ammonia has been added to the glue or sprayed onto the wood particles as a second component.

All these variants give results lying within a relatively narrow margin around the general line relating F-emission to molar ratio. Evidently, differences in reactivity between NH_2 groups, as in urea and melamine and even in ammonia (for our purposes calculated as $2NH_2$ equivalents), do not show up as clear differences in F-emission. For our purpose the reactivity of urea seems to be "high enough".

Although special methods, like separate spraying of an urea solution, certainly have some extra effect on F-emission, we concluded from the data given above that a real solution of the problem can only come from glue types with a strongly reduced gross molar ratio $F/(NH_2)_2$. To meet German E-1 limits with some certainty, a molar ratio of 0.9–1.0 seems necessary. In the following section some results of our approach are given.

5. MECHANICAL PROPERTIES OF LOW-FORMALDEHYDE-UMF PARTICLEBOARD; V-100

5.1. Introduction, unmodified systems

The F-emission data given in the preceding section are based on particleboard samples bonded with both unmodified and modified UMF glue systems. In the case of unmodified resins we have not limited ourselves to systems which give an acceptable board quality. In fact, bringing down the $F/(NH_2)_2$ molar ratio to levels below 1.2 and lower eventually results in a totally unacceptable quality of the board. Figure 3 shows the general picture for some glue systems.

V-100 values at first gradually go down as the molar ratio is reduced, after which there is a more or less precipitous fall to zero at $F/(NH_2)_2$ values below 1.2. In this context a remark should be made on one of our starting points in this research: a comparative evaluation of UMF systems of different compositions and of combined glue systems is always set up on the basis of equal cost price per m^3 board. So, in combinations differing in urea to melamine ratio, formaldehyde content, and blood albumin or isocyanate addition, the total amount of glue used as bonding agent is always chosen on this basis, unless stated otherwise. From this point of view it is clear (Figure 3) that reduction of the molar ratio *via* introduction of urea should be limited to $F/(NH_2)_2$ values of approx. 1.2; introduction of ammonia shows even worse results. Glues with a higher melamine content give us some extra margin, down to an $F/(NH_2)_2$ value of approx. 1.1. Molar ratio variations show a

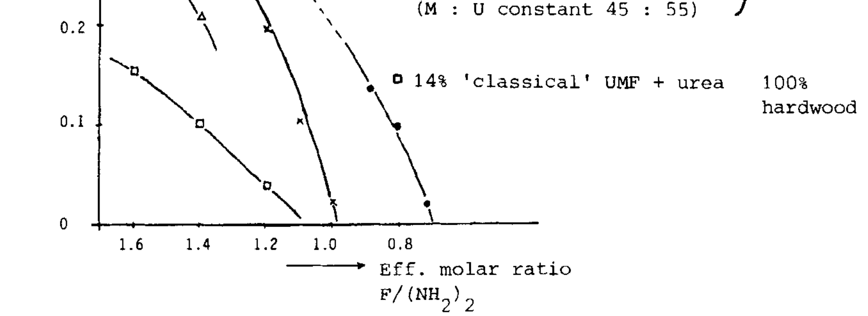


FIGURE 3 Tensile strength V-100 of UMF-bonded particleboard in relation to F/NH_2 molar ratio.

similar, but much less pronounced, effect on the swelling properties of the board; in order not to make matters too complicated we will limit ourselves to a discussion of V-100 results in this context.

5.2. UMF-isocyanate combinations

As mentioned earlier, the first indications that possibilities existed for a specific improvement of mechanical properties in low-F systems were found when blood albumin was used as an additive. Much more pronounced effects were obtained by introducing relatively small amounts of isocyanates. In Table I and Figure 4 a survey is given of some representative results† obtained with UMF glues of varying composition in combination with different amounts of PMDI.

The most important feature is the following: while addition of PMDI to the UMF glue has only a minor positive influence with "classical" UMF, the increase of the V-100 strength appears to be dramatic in the case of low-F systems.

TABLE I

V-100 tensile strength and F-emission of UMF/PMDI-bonded particleboards

$F/(NH_2)_2$ ratio	M content %, rel. to M+U	Glue content, %, rel. to dry chips: UMF	Glue content, %, rel. to dry chips: PMDI	V-100, N/mm^2	F-emission (DSM/Roffael), mg/m^2
1.6	40	14	—	0.35	5000
1.6	40	10	1	0.35	4000
1.3	40	14	—	0.30	1700
1.3	40	10	1	0.30	1500
1.0	40	14	—	0.10	400
1.0	40	10	1	0.30	400
0.9	40	14	—	0.05	200
0.9	40	12	0.5	0.20	200
0.9	40	10	1	0.30	200
0.9	40	8	2	0.25	200
0.9	50	9	1	0.30	200
0.8	40	14	—	0	100*
0.8	40	10	1	0.25	100*
0.7	40	14	—	0	50*
0.7	40	10	1	0.20	50*
0.55	45	10	1	0.15	<50*

* Below $F/(NH_2)_2 = 0.9$: preliminary experiments.

† Since this survey covers a substantial amount of experiments, in which different batches of wood particles were involved, a weighed average of V-100 data is given in order to provide a consistent picture.

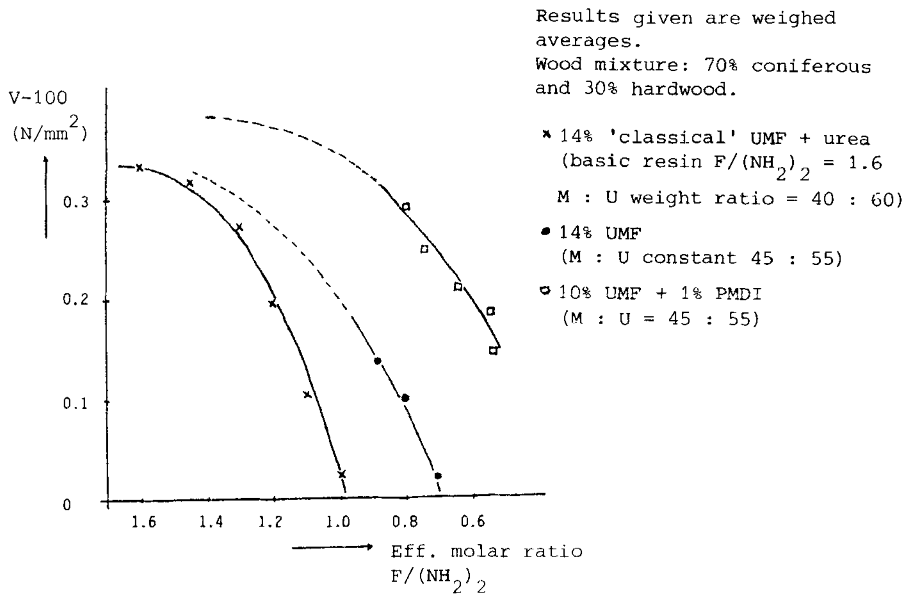


FIGURE 4 Tensile strength V-100 of UMF- and UMF/PMDI-bonded particleboard in relation to F/NH_2 molar ratio.

In fact, the strong fall in V-100 strength normally observed at $F/(NH_2)_2$ values below 1.2–1.1 is shifted to $F/(NH_2)_2$ values of 0.8–0.7 when approx. 4% UMF is substituted by 1% PMDI. Data in Table I show that there is an optimum in the UMF/PMDI ratio at approx. 10 to 1. Increasing the melamine content of the UMF component has some extra positive effect (glue application still being chosen on an equal-cost-price basis).

Referring to our objectives—$F/(NH_2)_2 < 1.0$; DSM-Roffael value <500–600 mg/m^2, to meet German E-1 limits—good possibilities seem to exist on a commercially acceptable basis.

Variations in the procedure of PMDI application in these combinations showed no significant effect: fully comparable V-100 and F-emission data were obtained when PMDI was introduced as a mixture with UMF or was separately sprayed onto the wood particles, both as first and as second component.

Also the type of PMDI used has no significant influence; different commercially available qualities of standard and emulsifiable PMDI were tested, with similar results.

With these combination systems of low PMDI content, no caul-adhesion problems were encountered in semi-technical scale work; evaluation on technical scale still has to be done.

5.3. Expected long-term behaviour

An important feature in UMF development is the behaviour of the particleboards in long-term tests. Although conflicting data can be found in literature, Deppe[8] has shown that the strength persistence of UMF-bonded boards as determined in a Xenotest procedure should be regarded as a critical criterion.

In order to give some provisional information on this point, we submitted some representative board samples to a V-100 test after prolonged boiling-up to 24 h; results are given in Table II.

TABLE II

Long-term behaviour of V-100 particleboards
V-100 tensile strength after prolonged boiling

Glue type	$F/(NH_2)_2$ ratio	M content rel. to M+U % wt.	Glue content rel. to dry chips, %		V-100 (2 h)	V-100 (4 h)	V-100 (24 h)
			UMF	PMDI			
UMF	1.6	40	13	—	0.23	0.19	0.10
UMF/PMDI	0.9	50	8.5	1	0.30	0.28	0.21
	0.7	50	8.5	1	0.20	0.20	0.13
PMDI	—	—	—	6	0.32	0.29	0.24

Although no more than an indication can be given by this test, the results seem promising; after 24 h of boiling the performance of a low F-UMF/PMDI-bonded board is much better than that of its "classical" UMF counterpart, and comparable to that of fully PMDI-bonded board samples, which were included in the testing programme.

In a Xenotest under conditions comparable to those described by Deppe,[8,9]

TABLE III

Xenotest results of UMF/PMDI- and PF-bonded particleboards (MPA results)

Glue type	$F/(NH_2)_2$ ratio	M content rel. to M+U % wt.	Glue content rel. to dry chips, %			V-100	V-100 after 12 weeks' Xenotesting
			UMF	PMDI	PF		
UMF/PMDI	1.1	50	9.5	1	—	0.19	0.21
	1.1	50	9.5	1	—	0.21	0.21
	0.9	50	11.0	1	—	0.20	0.19
	0.9	50	11.0	1	—	0.19	0.22
PF	—	—	—	—	10.5	0.21	0.20
	—	—	—	—	10.5	0.19	0.16

carried out by MPA in Dortmund, UMF/PMDI-bonded board with $F/(NH_2)_2 = 0.9$ showed no decrease in V-100 strength after 12 weeks (Table III).

A phenolic-bonded board produced from the same wood particles showed a decrease in V-100 of approx. 10% under identical conditions. A standardized Xenotest for these combinations is in progress at the BAM Institute in Berlin.

6. CHEMICAL/PHYSICAL BEHAVIOUR OF UMF/ISOCYANATE MIXTURES

The stability of UMF/PMDI mixtures is limited; a potlife of more than a few hours is not easily attained. Although this does not seem to be a serious handicap for technical application—separate spraying of components, application by means of, *e.g.*, a static mixer system or continuous mixing seem good alternatives—the chemical behaviour of these mixtures is yet of considerable interest. Without going into detail, we will give here some results of our preliminary work on this point.

The possibilities for analytical monitoring of the reactions of isocyanates in complicated systems like the one involved are limited. The only easily employable methods seem to be the determination of reactive isocyanate groups and the monitoring of CO_2 emission, which gives information on the reaction with water. Using both techniques, we obtained evidence that the reaction of MDI with water is dominant in this system, at least at room temperature. Comparison of NCO decrease and CO_2 emission over a few hours shows a good correlation between these two phenomena (Figure 5), if we make the plausible assumption that reaction of MDI with water results in the emission of one mole of CO_2, and in the NH_2 group set free quickly reacting with a second NCO group.

On a qualitative basis, the viscosity increase in these mixtures seems in line with the above observations.

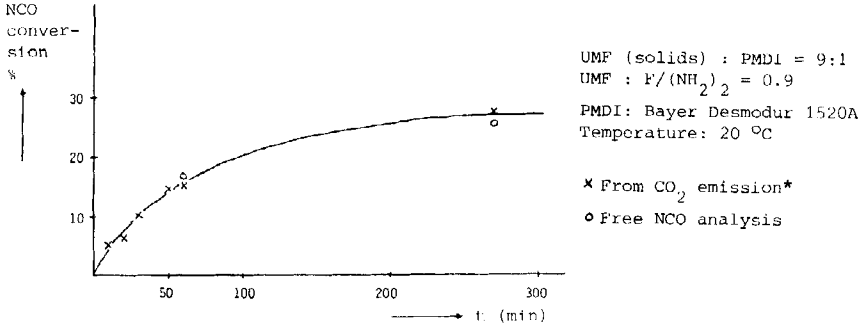
Some notes:

—As expected, temperature variations have a considerable effect on CO_2 emission and potlife of the mixture;

—PMDI/UMF mixtures show strongly increased CO_2 emission compared with PMDI-emulsions in water;

—Intensity of mixing plays a noticeable role (variations in CO_2 emission up to approx. 30%) the type of MDI used, however, does not seem to have an appreciable effect on CO_2 emission and potlife. The use of emulsifiable PMDI types does not distinctly prolong the potlife of UMF/PMDI mixtures, although it does facilitate mixing of the components.

It is an important point that the "potlife" of wood particles after glue



* Assuming one mole MDI to give one mole CO_2:

$$OCN-R-NCO \xrightarrow{H_2O} OCN-R-NH_2 + CO_2$$

$$OCN-R-NH_2 \xrightarrow{R(NCO)_2} OCN-R-\underset{H}{N}-\underset{O}{\overset{\|}{C}}-\underset{H}{N}-R-NCO$$

FIGURE 5 Conversion of MDI in UMF/PMDI mixtures.

application is good: when particles are stored for three hours at room temperature after spraying and pressed, the resulting board shows a mechanical quality which is not significantly lower than that of a "freshly" pressed analogue.

7. INFLUENCE OF THE GLUE TYPE ON THE COST PRICE OF THE FINAL PRODUCT

For commercial purposes it is very important to compare the relative price structures of the different glue systems. In this project the developmental work was concentrated on bonding systems for the particleboard industry. It does not make sense to look at the prices of the different bonding agents on a per-pound basis as such. As the basis for our calculations we took the equality of board properties such as internal bond, swelling, moisture resistance, durability, etc.

The basis of the combination system still is a relatively cheap formaldehyde-based aminoplast glue. To improve the mechanical properties of the boards it is necessary to introduce the expensive PMDI component into the glue system. It is shown however, that a very low PMDI addition already results in acceptable board properties. Summarizing, we can say that, based on a cost price comparison per m^3 board, the newly developed combinations seem well in line with other resin systems offered to the particleboard industry.

8. POSSIBILITIES OFFERED BY THE NEW COMBINATION SYSTEM

Before ventilating some of our ideas, we would do well to check in how far we have satisfied the most important demands to be made on a new bonding system. We think that our new resin system can be characterized as a fair compromise based on requirements as to F-emission, mechanical and physical properties, application opportunities and relative price. At a certain moment in our study of the possibilities to lower F-emission, we became aware of the limitations inherent in the normally-used aminoplasts preventing them meeting demands from the market. This caused us to take a look at the possibilities offered by the use of special types of aminoplast in combination with PMDI. In fact, we utilized the strong properties of one component to eliminate certain weak points of another.

The combined systems have been tested on laboratory and semi-technical scale so far. Further modification and optimization will be based mainly on experience to be gained under practical conditions. We are therefore primarily relying on cooperation with some particleboard manufacturers.

So far we have concentrated all our activities on the particleboard application. Perhaps the combined system offers new possibilities also as a structural adhesive system in the wood working industry, mainly as a laminating adhesive, and in the furniture industry. These industries generally make use of formaldehyde-based glues, and here, too, there are sometimes F-emission problems. In addition, properties such as durability and water resistance are important aspects also in these fields.

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