Indoor Air 99

Proceedings of the 8th International Conference on Indoor Air Quality and Climate held in Edinburgh, Scotland, 8–13 August 1999

Volume 1, Monday

SORPTION OF INDOOR FORMALDEHYDE BY WOOL

G Zwiener [1], G Wortmann [2], F J Wortmann [2], R Sweredjuk [3] and F Doppelmayer [3]

[1] ÖCO-Umweltinstitut GmbH, Cologne, Germany
[2] Deutsches Wollforschungsinstitut, Aachen, Germany
[3] Fritz Doppelmayer GmbH, Kempten, Germany

ABSTRACT

It is of great importance to minimise the concentration of formaldehyde in indoor air. Wool, a protein fibre, consists to approx. 97% of keratines; its smallest chemical constituent is the amino acid. Formaldehyde is able to react with the side chains of the amino acids leading, inter alia, to irreversible crosslinks between the peptide chains of the wool fibres.
Wool without surface treatment was placed in a test chamber. Tests at various concentrations of formaldehyde showed that a reduction of between 80% and 87% of the concentration of formaldehyde in the chamber air took place only after two hours after the test had begun. This is due to the chemical reaction of the formaldehyde with the wool proteins as shown by electrophoresis.
The experiments confirm that wool represents an extremely effective and ecological sorbent for eliminating formaldehyde from indoor air.

INTRODUCTION

Wood products, chipboard in particular, are the most significant source of formaldehyde in indoor air. The urea-formaldehyde-resins (UFR) make up most of the resins used. UFR are subjected to a slowly progressing hydrolysis, in the course of which formaldehyde is released as a function of the air humidity and as the inverse function of polymer formation.

According to estimates the German guide value for formaldehyde in indoor air (0.1 ppm) is exceeded by approx. 10% of German households (1), which means that several million people are affected. This is why it is of such great importance to minimize the concentration of formaldehyde in indoor air. The design of existing buildings, however, often renders it impossible to remove the sources of the emissions. In cases such as these, it is desirable to reduce the formaldeyde loading of the indoor air effectively and permanently by taking other measures which do not give rise to misgivings in respect of health and which are environmentally compatible.

Wool is part of the protein fibres and consists to approx. 97% of keratines; its smallest chemical constituent is the amino acid. The first bonding and reaction mechanisms of formaldehyde with different types of protein were described in detail in the 40's by Fraenkel-Conrat et al. (2). This was confirmed and supplemented, e.g. by Mason and Griffith in 1964, who carried out comparable investigations with wool proteins (3).

METHODS

A technically modified wool (doschaWolle®) of the company Fritz Doppelmayer GmbH, Kempten, was used for the experiments. The wool fleece is manufactured without surface treatment. A wool fleece (25 x 25 x 2 cm, pH 6.6, humidity 11%, weight 14 g) was introduced for the laboratory experiments into a test chamber made of glass with a volume of 250 l. The following climate conditions were set: rate of air change: 0 h^{-1}, temperature: 23°C, relative air humidity: 45%.

Before the individual experiments were carried out, the air chamber was rinsed with purified air and the formaldehyde blank was determined. The blanks were < 0.01 ppm formaldehyde. After the wool had been introduced into the chamber, high concentrations of formaldehyde were generated in the chamber air by injecting defined formaline solutions. The formaldehyde was absorbed in distilled water for analysis. Photometric evaluation was carried out at 570 nm after conversion with pararosaniline (VDI-Guideline 3484). The crosslinking of protein groups with formaldehyde in the formaldehyde-exposed wool was demonstrated by electrophoretic fractionating of the wool proteins as well as by means of HPDSC (High Pressure Differential Scanning Calorimetry).

RESULTS

When 300 ppm formaldehyde were applied, 96.7% ± 0.63% formaldehyde were absorbed by the wool in the test chamber within 24 hours. Decomposition of between 80% and 88% could already be observed after 2 hours (cf. Fig. 2 and 3).
In a further series of experiments, a formaline solution was sprayed - under the above-described marginal conditions - into the test chamber five times after every 24 hours; the formaline solution generated a formaldehyde concentration of 300 ppm in each case. After five days (5 x 300 ppm formaldehyde), a residual quantity of formaldehyde of merely 0.77 ppm was measured in the test chamber. The same sample was loaded an additional time with 5 x 300 ppm formaldehyde. 5 days after the last administration of formaldehyde, the concentration of formaldehyde in the test chamber was still only 0.21 ppm. A residual concentration of 0.1 ppm of formaldehyde was measured after a further 5 days.
All the tests which were carried out show an asymptotic curve pattern tending to zero (Example, cf. Fig. 2). The test sample which was dosed in this way was removed from the chamber and immediately subjected to an olfactory test. No foreign odours of any kind were perceived on the wool by the trained test persons.

The use of interior finishing panels which are lined with densely packed wool would be conceivable for the rehabilitation of formaldehyde-loaded buildings. So as to simulate this, the test chamber was divided into two identical spaces by a test sample lying in a frame closely adjacent to the chamber walls. On one side, a concentration of formaldehyde of 10 ppm was set. On the other side, the concentration of formaldehyde was determined after 24 hours. The values of four measurements after 24 hours in each case were: < 0.02, 0.03, 0.07 and 0.06 ppm.

The formaldehyde diffuses via the wool surface into the interior of the fibre. The molecules which have diffused in may react chemically with many amino acid side chains, in particular, with the side groups of the amino acids lysine, glutamine, asparagine, histidine, arginine, tyrosine, tryptophane, cystine and cysteine (4).

The complete decomposition of formaldehyde in the fibre takes place in two reaction steps (cf. Fig. 1):

1. Adding a reactive hydrogen atom to the carbonyl double bond of the formaldehyde. This first leads to an amino methlylol derivate.
2. Stable crosslinkings (methylene bridges) are formed by methylol groups which react in a condensation reaction with primary amino, amido, guanido, indol and other groups (5, 6).

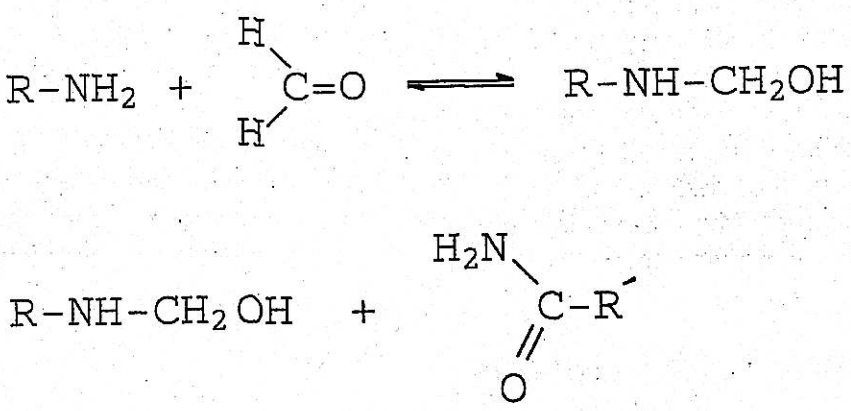

Fig. 1: Example of the reaction of formaldehyde with the amino acid side chains of the wool proteins

In the wool fibre, the formaldehyde molecules which have diffused in first react in the lysine- and glutamine-rich microfibril proteins (IF) and then with the amino acid residues of the sulphur-rich matrix (IFAPs) in which the IF are embedded (3).

When the wool proteins are electrophoretically fractionated, the proteins are first extracted from the fibre and then separated, e.g. according to molecular weight, in the electrical field. Protein groups which have been linked by formaldehyde can no longer be or can only incompletely be eluted from the fibre. Fig. 4 compares the results of electrophoretic fractionating of the proteins made from untreated and from formaldehyde-exposed wool. After they have absorbed formaldehyde, the protein groups of the IF are absent in the electrophoretic pattern of the wool, which reflects the preferred linking of this wool component.

The analysis of formaldehyde-exposed wool by means of HPDSC (High Pressure Differential Scanning Calorimetry) shows, in comparison with untreated wool, an increase in the melting temperature of the IF as a result of the linking of the microfibrillar regions of the wool (cf. Fig. 5).

Patent applied for: EP 0652318, PCT/EP 98/01691

SUMMARY AND PROSPECTS

The experiments confirm that wool without surface treatment represents an extremely effective sorbent for eliminating formaldehyde from indoor air. The design of buildings, however, often renders it impossible to remove the formaldehyde-emitting wood products or allows its removal only at a high cost, making the specific installation of wool an effective as well as environmentally compatible method of renovation. In addition, use of wool is also conceivable and desirable, particularly when considering the much discussed aspect of prevention.

REFERENCES

1. Bundesgesundheitsamt. Zur Gültigkeit des 0,1-ppm-Wertes für Formaldehyd. Bundesgesundhbl. (1992), 482
2. Fraenkel-Conrat, H L., Olcott, H S., The reaction of formaldehyde with proteins. J. Biol. Chem. Vol. 174 (1948), 827
3. Mason, P, Griffith, J C. Crosslinking of fibrous proteins by formaldehyde. Nature Vol. 203 (1964), 484
4. French, D., Edsall, J T. The reaction of formaldehyde with amino acids and proteins. Adv. Protein Chem. Vol. 2 (1945), 277
5. Alexander, P., Hudson, R F., Earland, C. Wool-its Chemistry and Physics, Chapman and Hall, London, 2nd edition (1963)
6. MacLaren, J A., Milligan, B. Wool Science, Science Press, Marrickville, Australia (1981), 186

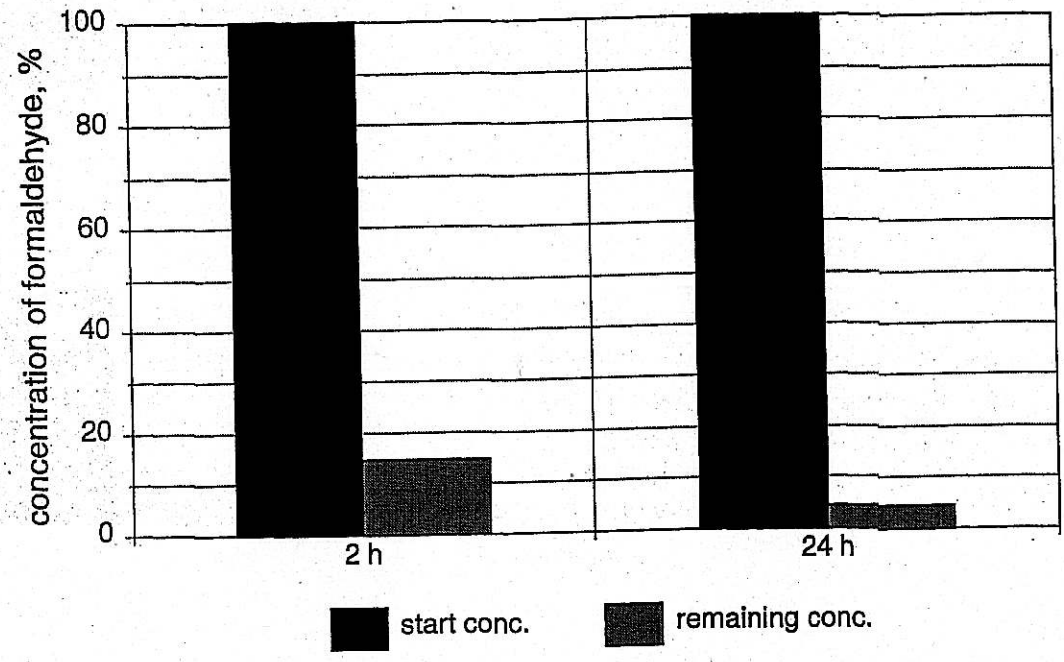

Fig. 2: Decrease of concentration of formaldehyde after 2 hours and 24 hours in the case of an initial concentration of 300 ppm formaldehyde (stating mean values)

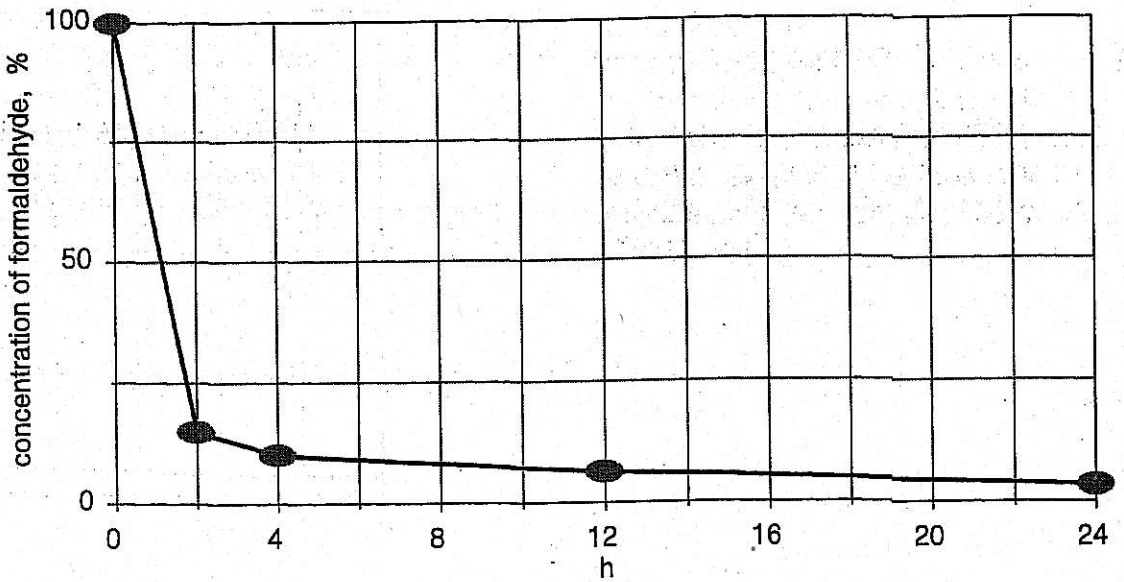

Fig. 3: Decrease of concentration of formaldehyde after 2, 4, 12 and 24 hours in the case of an initial concentration of 300 ppm formaldehyde (stating mean values)

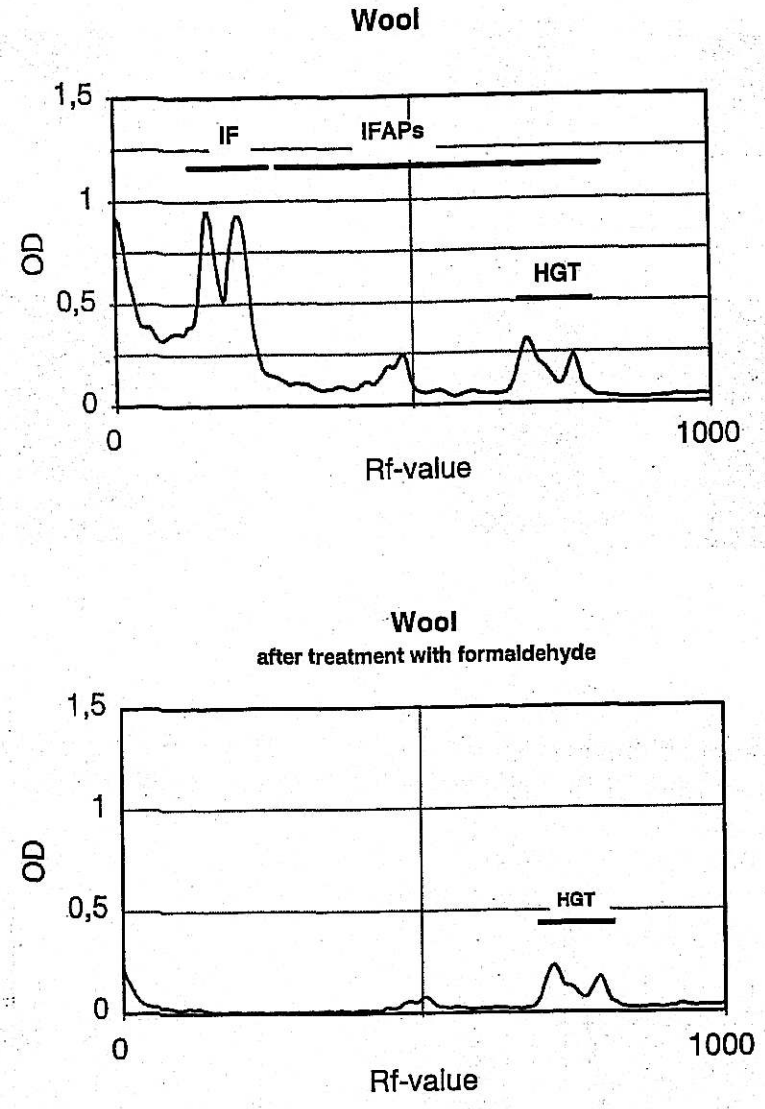

Fig. 4: Densitometric measurement of the electrophoretic fractionating (SDS-PAGE) of extracted proteins from untreated (above) and formaldehyde-exposed wool (down)

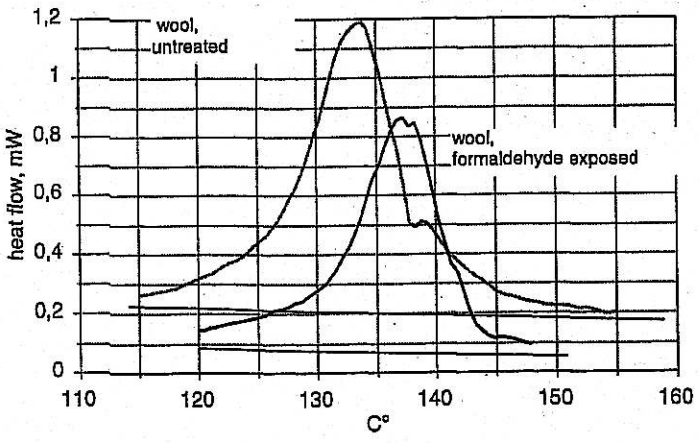

Fig. 5: Melting behaviour of the IF (HPDSC)