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Eco-Friendly Durable Press Finishing of Textile Interlinings

Abstract

In co-operation with the Slovene textile company ZVEZDA which produces textile interlinings, we studied the influence of different durable press finishers on the release of formaldehyde. This was measured by the standard method Law 112 (Control of Household Products Containing Harmful Substances, Law 112). The effect of durable press finishing was evaluated by measuring the dimensional stability of treated fabrics and by wrinkle recovery angle measurements (WRA). In our research we studied the addition of formaldehyde acceptors in the form of urea, N-ethylurea and 1H-benzotriazole to the treating baths, to reduce the amount of free formaldehyde on the knitted textile substrate.

Key words: *formaldehyde durable press finishing, interlinings, standard test method, formaldehyde acceptors, formaldehyde release.*

Introduction

Natural fibres include comfort, soft handle and tensile strength among their good properties, but also display some less desirable characteristics such as poor dimensional stability and crease resistance in laundering and wear. The most effective crosslinking reagents for durable press of cellulose fibres are formaldehyde adducts of urea, which unfortunately release formaldehyde during production and wear in clothes so treated [1-3].

The release of formaldehyde from durable press (DP) treated fabrics is a problem for human health and safety because formaldehyde is suspected to be carcinogenic. The short-term effects of exposure to formaldehyde include irritation of eyes and nose, rashes and headaches. The-long term effects have not been definitively established, but because of its innate harmfulness, not to mention legislation concerning the use of formaldehyde products (especially in some fields such as children's clothing), researchers have tried to develop new reagents, such as durable, low formaldehyde-content press finishers, and other alternative reagents with no formaldehyde in their structure [4-7].

Dimethylol dihydroxy ethylene urea (DMDHEU) and modified dimethylol dihydroxy ethylene urea (modified DMDHEU) are compounds which contain N-methylol and mainly N-alkoxymethyl groups (Figure 1) and they are extensively used in textile industry as durable press finishers.

During the finishing process the N-methylol compounds can react with hydroxyl groups of cellulose, which is the most preferable reaction; they may also react with themselves or with reactive NH groups. These latter two reactions are not desirable, because some reaction places on crosslinking reagents are lost, and the formaldehyde can be simply released from the N-methylol compounds (Figure 2). Splitting of acetalic bonds is catalytically accelerated by acids, and by the basis as well.

A mainly complete reaction with the hydroxyl groups of cellulose results in a very small free-formaldehyde value in the finished textile material, which means that a low free-formaldehyde value is a true indication of the quality of the crosslinking. For this reason, the fixed term 'free formaldehyde' is the quality criterion for many formaldehyde finishers. The crosslinking N-methylol systems contain some unreacted formaldehyde and formaldehyde adducts which are capable of releasing the formaldehyde.

In general, the formaldehyde-producing components of the finish can be presented in four main forms, as follows:

- free formaldehyde. These species are difficult to define; it is most appropriate to define them as extractable formaldehyde which is not in chemical combination with nitrogen;
- $=NCH_2OH$ groups. These are reasonably stable, but they release formaldehyde under more severe thermal or hydrolytic conditions. Under dry ambient conditions, crystalline N-methylol compounds have little odour, and they are stable for years.
- $=NCH_2OR$ groups, where R presents an alkyl or substituted alkyl group. These are more stable than $=NCH_2OH$. Direct release from $=NCH_2OR$ is not favoured. To minimise the release of formaldehyde from the crosslinking reagents and the finished textile fibres, derivatives of N-methylol compounds have recently been used as durable press finishing reagents. Nevertheless, some hydrolysis from N-alkoxy groups to N-methylol groups ($=NCH_2OH$), together with further release of formaldehyde, can be expected.
- when the N-methylol compounds react with cellulose, ($=NCH_2O$-Cell) groups chemically similar to N-alkoxymethyl groups are formed.

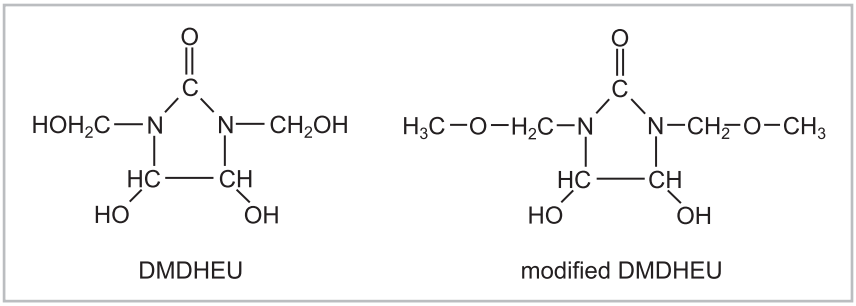


Figure 1. Chemical formula of DMDHEU and modified DMDHEU.

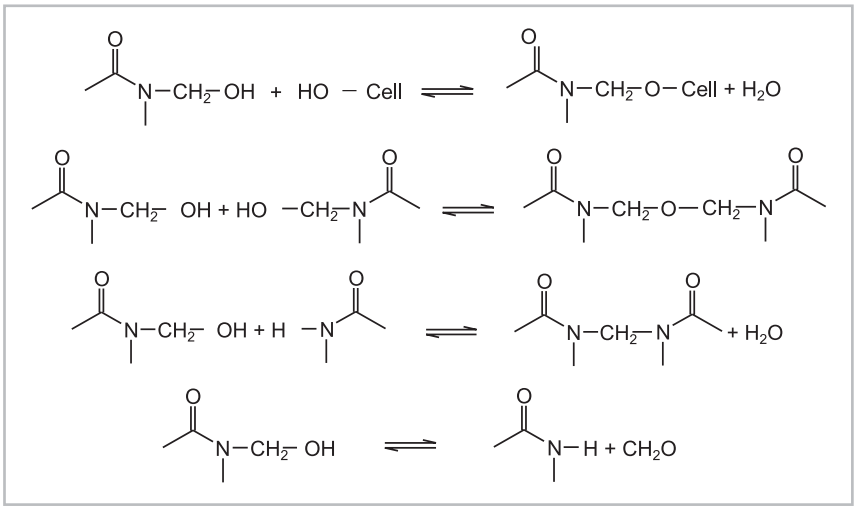


Figure 2. Equilibrium reactions of N-methylol compounds with hydroxyl groups of cellulose, with themselves, with reactive NH groups and the formaldehyde release.

Again, some formaldehyde release is expected to occur due to hydrolysis.

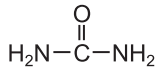
- $=NCH_2N=$ groups that are found in conventional finishers are expected to resist hydrolysis during the life of the fabric. However, under some test conditions, this group can be hydrolysed and formaldehyde can be released.

The free formaldehyde value in the finished textile material depends on the chemical structure of the crosslinking reagents and on the curing conditions. There are a number of test methods that are used for the formaldehyde release analysis, such as Japan Law 112, AATCC-112, the Shirley Methods and others.

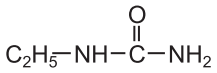
The Japan Law 112 method, which was used in our research, employed extraction that causes some hydrolysis of the finish as well as additional release of formaldehyde. Because of the relatively high extraction temperature (40°C), some hydrolysis of $=NCH_2OH$ and $=NCH_2O$-Cell can be expected. Therefore the Japan Law 112 method detects free formaldehyde and some amount of the formaldehyde released from the N-methylol groups due to hydrolysis. By this method the behaviour of crosslinking fabrics on skin can be simulated.

Formaldehyde Acceptors

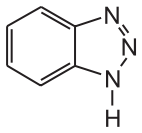
There are a number of substances which are capable of accepting the formaldehyde released from the textile substrate [8]. They form stable monomethylol compounds. In our research we studied the addition of formaldehyde acceptors in the form of urea, N-ethylurea and 1H-benzotriazole to the treating baths.



urea



N-ethylurea



1H-benzotriazole

Experimental

The main problem with formaldehyde as a durable press finisher in the textile industry is in its poor reproducibility of free formaldehyde measurements.

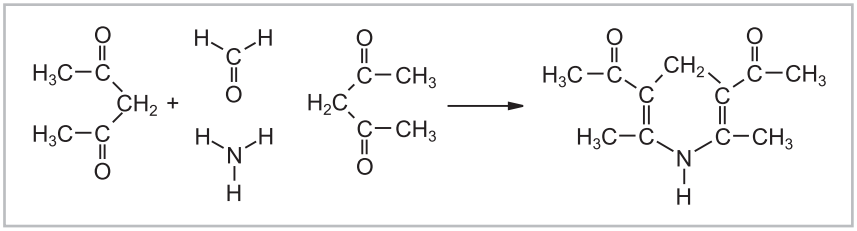


Figure 3. The conversion of formaldehyde with acetylacetone reagent to a yellow-coloured compound of 3,5-diacetyl-1,4-dihydrolutidin.

In co-operation with Slovene textile company ZVEZDA, which produces textile interlinings, we studied the behaviour of three durable press finishers with different formaldehyde content levels. The formaldehyde content in the finished cellulose fibres was measured by the standard method, Japan Law 112 (Control of Household Products Containing Harmful Substances Law 112) using UV/Vis spectrometry. The final effect of durable press finishing was evaluated by measuring wrinkle recovery angle (WRA) and by measuring the dimensional stability of the treated fabrics.

The conventional (experiment A), the low-formaldehyde (experiment B) and the formaldehyde-free (experiment C) finishing reagents were tested and the formaldehyde-free values were measured. The influence of different formaldehyde acceptors on the free formaldehyde content on the textile substrate was studied.

Textile material: warp knitted fabrics with polyester yarn 30% and viscose yarn 70%.

Chemicals:

- Crosslinking reagents:

Experiment A: modified DMDHEU, the free formaldehyde value is around 100 ppm:
42 g/l of modified DMDHEU (amount recommended by the producer)
20 g/l of recommended softener
0.5 g/ of recommended surfactant
11 g/l of recommended catalyst

Experiment B: modified DMDHEU, the free formaldehyde value is around 70 ppm
60 g/l of modified DMDHEU (amount recommended by the producer)
20 g/l of recommended softener
0.5 g/ of recommended surfactant
15 g/l of recommended catalyst

Experiment C: derivative of imidazolidinone, the free formaldehyde value supposed to be zero:
80 g/l derivative of imidazolidinone (amount recommended by the producer)
20 g/l of recommended softener
0.5 g/ of recommended surfactant
15 g/l of recommended catalyst

- ***Formaldehyde acceptors:***

Urea
N-ethylurea
1H-benzotriazole

Japan Law 112 standard test method
Formaldehyde is extracted from the textile sample with water at 40°C. In

Table 1. Types and concentrations of formaldehyde acceptors in the treating baths.

Treatment	Formaldehyde acceptors	Concentrations [g/l]
A1	-	-
A2	Urea	3
A3	Urea	6
A4	Urea	9
A5	N-ethylurea	6
A6	1H-benzotriazole	6

warm water, the extracted formaldehyde is converted by using acetylacetone reagent to a yellow-coloured compound. The mechanism of this aldoreaction and the formation of 3,5, -diacetyl –1,4-dihydrolutidin is shown in Figure 3 [9]. The amount of formaldehyde is then determined colorimetrically at the wavelength of 412 nm against water. A Cary 50 spectrophotometer from Varian was used for analyses of free formaldehyde on the cellulose substrate. The Japan Law 112 method detects free formaldehyde and some amount of formaldehyde released from the N-methylol groups due to hydrolysis.

Wrinkle recovery angle (WRA) measurements
The standard test method for wrinkle recovery of textile ISO 9867 was used to measure the conditioned wrinkle recovery angle [10].

Measurement of dimensional stability of textile substrate
This method according to the internal standard which simulates home laundering was used to determine the dimensional stability of untreated and treated textile fabrics [11].

Treatment of textile fabrics with crosslinking reagent
The fabric was immersed in the treating solution, passed through squeeze rolls, wetted again with treated solution and again passed through squeeze rolls to give a wet pick up of 100%. The fabric was suspended in a force draft oven, predried at 110°C for 5 minutes and cured for 30 seconds at 170°C.

Treatment of textile substrate was repeated with the crosslinking reagent which gave the highest formaldehyde content (the name of the treatment was Experiment A), and different formaldehyde acceptors were added (urea, N-ethylurea and 1H-benzotriazole). The types and the amount of formaldehyde acceptors in the finishing baths are shown in Table 1. After drying and curing, the amount of free formaldehyde on the crosslinked fabric was determined by the standard test method Japan Law 112. The final effect of crosslinking was studied by WRA measurements and dimensional stability measurements.

Results and Discussion

It is well known that the accuracy of different standard test methods for formaldehyde determination depends on the formaldehyde content in the textile sample analysed. As the formaldehyde content is lowered, so the accuracy of the method decreases.

With 95% probability, the relative values of formaldehyde on textile substrate are within the confidence range of 104.8 to 119.2 for experiment A, in the confidence range between 70.7 and 84.0 for experiment B, and in the confidence range between 10.4 and 14.0 for experiment C. The relative accuracy of the mean at the 95% confidence level are 7% for experiment A, 9% for B and 15% for C. The results are presented in Table 2.

In treatment C, where the formaldehyde content is supposed to be zero, the results show that some formaldehyde is present. When the formaldehyde content of untreated textile substrate was measured, some formaldehyde was also detected. The free formaldehyde value of untreated textile fibres was 10.5 ppm; therefore the formaldehyde on textile substrate which was finished with the non-formaldehyde crosslinking reagent (experiment C) can be presented as a consequence of formaldehyde in the textile substrate itself, and not as the consequence of the durable press finishing.

Formaldehyde acceptors in the finishing bath
The influence of acceptor concentration on free formaldehyde was studied. For this purpose different amounts of urea were added to the treating baths (Table 1). The amount of free formaldehyde on the treated textile substrate according to urea concentration in the treating baths is presented in the diagram in Figure 4.

From the above diagram it is possible to conclude that the optimum urea concentration in the finishing bath is 6 g/l. On this basis, the same concentrations of two further formaldehyde acceptors, N-ethylurea and 1H-benzotriazole, were used (Table 1). When the influences of different formaldehyde acceptors on formaldehyde release were studied, the following results were obtained (diagram in Figure 5).

The addition of formaldehyde acceptors in the form of urea, and the sometimes even more suitable ethylene urea, is a well-known procedure [12]. The amount of free formaldehyde on the knitted interlinings, made out of

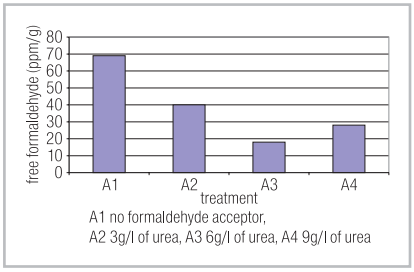


Figure 4. The influence of urea in the treating baths on free formaldehyde.

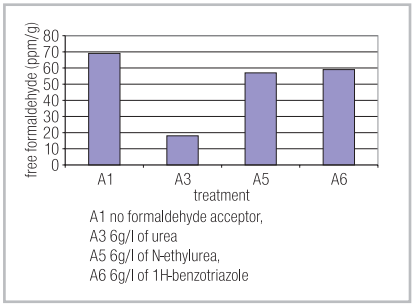


Figure 5. The influence of different formaldehyde acceptors on free formaldehyde.

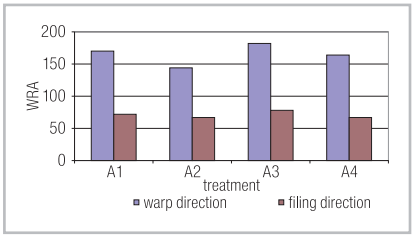


Figure 6. The influence of urea concentration on WRA measurements in warp and filing directions; where A1 means no addition of formaldehyde acceptor to the treating bath, A2 the addition of 3g/l of urea, A3 6g/l of urea, A4 9g/l of urea.

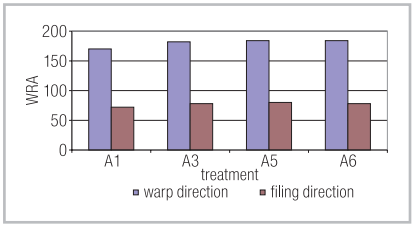


Figure 7. The influence of different formaldehyde acceptors on WRA measurements in warp and filing directions; where A1 means no addition of formaldehyde acceptor to the treating bath, A3 the addition of g/l of urea, A4 6g/l of N-ethylurea, A6 6g/l of 1H-benzotriazole.

Table 2. Formaldehyde contents in experiments A, B, C.

Formaldehyde in experiment A [ppm]	Formaldehyde in experiment B [ppm]	Formaldehyde in experiment C [ppm]
114.9	67.6	6.7
129.0	66.0	15.0
100.9	67.0	12.6
114.0	76.0	8.7
123.0	168.0	9.6
116.0	87.0	11.4
94.0	78.2	14.4
92.0	90.0	15.0
125.0	80.0	16.3
$\bar{x} = 112.0$	$\bar{x} = 77.0$	$\bar{x} = 12.2$
$s = 9.4$	$s = 9.2$	$s = 2.4$
confidence range [104.8 - 119.2] relative accuracy = 7%	confidence range [70.7 - 84.0] relative accuracy = 9%	confidence range [10.4 - 14.0] relative accuracy = 15%

Table 3. Dimensional stability of untreated textile substrate (A0), textile substrate treated with modified DMDHEU (A1) and with modified DMDHEU crosslinking reagent with addition of different formaldehyde acceptors.

Treatment	Shrinkage in warp [%]	Shrinkage in filling [%]
(A0) (untreated)	0.6	2.0
(A1) modified DMDHEU	0.6	0.4
(A3) modified DMDHEU + urea	0.6	0.4
(A5) modified DMDHEU + N-ethylurea	0.6	0.5
(A6) modified DMDHEU +1H-benzotriazole	0.6	0.5

PES/viscose blend treated with modified dimethylol-dihydroxy-ethylene urea, was improved with the addition of urea in the concentration of 6 g/l to the finishing baths. However the addition of ethylene urea, which was reported [12] to be an even better formaldehyde acceptor than urea, did not lower the amount of free formaldehyde in the textile substrate. The addition of benzotriazol to the finishing bath did not reduce the formaldehyde eider; in some cases the concentration of free formaldehyde even increased.

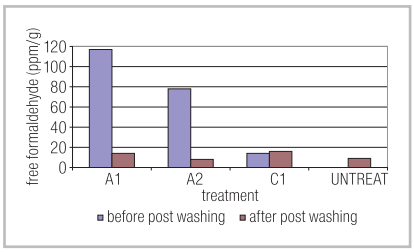


Figure 8. Decrease of formaldehyde content due to washing, where A1 and B1 signify a textile substrate finished with modified dimethylol-dihydroxy-ethylene urea (modified DMDHEU), and C1 a textile substrate finished with non-formaldehyde reagent: with the derivative of imidazolidinone.

To study the influence on crease resisting of urea concentrations in the finishing bath on the final effect of crosslinking, the WRA measurements were carried out. The changes of WRA measurements according to the urea concentration are presented in the diagram in Figure 6. The influence of different formaldehyde acceptors on WRA measurements on warp and filing directions is presented in Figure 7.

The main reason for the durable press finishing of knitting material (polyester/ viscose blend) was to assure the dimensional stability of treated material, so the dimensional test was carried out. The results are presented in Table 3. The dimensional stability of fabrics treated with the modified DMDHEU crosslinking reagent change filing direction (viscose fibres), and remain unchanged in warp direction (PES fibres).

Post-washing the durable press-finished textile substrate can quantitatively remove the formaldehyde. In the diagram in Figure 8 we see the decrease in formaldehyde due to washing. The main problem is that the rate of formaldehyde will increase again after a few days of storage.

Conclusions

In co-operation with the Slovene textile company ZVEZDA, which produces textile interlinings and manufactures materials for shoes such as knitted interlinings for forming and knitted, woven and non-woven interlinings for all parts of footwear, we studied the influence of different durable press finishers on the free-formaldehyde value of treated interlinings. The release of formaldehyde was measured by the Law 112 standard method, the effect of durable press finishing was evaluated by wrinkle recovery angle measurements and by dimensional stability measurements.

Results obtained from the research into the formaldehyde on the textile interlinings made out of the PES/viscose blend show that the confidence range for the free formaldehyde value is in the range of 4 to 15 ppm. The relative accuracy of the mean at 95% confidence level is the highest (around 15%) when the formaldehyde content is low (near zero).The relative accuracy for higher formaldehyde content is better, at around 7-9%.

The addition of a formaldehyde acceptor such as urea reduces the free formaldehyde value greatly, and at the same time the dimensional stability remained good.

Post-washing of the finished textile substrate can quantitatively remove the formaldehyde, but with time the free-formaldehyde value will increase again.

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