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Solvent Pre-Treated Wool Fabric Permanent Set and Physical Properties

Abstract
We present the results of an investigation which shows that the yellowing of wool fibre which occurs during light exposure and treatment with boiling water is reduced by pre-treatment of loom state wool fabric with perchloroethylene. The changes in light reflectance and the yellowing index of the treated wool fabric were found to correlate with the data of wool fibre strength, permanent set degree, solubility in urea-bisulphite solution, fluorescence emission and thermogravimetric analysis.

Key words: *wool, organic solvents, yellowness index, tryptophan, permanent setting.*

Introduction

Scouring wool fabric with perchloroethylene provides higher abrasion resistance [1,2]. When pre-scouring with perchloroethylene is carried out, the high physical performance of wool is retained after carbonisation [3-5].

Little is known about the influence of the pre-treatment of wool with organic solvents on the level of the damage to wool fibre which occurs during wet finishing processes or under weathering conditions, such as exposure to sunlight or treatment with boiling water.

In this paper, we report on the results of our investigation into the effect of the pre-treatment of wool fabric with organic solvents on the level of wool degradation caused by UV irradiation or treatment with boiling water.

Experimental

Materials

Loom state fabric (merino 18.7 μm), weave 2/2 twill weighing 270 g/m^2, was used.

Organic solvents

Perchloroethylene is a commercial product used for dry cleaning. Other solvents and chemicals (hexane, ethyl alcohol and diethyl ether) were reagent grade.

Fabric treatment

Loom-state wool fabric samples were scoured with perchloroethylene, or extracted subsequently with hexane and with ethyl alcohol, in a Soxhlet extractor. Scouring with perchloroethylene was carried out at 30°C. 3 wash cycles of 30 min each were carried out. The scoured samples were dried for 15 min at a temperature of 135°C to evaporate the excess solvent. The amount of soluble materials extracted from wool by different solvents is shown in Figure 1. All loom-state samples pre-treated with solvents were irradiated by using Xenotest 150S exposure (irradiation conditions: 20°C, 65% RH, 40 h and 120 h). The treatment of wool fabric samples with boiling water (1 hour) or dyed with C.I. Acid Orange 7 dye (pH 4.2, 100°C, 90 min) was used to examine the degradation level.

Testing methods

Reflectance spectra
The reflectance spectra of the wool fabric samples were measured using a Specol 11 (Carl Zeiss Jena) instrument in the wavelength range from 400 to 700 nm. The mean of three readings was recorded for each sample. The Yellowness Index *YI* was calculated using the following equation:

$$YI = 100 \cdot \frac{1.28X - 1.06Z}{Y} \qquad (1)$$

where *X*, *Y*, and *Z* are the CIE tristimulus values, which were calculated using the spectral reflectance characteristic R_λ of the wool fabric tested.

Fluorescence emission spectra
The fluorescence spectra of the wool fabrics were recorded by a MPF-4 fluorescence spectrophotometer (HITACHI) equipped with a solid sample holder. The yarn of wool was cut into small pieces using scissors. A powder of wool keratin was prepared using a laboratory pounder. The powder was transferred to the special quartz cell. The fluorescence intensity was recorded in the wavelength range from 310 to 400 nm (λ_{ex}=295 nm). All fluorescence measurements were carried out using the same arbitrary scale. The values of tryptophan (Trp)% were calculated as the ratios of Trp emission intensities (λ=346 nm) obtained before and after the Xenotest exposure (%Trp=IE/IU, where IE and IU represent the Trp emission intensities of the light exposed and unexposed respectively).

Measurement of permanent set degree
For permanent setting experiments, pieces of wool fabric were folded across the warp, and a crease was sewn into the test fabric. After an irradiation test and treatment with boiling water or after dyeing, the snippets were removed, relaxed in water for 30 min at 70°C, and the yarn angle *Θ* measured. The level of set was calculated using equation 2 [6]:

$$Set(\%) = (180 - \Theta)/180 \times 100 \qquad (2)$$

The average angle between the arms of snippets was established from 20 measurements.

Tear strength and extension at break

Fibres were immersed in distilled water at 20°C for 24 hours before testing. Tensile testing was performed using a Digital Electronic Fibre Tester FM-27. The distance between squeezes was 10 mm, the drawing rate was 10 mm/min, and the original load was 225 mg. An average value of mechanical indexes was calculated from 100 measurements.

Solubility in urea-bisulphite (UBS) solution

These treatments were made according to the I.W.T.O. method [7].

Thermogravimetric analysis

We used the A.F. Paulik, J. Paulik and L. Erdey thermoanalyser. The standard material was Al_2O_3, helium atmosphere, the temperature was increased from 20 to 300°C at a rate of 10°C/min.

■ Results

The wool fabric was pre-treated with organic solvents, which remove grease, surface lipids, other contaminants and enhance the degree of yellowness and dyeability. The amount of extracted material from wool fabric with perchloroethylene is equal to that obtained by subsequental extraction with hexane and ethanol (Figure 1).

The results presented in Figure 2 show that the pre-treatment of loom state fabric with perchloroethylene increases the reflectance to a greater extent than in the case of subsequent extraction in the Soxhlet extractor with hexane and ethanol. Eliminating the solvent soluble lipids and other contaminants from wool fibre increases the resistance of wool to the degradation occurring during treatment with boiling water, which leads to the increase in yellowness (Table 1).

It is evident from Table 1 that the irradiation (up to 120 hours) provides a decrease in the yellowness index in the case of perchloroethylene (PCHE) pre-treated wool. This effect for hexane and ethanol (HE + EtOH) pre-treated wool fabric samples is small. The higher resistance of wool fibre to yellowing which occurs during irradiation or subsequent irradiation and treatment with boiling water is obvious in the case of wool pre-treated with perchloroethylene (Table 1).

The data shown in Figure 3 illustrate the effect of wool fabric pre-treatment with solvents on the extent of Trp decomposition

caused by Xenotest exposure. All the samples examined exhibit rapid Trp decomposition, with about 33-36% of Trp residues remaining after 60 min irradiation.

The data presented in Figure 3 demonstrates that Trp decomposition is activated by Xenotest exposure. The sensitivity to photodegradation is slightly increased for the wool extracted with hexane and ethanol, compared with that of perchloroethylene pre-treated wool.

After irradiation, the breaking strength of single wool fibre is reduced (Table 2). When the time of irradiation is 120 h the loss of strength is more evident for loom state fibres compared with the solvent pre-treated samples. A slightly higher fibre strength after irradiation is observed for the samples pre-treated with perchloroethylene.

Table 3 presents the loss of weight of wool fibre while it is heated under conditions of TGA at temperatures ranging from 200°C to 250°C. Perchloroethylene pre-treated wool is more stable when heated under TGA testing conditions or irradiated compared with wool or loom state wool subsequently extracted with hexane and ethanol.

The investigations of the permanent setting which occurs during treatment of wool fabric with boiling water were carried out using wool fabric samples pre-treated with solvents and irradiated. The results presented in Table 4 indicate that for all the samples examined the level of permanent set is reduced with an increase in irradiation up to 40 hours. This reduction correlates with the change in fibre strength (Table 2). When irradiation is increased up to 120 hours, the permanent set degree for hexane and ethanol pre-treated fabric increases, as does that for loom-state fabric. However, the gradual reduction of permanent set level with an increase in irradiation time up to 120 hours is distinct for the wool fabric samples pre-treated with perchloroethylene.

The results of the wool UBS solubility experiments presented in Table 5 indicate that the solubility in UBS of solvent pre-treated wool is significantly lower than that of loom-state fabric. The solubility in UBS of perchloroethylene pre-treated wool is slightly higher compared to that of the wool extracted with hexane and ethanol.
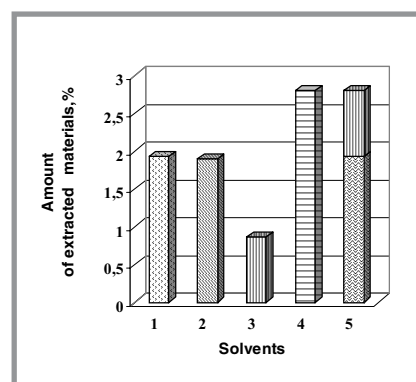

Figure 1. Amount of materials extracted by the solvents; 1 - hexane; 2 - diethyl ether; 3 - ethanol; 4 - perchlorethylene; 5 - hexane and subsequently ethanol.
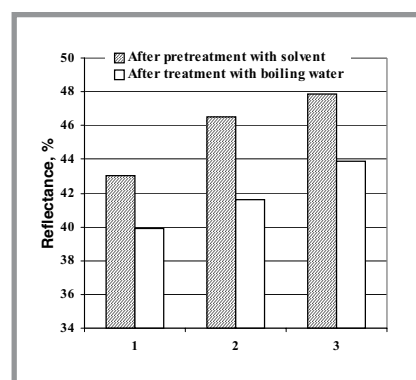

Figure 2. Light reflectance of wool fabric pre-treated with solvents; 1 - loom state fabric; 2 - fabric after subsequent extraction with hexane and ethanol; 3 - pre-treated with perchlorethylene fabric; (λ=460 nm).
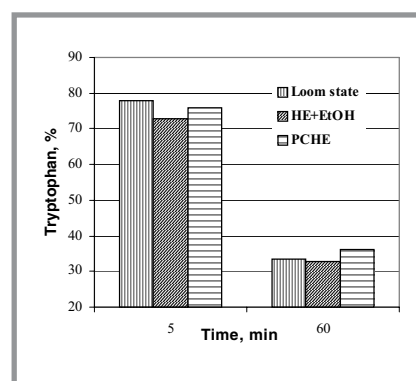

Figure 3. Tryptophan decay for Xenotest-exposed fibres.

Irradiation of wool fabric pre-treated with hexane and ethanol reduces the UBS solubility. However, the solubility of pre-treated with perchloroethylene wool fibre after irradiation increases. After combined treatment of wool fabric using irradiation and boiling in water, the UBS solubility of wool is significantly reduced. The least solubility was observed in the case of wool fabric pre-treated with hexane and ethanol.

Table 1. *Changes in the Yellowness Index (ΔYI).*

Fabric	YI before irradiation	After irradiation		After irradiation and subsequent boiling in water 1 hour		
		40 h	120 h	0 h	40 h	120 h
Loom state	41.03	1.86	0.60	5.60	3.47	4.93
Pre-treated:						
HE+EtOH	34.28	4.34	4.27	7.45	6.90	6.38
PCHE	37.55	-0.15	-0.24	3.93	1.93	1.29

Table 2. *Tear strength of single fibre, dN (*compared with the loom state fibre strength 58.7 dN).*

Fabric	Irradiation, hours			Retained strength* after 120 h irradiation, %
	0	40	120	
Loom state	58.7	53.1	47.7	81.2
Pre-treated:				
HE+EtOH	55.7	48.8	51.7	88.1
PCHE	64.5	49.5	53.6	91.3

Table 3. *Weight loss of wool fibre in TGA* and mechanical properties of solvent pre-treated and irradiated wool (*temperature interval taken in consideration 200-250°C; **Xenotest exposure 120 h; ***compared with the loom state fibre strength 55.3 dN and extension 45.79% respectively).*

Fabric	Weight loss in TGA %	Weight loss of irradiated** wool in TGA %	Retained strength*** after irradiation %	Retained extension after irradiation %
Loom state	5.26	4.85	85.23	92.77
Pre-treated:				
HE+EtOH	5.46	5.32	79.75	67.18
PCHE	4.90	3.34	89.51	87.77

Table 4. *Permanent set* of wool after irradiation and treatment with boiling water, %; (means ±0.5%).*

Fabric	Irradiation, hours		
	0	40	120
Loom state	72.1	69.4	74.7
Pre-treated:			
HE+EtOH	67.3	64.9	68.4
PCHE	68.3	66.9	64.9

Table 5. *Solubility in urea-bisulphite (UBS) solution of wool fibre after degradation causing treatments, % (* Xenotest exposure 34h; **dyeing with C.I.Acid Orange, pH 4.2, 100°C, 90 min).*

Fabric	Untreated	After light exposure*	After light exposure* and boiling with water	After dyeing**
Loom state	47.50	42.36	16.21	36.40
Pre-treated:				
HE+EtOH	35.70	28.00	9.72	30.80
PCHE	37.54	43.56	11.15	36.00

■ Discussion

Background

The results of previous studies indicate that the crimp of the warp yarn in wool fabric after scouring with perchloroethy-lene decreases, and significant reductions in shear rigidity and hysteresis are also observed [8,9]. However, a slightly higher degree of hygral expansion and shrinkage resistance after scouring of wool fabric is noted. In the same study, a higher cystine content in wool fibres after scouring with perchloroethylene was detected. These observations give a hint that the wool fabric after scouring with perchloroethylene could be slightly set.

The setting of wool fibre can be initiated by thermal or photo-oxidation involving thiol groups that are always found in the initial wool. It has been shown recently that the fission of both -S-S- and -C-S- bonds in keratin occurs with an increase in light exposure, and that this leads to an increase in thiol groups [10]. Thiol groups can be transformed into thiolate anions (RS⁻) or thiyl radicals (RS•) during the autooxidation of cysteine in the presence of oxygen and a photoirradiation source [11,12].

It might be expected that to a certain extent strained covalent bonds in the wool fibre of warp yarn of wool fabric would be more easily broken with the formation of free radicals. This could release the strained bonds, relax and form new covalent links, resulting in increased stability of wool fibre structure.

Changes in wool colour upon irradiation and treatment with boiling water

The changes in wool colour and yellowing in particular are important indications of the degradation of pre-treated wool keratin. After removing soluble internal lipids and other contaminants from the wool solvent, the extent of measured reflectance significantly increases (Figure 2) and the yellowing index decreases (Table 1). These changes can be related to the removal of the coloured species such as pigments of different chemical structures formed by oxidation of waxes & fats and pigments produced by micro-organisms. The treatment of wool with boiling water leads to the degradation which causes yellowing. The change in colour of the samples pre-treated with hexane and ethanol after treatment with boiling water is greater, compared with that of the loom-state sample. The change in yellowing index for wool fabric pre-treated with hexane and ethanol is more distinct after irradiation also. Apparently some components of non-proteinous materials such as greases, pigments, fats or solvent soluble internal lipids in the loom-state wool can serve as a protective barrier in degradation reactions occurring in wool fibre.

Different behaviour was observed for perchloroethylene pre-treated wool. After irradiation for 40 or 120 hours, the yellow-

ness index did not increase. The colour change (yellowing) is known to be induced by the photodegradation, hydrothermal or thermal degradation which also involves the decay of perceptible tryptophan residues. The measurement of the decay of Trp in wool is recognised as a useful instrument in assessing the keratin fibre's degradation level [13]. Our data shows (Figure 3) that substantial decay of Trp takes place after 60 min of Xenotest exposure. The examination of solvent pre-treated samples using fluorescence emission spectra in our study indicates that, in the case of perchloroethylene pre-treated wool, the decay of Trp is less compared with that of hexane and ethanol pre-treated wool.

These results suggest that the stabilisation effect induced by the pre-treatment of wool with perchloroethylene is distinct both after irradiation and after treatment with boiling water, and provides a possibility to improve the resistance of wool fibre to the colour deterioration which occurs under conditions causing wool keratin degradation.

Degradation and permanent setting

It is well known that sunlight irradiation weakens the non-keratinous domains of wool fibre, and the disintegration of the cell membrane complex is a criterion of the beginning of mechanical damage to the wool fibre as a result of photochemical reactions [14]. Our results of the strength measurements of single fibres (Table 2) for Xenotest-exposed wool fabric do not contradict this statement. The tear strength of wool fibre after treatment with solvents, i.e. free of solvent soluble internal lipids, is higher after 120 hours irradiation than after 40 hours of irradiation. The strength of perchloroethylene pre-treated wool fibre decreases after irradiation for 40 hours to a lesser extent compared with that of the sample pre-treated with hexane and ethanol.

Untreated loom-state wool fibres and irradiated fibres showed lower weight losses in TGA experiments compared with those pre-treated with hexane and ethanol (Table 3). The values of retained strength and extension at break of fibres after irradiation correlate with the data of TGA. These data show that the wool fibre after pre-treatment with hexane and ethanol becomes less resistant to the factors causing degradation than loom-state fibre. Therefore it seems unlikely that the pho-

tooxidation of solvent soluble internal lipids is a decisive factor in the sensitising the photochemical reactions of wool keratin.

Photodegradation of wool fibre causes the deterioration of mechanical properties, and also leads to the change of permanent setting which occurs during subsequental hydrothermal treatment.

The results presented in Table 4 show that the most distinct permanent setting after treatment with boiling water is characteristic of loom-state fabric. After 40 hours irradiation for all wool fabric samples, a decrease in permanent set degree is distinct, as is the increase in the yellowness index (Table 1), and the decrease in single fibre strength (Table 2). This suggests that at the initial stage of photoirradiation causing degradation of wool fibre, permanent setting is not enhanced and new cross links are not formed. Increasing irradiation up to 120 hours continues to enhance the setting in loom-state and hexane & ethanol pre-treated fibres, but inhibits the setting in perchloroethylene pre-treated wool fibre.

The data of testing on wool fabric change in yellowness index (especially the results of single-fibre tear strength testing), as well as in the permanent set degree show that the stabilisation of wool fibre structure takes place when the fabric is pre-treated with perchloroethylene.

Crosslinking and solubility in urea-bisulphite solution

The results of investigating the UBS solubility of wool are presented in Table 5. They support the idea that photoirradiation alongside the degradation of wool fibre causes formation of new cross links between amino-acid residues [15]. In our study, the UBS solubility of loom-state fabric or fabric pre-treated with hexane and ethanol after irradiation for 32 hours decreased. However, the solubility for perchloroethylene pre-treated samples after irradiation increases. These results are consistent with the decrease in strength of fibre which goes through a minimum with the increase in irradiation up to 120 hours (Table 2). This observation also suggests that a loss of cross links in fibre pre-treated with perchloroethylene after 32-40 hours irradiation takes place. Wool extracted with hexane and ethanol is more inclined to form the cross links compared with that pre-treated with perchloroethylene.

The higher resistance with respect to photodegradation of perchloroethylene pre-treated wool is obvious, irrespective of the aftertreatment of the sample (treatment with boiling water or treatment under the dyeing conditions).

■ Conclusions

Pre-treatment of wool fabric with perchloroethylene causes some improvement in the resistance of wool fibre to photodegradation or hydrothermal degradation. Yellowing, fibre strength loss and setting of wool, which occur during light exposure and treatment with boiling water, can be reduced by the pre-treatment of wool fabric with perchloroethylene.

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References

1. H.K. Rouette, G. Kittan. Leitfaden der Woll-Ausrüstung, Konradin, Aachen, Germany, 1990.
2. J.A. Rippon, D.M. Lewis, et al., Wool dyeing. Society of Dyers and Colourists, West Yorkshire, England, 1992.
3. P. Zanaroli, International Dyer, 1998 April, pp. 28-30.
4. P. Zanaroli, Melliand Textilberichte, 1998, vol. 6, pp. 446-448.
5. E. Ciapini, 17th IFVTCC Congress, 1996, June 5-7, pp. 93-96.
6. A. G. De Boos, A. M. Wemyss, J. Text. Inst., 1993, vol. 84, No. 4, pp. 506-519.
7. I.W.T.O. Technical Committee, Venice, May, 1960.
8. J.E. Garcia, M.T. Pailthore, R. Postle, Textile Res. J., 1994, vol. 64 (8), pp. 466-475.
9. J. Garcia, R. Postle, M. T. Pailthore, Textile. Res. J., 1995, vol. 65 (8), pp. 477-485.
10. D.C. Jones, C.M. Carr, W.D. Cooke, D.M. Lewis, Textile Res. J., 1998, vol. 68 (10), pp. 739-748.
11. K.R. Millington, JSDC, 2000, vol. 116, pp. 266-272.
12. L.J. Kirschenbaum, Q.U. Xinhua, E.T. Borish, J. Cosmet. Sci., 2000, vol. 51, pp. 169-182.
13. McMullen, J. Cosmetic Sci., 1998, vol. 49 (July/August), pp. 223-244.
14. M. Zimmermann, H. Hocker, Textile Res. J., 1996, vol. 66 (10), pp. 657-660.
15. S. Ratnapandian, S.B. Warner, Y.K. Kamath, J. Cosmet. Sci., 1998, vol. 49, pp. 309-320.