

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Lipid Role in Wool Dyeing

Meritxell Martí, José Luis Parra and Luisa Coderch
*Institute of Advanced Chemistry of Catalonia (IQAC-CSIC), Barcelona
Spain*

1. Introduction

The textile industry uses different fibers obtained from various animals, of which the wool from domesticated sheep *Ovis aries* is commercially the most important. Dyeing is one of the most important finishing procedures of wool processing. It almost invariably involves absorption of water-soluble colorants from aqueous solutions by the fibers. Diffusion is the process by which the colorant molecules penetrate the interior of the fibers.

Earlier workers studying the dye uptake of dyes by wool were mainly interested in the thermodynamics of the process, treating the wool fiber as a cylinder of uniform composition. Over the last decades there has been growing recognition of the importance of the diverse morphological structure of wool in determining its dyeing behavior (Rippon, 1992). Therefore a short wool structure description will be followed by a review of the role of this structure in wool dyeing.

The importance of the non-keratinous components of the fiber, specially the study of lipids present in the cell membrane complex prone us to emphasize in the lipid depleted wool, the modification of many properties and its behavior in the dyeing process. Besides the study of the mechanism of liposomes (made up with phospholipids) on wool dyeing could also help to elucidate the lipid role in wool dyeing.

1.1 Wool structure

Structurally, a wool fiber is an assembly of cuticle and cortical cells held together by the "cell membrane complex" (CMC). The surface of wool fibers consists of overlapping cuticle cells (Rippon, 1992). These are composed of two distinct major layers: the exocuticle and the endocuticle. The exocuticle consists of two sub-components, the A-layer, which is approximately 0.3 microns thick, and the B-layer, which is approximately 0.2 microns in thickness. These components differ mainly in the concentration of disulfide crosslinks (A-layer 35% half-cystine, B-layer 15% half-cystine and endocuticle 3% half-cystine).

Individual cuticle cells are surrounded by a thin membrane, the epicuticle, which is approximately 3–6 nm thick and accounts for around 0.1% of the total mass of the fiber. Although the epicuticle is proteinaceous, the surface of clean, untreated wool is hydrophobic. This property is the result of a thin layer of fatty acids (lipids) which are covalently bound to the surface of the epicuticle (the F-layer) (Naebe et al., 2010).

The cortex is made up of approx. 90% of keratin fibers, and is largely responsible for their mechanical behavior. It consists of closely packed overlapping cortical cells arranged

parallel to the fiber axis. Cortical cells are approximately 100 μm long and 3–6 μm wide, and they are composed of rod-like elements of crystalline proteins (microfibrils) surrounded by a relatively amorphous matrix. The low-sulphur material, with a simple regular structure and without disulphide crosslinks, forms crystalline fibrils, which are embedded in a matrix of more complicated and crosslinked high-sulphur material. The fibrillar protein forms first, and the low-sulphur parts of the natural block copolymer crystallize in parallel rods separated by the high-sulphur domains. Then the rest of the high sulphur protein is formed and solidifies the matrix. Nature joins the two constituents of this natural composite in a special way. The low-sulphur protein molecules in the fibrils have high-sulphur domains that come out of the fibrils at intervals and are crosslinked to the rest of the amorphous matrix (Hearle, 1991).

As stated above, the cuticle and cortical cells are separated by a continuous network, the cell membrane complex. This accounts for approx. 3.5% of the fiber, is around 25 nm in width, and provides adhesion between the cells. The CMC has three major components: (i) an easily swollen “intercellular cement” (1.5%) of a crosslinked nonkeratinous protein (δ -layer); (ii) a lipid component (1%), which may be associated with β -layers; and (iii) a chemical resistant proteinaceous membrane (1%), which surrounds each cortical and cuticle cell.

1.2 Role of fiber structure in wool dyeing

This diversity of morphological structure is very important to determine the dyeing behavior of wool. Generally, when a textile substrate is dyed by an exhaustion method, the dyeing operation proceeds in three stages (Crank, 1956; Rippon, 1992):

1. diffusion of dye through the aqueous dyebath to the fibre surface
2. transfer of dye across the fibre surface
3. diffusion of dye from the surface throughout the whole fibre.

In order to obtain satisfactory shade development and fastness properties, complete penetration of dye into the fibre is essential. The rate at which this occurs is controlled by the rate of dye diffusion across the fibre surface and then throughout the whole interior. The rate can be markedly affected by altering the net charge on the fibre, by modifying the epicuticle or by altering the rate of diffusion within the fibre.

If the wool fibre is treated as a uniform cylinder, Fick's laws of diffusion (Crank, 1956) dictates that a plot of dye uptake versus the square root of time should be a straight line over most of the dyeing curve (Medley & Andrews, 1959). In the case of wool, however, the dyeing curve is initially concave and only becomes linear after some time. This observation led to the assumption that a “barrier”, with a small capacity for dye, exists at the fiber surface (Medley & Andrews, 1959). The barrier was believed to be responsible for the non-Fickian dyeing isotherms obtained with wool (Medley & Andrews, 1959; Leeder, 1999).

Earlier workers identified the epicuticle with the barrier to dye penetration, thinking that this component constitutes a continuous membrane around the whole fibre (Lindberg et al., 1949; Milson & Turl, 1950). The barrier has also been ascribed to the whole cuticle (Makinson, 1968) and to the highly crosslinked A-layer of the exocuticle (Hampton & Ratte, 1979). All these suggestions regarding the nature of the barrier were based on a common belief that dyes must diffuse through the cuticle cells in order to reach the fiber cortex (i.e. the transcellular route shown in Figure 1. The epicuticle is not a continuous membrane,

however, but surrounds each individual cuticle cell. Thus, gaps exist between the scales where the intercellular material extends to the exterior fiber surface (approximately 0.05% (Joko et al., 1985)).

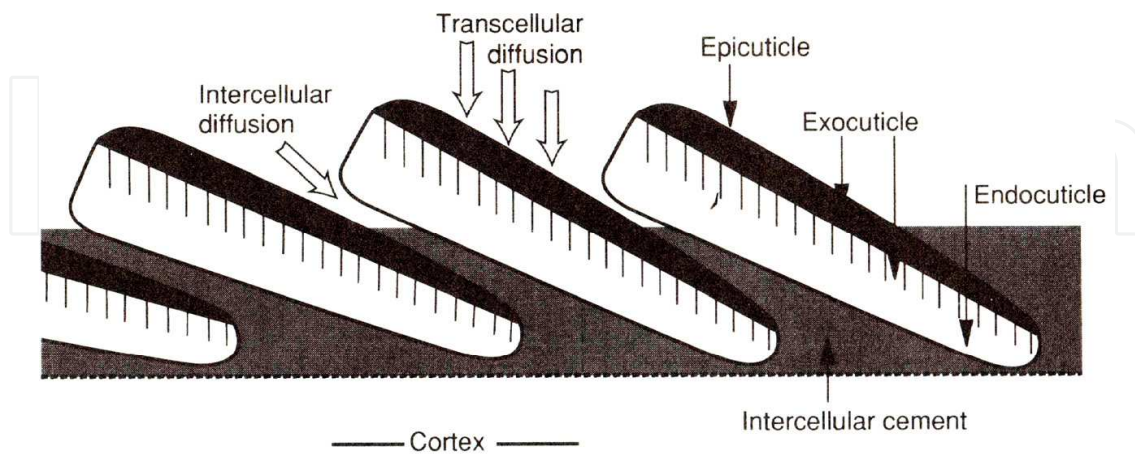


Fig. 1. Diffusion pathways for dyes into wool (Simmonds, 1955).

It has been suggested that lipids present at the cuticular junctions may hinder entry of dye into the fiber (Joko et al., 1985; Leeder et al., 1985a); for example, treatment of wool with potassium *t*-butoxide in anhydrous *t*-butanol, markedly improves the dyeing rate. This observation appears to be inconsistent with the fact that the anhydrous treatment is confined to the fiber surface, where it removes the F-layer from the epicuticle (Rippon & Leeder, 1986). The anhydrous alkali treatment would, however, be expected to remove lipids from the CMC at the point where this component extends to the fiber surface (Joko et al., 1985).

Different methods have been studied for comparative assessment of surface lipid removal from wool fabric; methanolic potassium hydroxide, anhydrous *t*-butoxide in *t*-butanol, and aqueous hydroxylamine (Negri et al., 1993; Ward et al., 1993; Dauvemmann-Gotsche et al., 2000; Baba et al., 2001). Plasma treatments, which utilize a gaseous electrical discharge, are reported to be surface specific for wool fibers (Kan et al., 2004) and offer the potential of simple, clean, solvent-free, and inexpensive treatment (Thomas et al., 2005; Körner & Wortmann, 2005; Klausen et al., 1995; Kalkbrenner et al., 1990).

All these treatments (Thomas, 2007; Wakida et al., 1993, 1996, 1994; Lee et al., 2001; Höcker et al., 1994; Yoon et al., 1996; Jovic et al., 2005; Kan et al., 1998; Kan & Yuen, 2008; El-Zawahry et al., 2006; Kan, 2006) have shown to invariably increase the rate of uptake of dyes by wool. Some studies have revealed that little or no physical change to the surface structure of wool fibers results from treatment with plasma, whereas others have found significant damage (Thomas, 2007; Wakida et al., 1993; Yoon et al., 1996; Kan, 2006; Erra et al., 2002). The methods for producing plasmas vary considerably, and generally rely on the use of purpose-built equipment.

To obtain a better understanding of the uptake of dyes by plasma treated wool several aspects must be considered. A recent study has: (a) established conditions where only surface changes occur to wool fibers using a pilot-scale, commercial, atmospheric pressure plasma machine, and characterized those changes; and (b) examined the impact of the plasma treatment on the uptake of selected acid, 1:2 metal-complex and reactive dyes -

under adsorption conditions at 50 °C, as well as absorption conditions at 90 °C – with the aim of rationalizing the relationship among surface properties, dye structure and dye uptake (Naebe et al., 2010).

The dyes used were typical, sulfonated wool dyes with a range of hydrophobic characteristics, as determined by their partitioning behavior between water and n-butanol. Dye adsorption is a complex phenomenon involving both hydrophobic and electrostatic interactions. No significant effects of plasma on the rate of dye adsorption were observed with relatively hydrophobic dyes. In contrast, the relatively hydrophilic dyes were adsorbed more rapidly (and uniformly) by the plasma-treated fabric. It was concluded that adsorption of hydrophobic dyes on plasma-treated wool was influenced by hydrophobic interactions, whereas electrostatic effects predominated for dyes of more hydrophilic character. On heating the dye bath to 90 °C in order to achieve fiber penetration, no significant effect of the plasma treatment on the extent of uptake or levelness of a relatively hydrophilic dye was observed as equilibrium conditions were approached.

Extraction of normally scoured wool with lipid solvents also increases the dyeing rate (Medley & Andrews, 1959; Joko et al., 1985; Lindberg, 1953). This observation supports the concept that a lipid barrier to wool dyeing exists located at, or near, the fiber surface. A significant finding is that surface lipids appear to be concentrated mainly at the edges of the cuticle cells (Aicolina & Leaver, 1990).

Leeder, et al. (Leeder et al., 1985b) used specially synthesized dyes to study the mechanism of wool dyeing. The metal-complex dyes contained platinum, palladium or uranium atoms, but in other respects were similar to conventional anionic wool dyes. The nuclear-dense, heavy metal atoms in the model dyes have a high electron-scattering power. This property enabled their location in the fiber to be determined with the transmission electron microscope at different stages of the dyeing process. This investigation provided the first unequivocal evidence that dye does, in fact, enter the wool fiber between cuticle cells, and also showed that dye diffuses along the nonkeratinous endocuticle and CMC early in the dyeing cycle.

The above finding supports the view that the cuticle (Makinson, 1968), probably the highly crosslinked A-layer of the exocuticle (Hampton & Rattee, 1979; Baumann & Setiawan, 1985), is a barrier to dye penetration, in that dyes are directed to the gaps between the scales in order to reach the cortex. It appears, however, that lipids present at the intercellular junctions are also a barrier to the diffusion of dyes into the nonkeratinous regions of the CMC (Leeder et al., 1985a).

After initial penetration into wool fibers, dyes must diffuse throughout the entire cross-section in order to obtain optimum colour yield and fastness properties. Several workers have suggested that the continuous network of the CMC provides a pathway for the diffusion of reagents into wool. Leeder and Rippon (Leeder & Rippon, 1982) have shown that the CMC swells in formic acid to a much greater extent than does the whole fiber. They suggested (Rippon & Leeder, 1986) that this disproportionately high swelling is the reason why dye is taken up very rapidly from concentrated formic acid.

The situation regarding the pathway for the dye diffusion into wool remained unresolved until the study by Leeder et al. (Leeder et al., 1985b) involving the transmission electron microscope, described above. This investigation demonstrated unequivocally the importance of the nonkeratinous components of the fiber in wool dyeing. After dye has entered the fiber between the cuticle cells, diffusion occurs throughout all the

nonkeratinous regions of the CMC, the endocuticle and the intermacrofibrillar material. It is interesting that dye also appears in the nuclear remnants very early in the dyeing cycle, before dye can be seen in the surrounding cortical cells. The mechanism by which this occurs is not clear, but dyes may diffuse along "membrane pores". Kassenbeck (Zhan, 1980) has suggested that these pores connect the nuclear remnants with the endocuticle and the CMC.

The above findings on the importance of the nonkeratinous regions as pathways for diffusion of dyes into wool and other animal fibers have been confirmed by fluorescence microscopy (Leeder et al., 1990, Brady, 1985, 1990). However, the lower resolution of the light microscope, compared with the transmission electron microscope, restricts the amount of information that can be obtained by this technique.

Wortmann et al. (Wortmann et al., 1997) summarized different ideas about this subject. They justified that due to the CMC size in the fiber, intercellular pathway appears questionable. CMC makes up at most about 4-6% of the fiber structure, of which 1.5% are resistant membranes, 1.5% are lipids, and 1-3% are intercellular cement (Rippon, 1992). But only the two latter ones may be assumed to play a role in the intercellular pathway. After a revision of different experiments from several authors (Wortmann et al., 1997) and further references therein, they suggested that there is, in fact, little evidence for the intercellular pathway, which identifies intercellular diffusion as the primary pathway for dyes into fibers. Instead the results support their view that under normal dyeing conditions, diffusion proceeds through the nonkeratinous components of the fiber according to a restricted transcellular diffusion mechanism. With fibers that exhibit an intact epicuticle as a diffusion barrier, dyes will enter at the distal cuticle cell edges and will diffuse along the endocuticle and the CMC. Having reached the cortex, they then largely follow the intermacrofibrillar material and from there enter the nuclear remnants.

Swift (Swift, 1999) supports Wortmann et al. arguments with his microscope studies about precipitate silver sulphide in human hair by allowing aqueous silver nitrate to diffuse into fibers previously saturated under high pressure with gaseous hydrogen sulphide.

Rippon described the mechanism in his review (Rippon, 1992): after entering the fiber between cuticle cells, dye diffuses throughout all the nonkeratinous regions, including the CMC, endocuticle, and intermacrofibrillar material. Dye also appears in the nuclear remnants early in the dyeing cycle. Dye molecules progressively transfer from the nonkeratinous regions into the sulphur-rich proteins of the matrix surrounding the microfibrils within each cortical cell, and also from the endocuticle into the exocuticle. At equilibrium, the nonkeratinous proteins, which were involved in the early stages of dyeing, are virtually devoid of dye. Rippon also enhanced that the intercellular cement component of the CMC, the only continuous phase in wool, provides a pathway for dyes to reach the cortical cell located inside the fiber, this occur while dye is simultaneously diffusing along the other nonkeratinous regions of the fiber, and indeed, while dye is also diffusing to its equilibrium location within the high-sulphur proteins of the matrix (Rippon, 1999).

2. Results and discussion

2.1 Wool modification due to internal lipid extraction

A number of studies have been performed in our laboratories based on the extraction, analysis and structure of the internal lipids and isolated ceramides from wool (Ramírez et al.,

2008a, 2008b; Coderch et al., 2002, 2003; Méndez et al., 2007; Fonollosa et al., 2004). Internal wool lipids have been shown to form stable liposomes (Fonollosa et al., 2000; Körner et al., 1995; Ramírez et al., 2009a) and are supposed to be arranged in the wool fiber as lipid bilayers.

Raw Spanish Merino wool was Soxhlet-extracted with chloroform/methanol azeotrope (Martí et al., 2010), in order to obtain wool mostly depleted of internal lipids. The lipids extracted were quantitatively analyzed by TLC-FID so that the main lipid families were separated and quantified.

It was observed that the percentage of lipids analyzed was 0.96% o.w.f., and the main compounds are free fatty acids 19.68%, sterols 6.45% and polar lipids where the ceramides 65.03% are included. It is important to bear in mind that the total internal lipids account for 1.5% of total fiber weight (Rivett, 1991) and the total extracted internal lipids only account for 0.96% of the total fiber.

Analytical and physicochemical studies reveal considerable resemblance between the internal wool lipids (IWL) and the lipids from the stratum corneum of the human skin (Coderch et al., 2003; Schaefer & Redelmeier, 1996; Schürer et al., 1991; Kerscher et al., 1991). IWL are present in about 1.5% of fiber weight and are rich in ceramides, cholesterol, free fatty acids and cholesteryl sulfate (Hearle, 1991). The intercellular lipids of the stratum corneum play a vital role in the barrier function of human skin by protecting it from the penetration of external agents, as well as by controlling the transepidermal water loss, which maintains the physiological skin water content (Kerscher et al., 1991; Rivett, 1991; Elias, 1981). In order to obtain IWL extracts with a large amount of ceramides, different extraction methodologies such as Soxhlet with diverse organic solvent mixtures or supercritical fluid extraction with CO₂ and several polarity modifiers have been optimized at laboratory and pilot plant levels (Ramírez et al., 2008a, 2008b; Coderch et al., 2002; Petersen, 1992).

Besides the chemical analyses of wool extracts, chemical and mechanical evaluations of extracted wool have been carried out. Residual grease, whiteness index, fiber diameter, fiber length, cleaning tests, alkaline solubility, bundle tenacity and drafting forces, abrasion resistance, pilling tests, and pore size have been determined. Few significant changes have been obtained in most of the assays between non-extracted and solvent extracted fibers. However, the higher abrasion resistance of extracted fabrics, the longer fiber length and the lower alkaline solubility of most lipid extracted wools should be noted (Ramírez et al., 2008b, 2009b; Petersen, 1992).

Additional analyses of the extracted fibers have been performed. Parameters such as yield, fibril and matrix viscoelastic behavior, deformation work and breaking elongation have highlighted the effect of IWL on the fiber mechanical properties. The IWL extraction has increased yield tenacity and decreased the elongation at break of the fibers, maintaining the feasibility of extracted wool for textile purposes (Martí et al., 2007).

Changes in hydrophobicity in IWL extracted fibers could be important in the dyeing process. Therefore, hydrophobicity of extracted and untreated wool fabrics was assessed by the wetting time test in order to ascertain whether the epicuticular lipids were removed during chloroform/methanol Soxhlet extraction. The results obtained were the same in two samples. The extracted and the non-treated wool fabrics remained on the water surface for more than 48 hours. This finding indicates that the epicuticular lipid layer is intact despite Soxhlet IWL extraction (Martí et al., 2010).

Accordingly, a contact angle of wool fibers was also performed. Five non-treated and five extracted fibers were analyzed and the mean values of perimeter and contact angle evaluated. The contact angles of the two wool fibers are similar, $87.51^\circ (\pm 3.1)$ for the non-treated and $86.94^\circ (\pm 3.8)$ for the extracted sample. Despite a non-significant reduction in hydrophobicity of extracted wool fiber, it may be concluded that the superficial hydrophobicity of extracted wools was not modified under these experimental conditions (Martí et al., 2010).

Moreover, in the absence of IWL, the extracted wool fibers absorbed more water. This behaviour was demonstrated by TG (Thermogravimetry) study and the DSC analysis (Differential Scanning Calorimetry), where the amount of water increases when the extraction time is longer (Martí et al., 2007). DSC is a method commonly used to determine crystallinity in polymers and involves measuring the melting enthalpy. Wool fibres have been studied by this technique in several papers (Cao et al., 1997; Spei & Holzem, 1987; Wortmann & Deutz, 1993, 1998; Wortmann, 2005). There are currently difficulties in accurately measuring the melting transition of wool owing to the fibrous nature of the sample, (for example the level of cystine content could have an influence on DSC analysis (Rivett, 1991), and to the moisture sensibility of the thermal transitions (Haly & Snaith, 1967). The differences in DSC parameters can be related to differences in the matrix material that is the non-helical parts of the intermediate filaments (IFs), the material existing between the IFs, and all other amorphous, morphological components (Wortmann, 2005).

For Merino wool the endotherm is often bimodal. Wortmann et al. confirmed that ortho-cortical cells have a lower melting point than para-cortical cells (Wortmann & Deutz, 1998), which could account for the bimodal peak. (Cao et al., 1997) have investigated the origin of this bimodal endotherm and have presented an alternative interpretation, in which the bimodal peak arises from the overlapping of the melting endotherm of α -form crystallites with the thermal degradation of other histological components.

A research was focused on the changes in the wool structure when IWL were extracted in order to better understand the bimodal endotherm peak behaviour when other histological compounds were extracted from wool. The decreased ΔH_D could mean that methanol extracts part of the amorphous α -form keratin, whereas the high temperature could mean that the rest of crystalline material was more stable than that of the non-extracted wool. This phenomenon could be related to the high abrasion resistance obtained for these samples (Martí et al., 2005). In this work, weakly marked endotherms were obtained in all the samples studied with small enthalpy differences. Therefore, it seems that our results may lend support to the melting endotherm corresponding to the differential melting behavior of the α -form crystallines in the domains of ortho- and para-cortical cells as affirmed by Wortmann et al. (Wortmann & Deutz, 1993, 1998) and by the results of Manich et al. (Manich et al., 2005).

An additional part of our study was focused on the determination of pore size of treated wools in order to analyse the possible pore modification due to lipid extraction. The technique used was thermoporometry, which is based on the determination of the melting temperature of imbibed water for different pore sizes. The cumulated pore volume of the extracted wool fibers increased, indicating that extraction of material from the CMC occurred. From all these results it seems that the morphological modification of extraction would exert an influence on the dyeing of wool lipid extracted fibers.

2.2 Dyeing process of lipid depleted wool fibers

As it was previously mentioned in section 1.3, a number of theories have been proposed concerning the influence of different wool compounds on the dyeing process. According to Wortmann (Wortmann et al., 1997) and Swift (Swift, 1999) the main pathway for dye diffusion is through the nonkeratinous components (endocuticle, intermacrofibrillar matrix and nuclear remnant zones) according to a restricted transcellular diffusion mechanism. However, for Rippon (Rippon, 1999) and Leeder (Leeder, 1999), the intercellular cement is the pathway by which dye molecules reach cortical cells. Therefore, a study of the influence of lipid extraction on the dyeing behavior of wool could help to lend support to one of these two theories.

Extracted and untreated raw wools were conventionally dyed with two acid dyes in order to elucidate the interaction of the dyes and the chemical wool structure with and with less internal wool lipids (0.96% of lipids extracted (Martí et al., 2010)).

The kinetics of extracted and non-extracted wool dyed at 98°C under conventional conditions by two dyes Acid Green 25 (hydrophilic) and Acid Green 27 (less hydrophilic) (Martí et al., 2004) were compared (Figure 2).

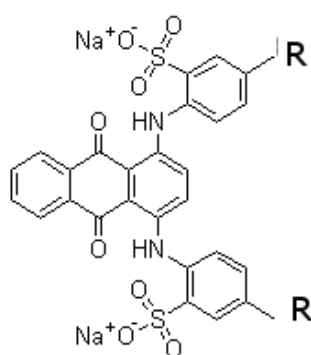


Fig. 2. Molecular structure of the acid dyes used: C.I. Acid Green 27 (R=C₄H₉) and C.I. Acid Green 25 (R= CH₃)

Partition coefficient measurements of the dyes were previously evaluated (Martí et al., 2004) and results (4.2 for Acid Green 25; 1.3 for Acid Green 27) indicated a large difference between these two dyes in their affinities to the polar or non-polar environment. Some bath aliquots were analyzed as the temperature increase. Figure 3a shows the dye exhaustion of Acid Green 25 in untreated and extracted wool. It can be seen that the more hydrophilic dye has high dye exhaustion (about 99%), at 70°C, and the untreated wool attained the highest dye exhaustion at 98°C.

Acid Green 27 (Figure 3b), the big molecular structure dye (less hydrophilic), had a different behavior when the temperature increases; the extracted wool had lower dye exhaustion than the untreated wool during the dyeing process. The diminution of lipids could account for the faster penetration of the small molecular structure dye into the extracted wool fibers than into untreated wool (which retains its original composition). The interaction of this dye with short carbon chains (-CH₃) and its penetration into the fibers without IWL were increased, because the lipids may act as a barrier for more hydrophilic. This contrasts with the big molecular structure dye (-C₄H₉) which had lower affinity with the modified wool fiber, because the hydrophobic forces were absent, resulting in a decreased dye exhaustion.

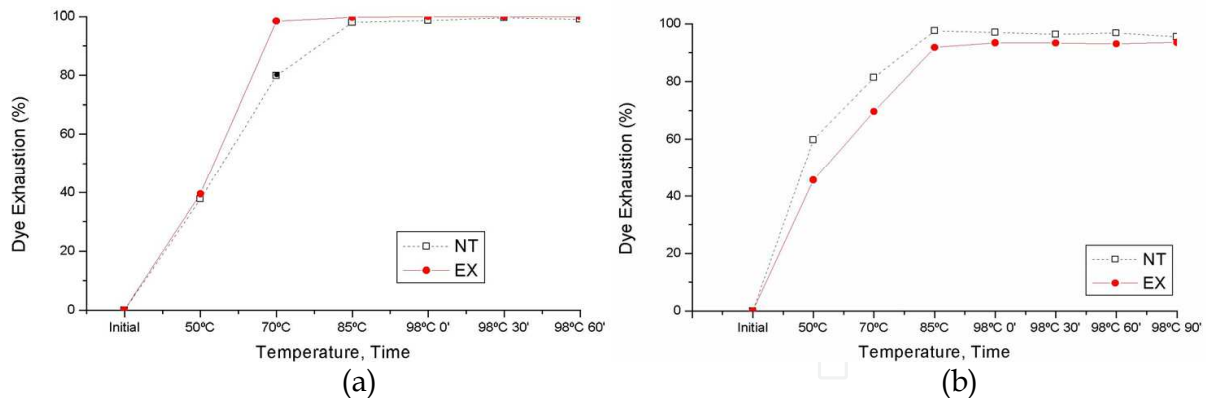


Fig. 3. (a) Acid Green 25 kinetic dyeing at 98°C and (b) Acid Green 27 kinetic dyeing at 98°C.

In order to corroborate these results, another kinetic study was performed in which a final temperature of 70°C was attained, given that a maximum exhaustion was obtained for Acid Green 25 at this temperature. Therefore, two dye processes at 70°C were performed with the same dyes (Figures 4). The dyeing conditions were the same as the earlier kinetic dyeing except for the final temperature of 70°C.

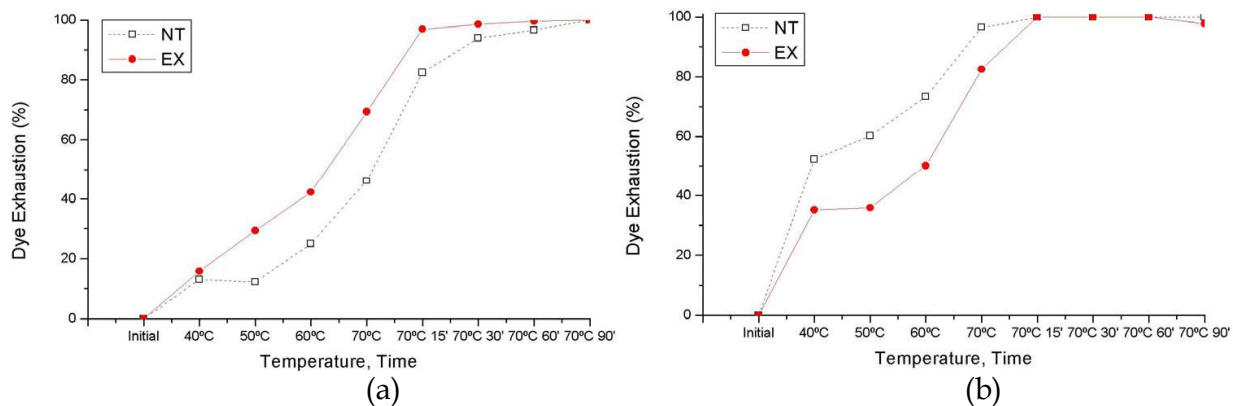


Fig. 4. (a) Acid Green 25 kinetic dyeing at 70°C and (b) Acid Green 27 kinetic dyeing at 70°C.

Again, the extracted fiber was dyed faster than the untreated fiber with Acid Green 25, yielding 92% of dye exhaustion after 15 minutes at 70°C (Figure 4a). These results confirmed the faster penetration of the hydrophilic dye when the fiber is mostly depleted of lipids and becomes more hydrophilic.

In Figure 4b, the dye behavior contrasts with that shown in Figure 4a. The less hydrophilic dye, the faster the penetration into the fiber in the untreated sample, which maintains its lipid internal structure and has a hydrophobic character.

In order to assess dye penetration mechanism of the lipid depleted wool fibers, a microscopic study of the Acid Green 25 and Acid Green 27 dye diffusion was performed (Figure 5). Similar staining behavior was obtained for the two dyes when applied to lipid-extracted wool at the end of the dyeing processes. High penetration was observed with no ring dyeing, which supports a correct penetration for the two dyes on the lipid-extracted wool fibers.

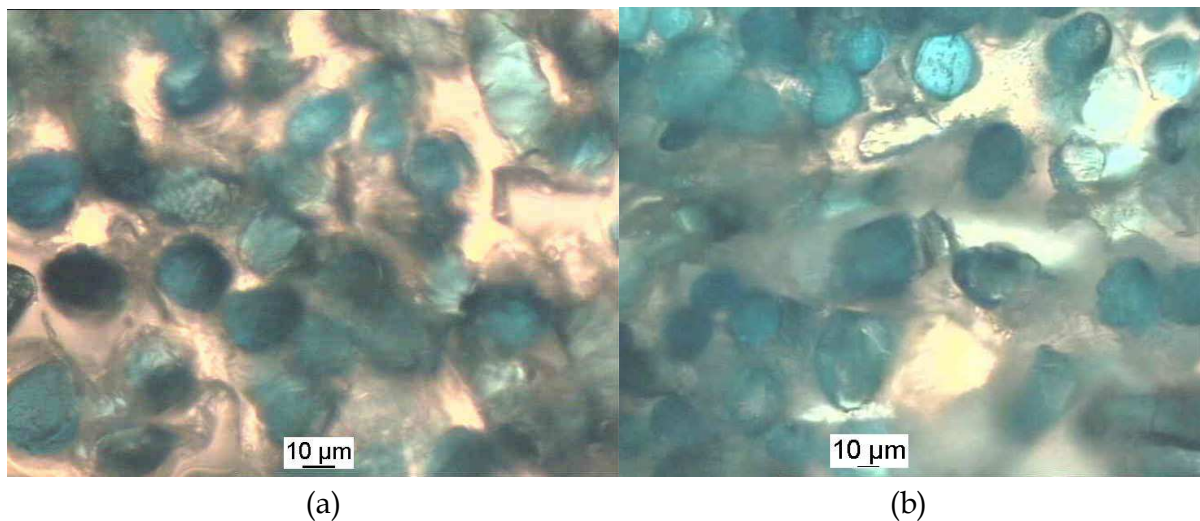


Fig. 5. Micrographs of cross sections of Acid Green 25 (a) and Acid Green 27 (b) lipid extracted wool dyed samples.

K/S values of final dyed goods were also evaluated for the fibers with and with less internal lipids at the two final dyeing temperatures of 98°C and 70°C with the two dyes. Results indicate the same tendency as the dye exhaustion values; however, the dyeing differences are much marked. While the extracted fibers present a lighter color when dyed with the less hydrophilic dye Acid Green 27, the opposite occurs with the more hydrophilic one, Acid Green 25. This higher affinity for the hydrophilic dye to the extracted fiber is even maintained at 70°C, the final dyeing temperature.

To evaluate the visual appearance of the final dyed flock samples, the CIELAB L^* a^* b^* values were obtained. Hue becomes more blue-green in this case for the two dyestuffs. In the case of Acid Green 27, the influence of the extraction is more marked in the final color, between non-extracted and extracted samples, than with the Acid Green 25.

Color fastness was also followed to evaluate dye fastness of wool fabrics with or with less internal lipids. Slightly lower color-fastness values were obtained for the dyed fibers with less internal lipids in the staining degree onto diacetate, polyamide and polyester. In addition, the fastness values for less hydrophilic dye Acid Green 27 are in general slightly lower than for Acid Green 25; this might be due to low interaction between more hydrophilic extracted fiber and the less hydrophilic dye (Acid Green 27). In this case, when the dyed fabric undergoes washing conditions the dye is easily released from the lipid-free fibers. Slight differences in the staining degrees are observed between Acid Green 25 dyed fabrics.

According with the two theories proposed concerning the influence of different wool compounds on the dyeing process, the null hydrophobic surface modification due to lipid extraction and the dyeing results obtained lend support to the intercellular cement as the main dye pathway. The internal lipids, which account for only 33% of the continuous phase of wool and about 1.5% o.w.f., play a major role in the dyeing mechanism.

The results obtained show the different dye behaviors of wool fibers with and almost without IWL. Two dyestuffs were used, the only difference being in the length of their chains; a shorter one that was more hydrophilic (Acid Green 25) and a longer one that was more hydrophobic (Acid Green 27). Maximum dye exhaustion, (about 98%), was achieved at

70°C in extracted wool when a hydrophilic dye was used, with 100% of final exhaustion and a small difference in the hue (CIELAB values). However, slightly lower dye exhaustion values (93% *versus* 96%) were obtained at temperatures over 85°C in the dyeing process in extracted wool when a hydrophobic dye was applied. These different dyeing behaviors may be attributed to the interaction between IWL and the dyestuff.

It may be deduced that the depletion of the hydrophobic internal lipid structure in wool leads to a more hydrophilic pathway. Therefore, the hydrophilic dye easily penetrates into the extracted fiber in contrast to the dye with longer alkyl chains. Since contact angle and wetting time measurements show no modification in the hydrophobicity character of the surface, these results support the theory that the intercellular cement is the main pathway for dyes, highlighting the role of the IWL in this process.

These findings indicate a similar dyeing behavior of wool fibers mostly depleted of internal lipids when a hydrophobic dye was used, and a marked increase in dye exhaustion when a hydrophilic dye was applied. This strategy proves useful in reducing the final dyeing temperature and in mitigating the fiber damage without impairing the washing fastness of the fibers. However, consideration should be given to the color differences obtained between the dyed samples at different temperatures.

In the same way, Telegin et al. (Zarubina et al., 2000) have indicated that hydrophilic/lipophilic properties of acid dyes predetermine the mechanism of their interaction with wool fibers. Temperature changes in sorption of hydrophilic dye and high values of affinity of lipophilic dye support the idea that nonkeratinous components control the transport of acid dyes into the fiber.

2.3 Wool dyeing with liposomes

In our laboratories the role of wool lipid on wool dyeing was already detected on the dyeing process using phosphatidylcholine liposomes as a dyeing auxiliary (Martí et al., 2004). The same two acid dyes of the work presented in the previous section with the only difference being in the length of their chains; the shorter one being more hydrophilic (Acid Green 25) and the longer one being more hydrophobic (Acid Green 27) were used to study the mechanism of wool dyeing.

Liposomes are vesicular colloidal particles with inner water volume separated from bulk water with self-closed lipid bilayers. Having both hydrophilic and hydrophobic compartments in their structure, liposomes can be loaded with substances of different polarity ranging from water-soluble molecules, which are entrapped in the inner aqueous space of liposomes, to hydrophobic molecules which can be dissolved in non-polar bilayer interior. Due to their effective encapsulation capacity liposomes have found numerous applications in various fields, as drug delivery vehicles (Lasic, 1993). In recent years, liposomes have been used in textile industry as dyeing auxiliaries, mainly for wool dyeing (Martí et al., 2001; Montazer et al., 2006; Barani & Montazer, 2008). Dyeing of wool and wool blends along with liposomes has demonstrated better quality, energy saving, and lower environmental impacts. The temperature of dyeing of pure wool and wool blends could be reduced and there was less fiber damage. Moreover, dye bath exhaustion was shown to be greater than 90% at the low temperature (80°C) used resulting in significant saving in energy costs. The impact of the dyeing process on the environment was also much reduced with chemical oxygen demand (COD) being reduced by about 1000 units (Rocha Gomes et al., 1997; Coderch et al., 1999a, 1999b; Martí et al., 1998, 2001; de la Maza et al., 1998; Montazer et al., 2007).

The self-assembling behavior of liposomes and their physicochemical stability at acidic pH values (4.0-5.0) and temperature range (40-90 °C) demonstrated that the liposomes are stable under experimental conditions of the dyeing process. The temperatures used in the dyeing process are always higher than the transition temperature of lipids forming liposomes (~10°C). This implies the continuous fluid state of these lipids maintaining the vesicles without structural modifications.

Transition temperature of the internal lipids was previously evaluated (~ 45°C) (Méndez et al., 2007); this is important to modulate dye diffusion because they are the main components of the CMC (Cell Membrane Complex) which is presumably the dye pathway.

Liposomes can influence the dyeing process through their interactions with the wool fibers and at the same time with the dyestuffs. To elucidate the effects of liposomes on each of these substrates, the dyeing kinetics for the dyes Acid Green 25 and Acid Green 27 were compared in three experimental protocols: (i) in the presence of phosphatidylcholine (PC) liposomes, (ii) without liposomes, and (iii) with wool previously treated with PC liposomes. For untreated wool fibers, a retarding effect of liposomes at the first stages of the dyeing process was observed in the case of the hydrophobic dye Acid Green 27 when the liposomes were present in the bath. At the end of the process, the same (Acid Green 27) or higher (Acid Green 25) dye exhaustion values were obtained when compared with the dyeing process without liposomes in the bath (Figure 6). At the first stages of the dyeing process, the higher retarding effect of the liposomes with the Acid Green 27 could be due to the higher affinity of the hydrophobic dye to the liposomes present in the bath in comparison with the wool fiber. In fact, the previous studies on the liposome-dye interaction and its influence on dyeing kinetics demonstrated a retarding effect on the dye exhaustion due to dye accumulation in liposomes, which takes place in measurable amounts even in the presence of wool (Simonova et al., 2000).

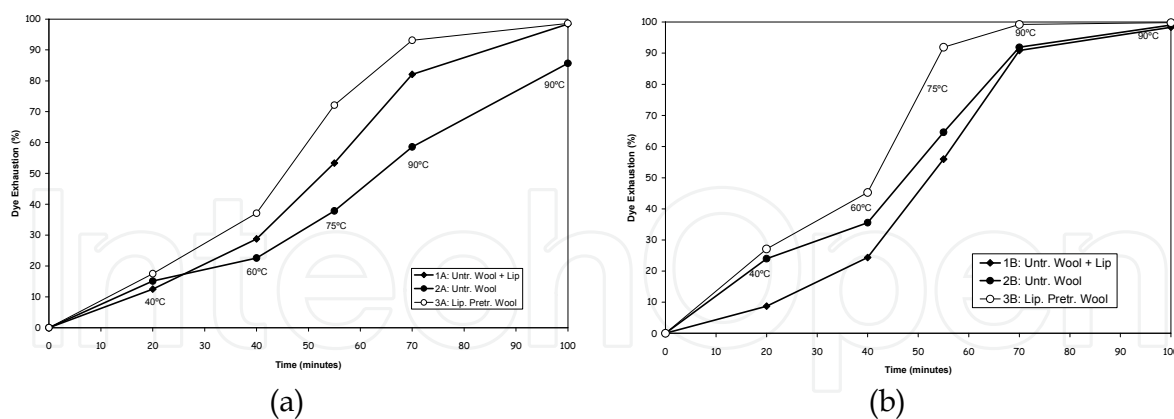


Fig. 6. Exhaustion kinetics of Acid Green 25 (a) and Acid Green 27 (b). 1: Untreated wool in the presence of liposomes, 2: Untreated wool, 3: Liposome pretreated wool.

However, the most striking feature is an increase in the dye exhaustion for the two dyes at all stages of the dyeing process when wool was previously treated with liposomes. The liposome-wool interaction responsible for this behavior could be explained by possible structural changes in the CMC of the fiber due to the previous PC absorption and/or the eventual wool lipid solubilization, which could increase wool permeability for the dye molecules.

Therefore, different experiments were performed to elucidate the liposome–wool interaction in the wool dyeing process. Liposome absorption by the wool fibers was followed by quantifying the amount of the total phosphorus in the bath at different stages of the liposome pretreatment. In addition, DSC measurements were carried out using dimyristoylphosphatidylcholine (DMPC) liposomes as a probe to monitor changes in their thermotropic behavior that may be related to the liposome–wool interaction. Structural changes in the CMC of wool fiber were also evaluated by analyzing the lipids extracted from the liposome-treated wool fibers in order to determine whether PC is actually absorbed by the wool fibers and whether the composition of the internal wool lipids is modified.

Liposome absorption by the wool fibers was determined by the quantitative total phosphorus analysis in aliquots taken from the bath under conditions of the liposome pretreatment. A very quick PC absorption (24%) in the first stage of the process was observed, being also especially important in the last 30 min of incubation at 90 °C to achieve a 39% PC absorption.

The influence of wool on the thermotropic properties of liposomes was studied using the DMPC liposomes as a DSC probe. Heating of the DMPC liposomes (1% oww) with wool at 70-90 °C resulted in complete disappearance of the DMPC signal from the DSC thermograms.

A deep DSC study showed that some liposome-active material is actually solubilized from wool, even at low temperatures, the releasing process being more efficient in the presence of liposomes. A strong effect of this solubilized material on the phase behavior of liposomes implies that this substance has a high affinity to lipid bilayers and thus may originate from the lipid constituents of the cell membrane complex of the wool fibers.

In fact, the experiments performed with liposomes prepared from IWL have clearly shown that these lipids also exert a strong broadening effect on the DMPC thermogram (Figure 7). This supports our supposition that wool being incubated with liposomes releases into the incubation bath some lipid material (presumably polar lipids) that enters the liposome membrane and affects drastically its properties.

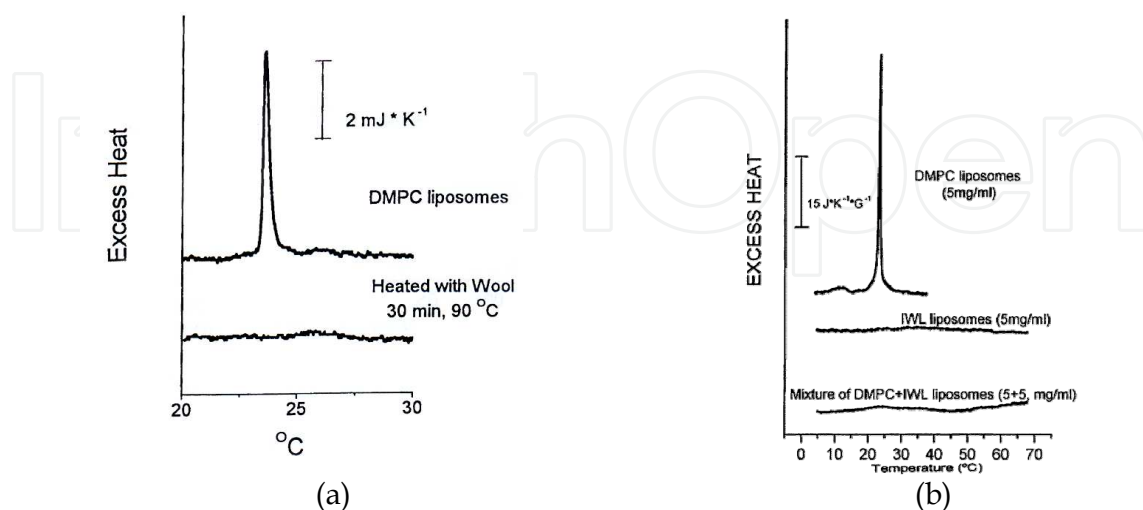


Fig. 7. (a) DSC thermograms of DMPC liposomes heated at 90°C for 30 min in the presence or absence of wool, (b) DSC thermograms of DMPC liposomes, IWL liposomes, and a mixture of DMPC and IWL liposomes.

A release of the lipid material from wool should be accompanied by changes in the lipid composition of wool fibers. The results of lipid extracted from different treated wool performed by TLC/FID (Martí et al., 2004), confirmed that the decrease in the liposome content of the incubation bath observed on pretreatment of wool with liposomes was actually accompanied by the PC absorption by the wool fibers. Being this PC strongly bound to the wool fibers, seemingly due to its incorporation into the lipid domains of the CMC.

The amounts of free fatty acids and sterols extracted from all wool samples were very similar regardless of the experimental dyeing conditions used and the presence of liposomes in the bath. However, a substantial decrease in polar lipids was detected even when wool was subjected to the dyeing conditions in the absence and in the presence of PC liposomes in the incubation bath. These experiments also showed that the removal of polar lipids from wool was accompanied by simultaneous penetration of PC into the wool fibers when incubation was carried out in the presence of liposomes. Since the polar lipids consisting mainly of ceramides and cholesterol sulfate significantly differ from PC in chemical structure and membrane behavior, the authors supposed that such a substitution should greatly affect those properties of the CMC that govern the permeability of wool to dye molecules.

Indeed, it had been shown by electron paramagnetic resonance (EPR) measurements on mixed IWL/PC liposomes that the presence of PC, especially at low amounts (10 wt %), greatly fluidized the lipid bilayer at any temperature and decreased the enthalpy of the main phase transition of IWL from an ordered gel state to a liquid-crystalline fluid state (Fonollosa et al., 2000). If the dye, owing to its amphiphilic nature and some affinity to the lipid bilayer, was able to diffuse along the CMC through lipid domains, then an agent that increases their fluidity would facilitate the dye penetration deep into the wool fiber.

This was the effect that had been observed for the liposome pretreated wool (see Figure 6), which contains the highest amount of PC absorbed by the wool fibers. However, when the dyeing was performed in the presence of PC liposomes two different processes seemed to compete against each other. On one hand, PC tend to enter the wool fibers, and on the other hand, dye had affinity to the liposomes, the latter process being more pronounced for the more hydrophobic dye. Therefore, at initial stages of the dyeing process, when the amount of PC incorporated into wool was low, the retarding effect of liposomes on the dye exhaustion kinetics predominates, which was especially obvious in the case of the hydrophobic dye Acid Green 27.

Our findings indicated that the presence of liposomes in the dyeing bath promotes retention of the two dyes investigated at low temperature, this effect being more important in the case of the hydrophobic dye. It appears that the hydrophobicity of liposomes competes with that of the wool fibers so that the more hydrophobic dye was retained in the dyeing bath to a greater extent. This study had also shown that liposomes and wool interacted actively with each other mainly at high temperature (above the internal lipid transition temperature $\sim 45^{\circ}\text{C}$) with wool polar lipids / PC interchange resulting to a high fluid lipid bilayer in the CMC. This interaction resulted in such a modification both of liposomes and wool fibers that eventually favors the dyeing process, with a dye retardant effect at the beginning of the process and an increase of final dye exhaustion (Figure 8).

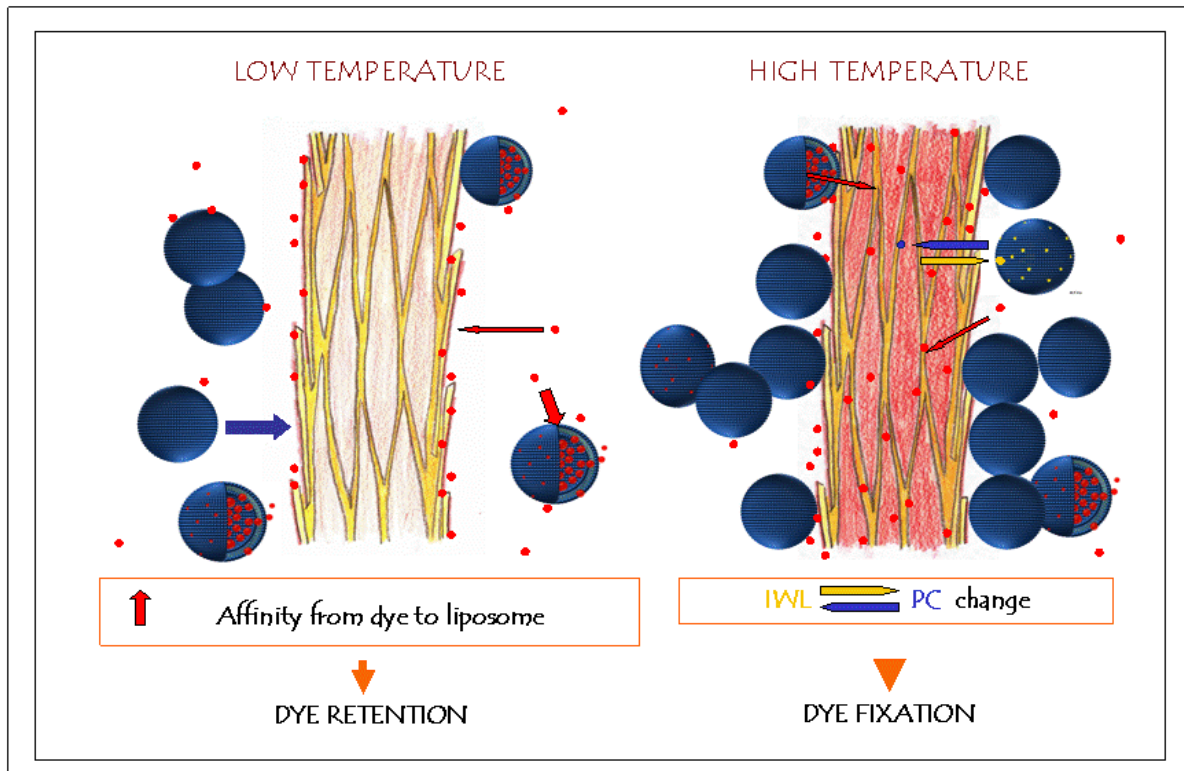


Fig. 8. Liposome–wool-dye interaction.

The detailed study of the liposome–wool interaction with the physicochemical methods revealed that an exchange of some lipid material between liposomes and wool fibers might occur (Figure 8). It was demonstrated that phosphatidylcholine from liposomes was absorbed by wool when wool fibers were subjected to the liposome treatment. On the other hand, a membrane-active factor was released from wool into the water phase, the release being highly intensified in the presence of liposomes. The strong effect exerted on the phase behavior of liposomes implied that this material has a high affinity to lipid bilayers and may originate from the lipid constituents of the cell membrane complex of the wool fibers. This assumption was confirmed by model experiments with liposomes prepared from internal wool lipids. As far as the cell membrane complex plays a key role in penetration and diffusion of dyes into the wool fibers, these results may be helpful in a better understanding of lipid pathways of wool dyeing (Martí et al., 2004).

3. Conclusion

Most plasma treatments invariably increase the rate uptake of dyes by wool. They do not only remove the covalently bond fatty layer (F-layer) which end up to a less hydrophobic wool surface, but also results in exposure of the underlying hydrophilic protein material, which increase the effectiveness of the ionic interaction between protein of the epicuticle and exocuticle and the more hydrophilic molecules. Modification of external linked lipids from the epicuticle showed the importance of both hydrophobic and electrostatic interactions in the dye absorption (Naebe et al., 2010). Hydrophobic dye had little impact of the plasma treatment on dye uptake. It appeared that, for the plasma-treated wool, there was still a

sufficient number of hydrophobic groups on the exposed surface of the epicuticle to facilitate this mechanism of dye adsorption. For the more polar disulfonated and trisulfonated dyes, it appeared that electrostatic effects were more important for adsorption than were hydrophobic effects.

With respect to modification of internal wool lipids, the fundamental role of the internal lipids in the penetration of dyestuffs into fibers should also be noted. A very different dye behavior was obtained for wool fibers with and without internal lipids. Maximum dye exhaustion was achieved in extracted wool when a hydrophilic dye was used. However, lower dye exhaustion was obtained in the dyeing process of extracted wool when a hydrophobic dye was applied. These different dyeing behaviors may be attributed to the interaction between the internal wool lipids and the dyestuff. It was deduced that the depletion of the hydrophobic internal lipid structure in wool leads to a more hydrophilic pathway. Therefore, hydrophilic dye may easily penetrate into the extracted fiber in contrast to the dye with longer alkyl chains.

The presence of liposomes in the dyeing bath promoted retention of the two dyes investigated, this effect being more important in case of the big molecular structure dye. It appears that the hydrophobicity of liposomes competes with that of the wool fibers so that the bigger molecular structure dye was retained in the dyeing bath to a greater extent. This study (Martí et al., 2004) also showed that liposomes and wool interact actively to each other. This interaction resulted in such a modification both of liposomes and wool fibers that eventually favors the dyeing process.

According to the arguments above exposed and taking into account the complexity of the fiber structure, it can be concluded that there are several barriers for dyeing penetration being important the F-layer of the epicuticle for the diffusion of dye through the aqueous dye bath to the surface. However, the results obtained from the study of the dye process of lipid depleted wool fibers and the liposome assisted dye uptake support the theory that the intercellular cement is the main pathway for dyes, highlighting the role of the internal wool lipids in this process mainly in the transfer of dye across the fibers.

4. Acknowledgment

The authors are indebted to Ms. I. Yuste for technical support. And part of this work was supported by funds from the INTAS Project 97-0487 and by Spanish National Project (Ministerio de Educación y Ciencia) CTQ-PPQ2009-13967-C03-01.

5. References

- Aicolina, L.E. & Leaver, I.H. (1990). *Proceedings of 8th Int. Wool Text. Res. Conf.*, Vol. 4, pp. 297, Christchurch, NZ, February 1990.
- Baba, T.; Nagasawa, N.; Ito, H.; Yaida, O. & Miyamoto, T. (2001). Changes in the Covalently Bound Surface Lipid Layer of Damaged Wool Fibers and their Effects on Surface Properties, *Textile Res J.*, Vol. 71, No. 4, pp. 308-312, ISSN 1746-7748.
- Barani, H. & Montazer, M. (2008). A review on applications of liposomes in textile processing. *J. Liposome Res.* Vol 18, No.3, pp. 249-162, ISSN 0898-2104.
- Baumann, H. & Setiawan. (1985). Topochemistry of Dyeing and Chemical Processing of Wool. *Proceedings 7th Int. Wool Text. Res. Conf.*, Tokyo, Vol.5, pp.1-13.

- Brady, P.R. (1985). Dyeing Wool at Low Temperature for Minimum Damage. *Proceedings of 7th Int. Wool Text. Res. Conf.*, Tokyo, Vol. 5, pp. 171-180.
- Brady, P.R. (1990). Penetration Pathways of Dyes into Natural Protein Fibres. *Proceedings of 8th Int. Wool Text. Res. Conf.*, Christchurch, NZ, February 1990, vol. 4, pp. 217-226.
- Cao, J.; Joko, K. & Cook, J.R. (1997). *Textile Res. J.* Vol.67, pp. 117-, ISSN 1746-7748
- Coderch, L.; Manich, A.M.; Martí, M.; de la Maza, A.; Parra, J.L. & Serra, S. (1999a). Complementary study of optimizing a wool dyeing process with commercially available liposomes. *Textile Res J.*, Vol. 69, No. 10, pp. 789-790, ISSN 1746-7748.
- Coderch, L.; Martí, M.; de la Maza, A.; Manich, A.M.; Parra, J.L. & Serra, S. (1999b). Potencial of liposomes to aid the quest for cleaner dyeing. *Wool Record*. Dec: 26.
- Coderch, L.; Fonollosa, J.; Martí, M.; Garde, F.; de la Maza, A. & Parra, J.L. (2002). Extraction and analysis of ceramides from internal wool lipids. *J. Am. Oil Chem. Soc.* Vol. 79, pp. 1215-1220, ISSN 0003-021X.
- Coderch, L.; Bondia, I.; Fonollosa, J.; Méndez, S.; and Parra, J.L. (2003). Ceramides from Wool: Analysis and structure, *IFSCC Mag.*, 6, 117-123, ISSN 1520-4561
- Crank, J. (1956) *The mathematics of diffusion* (Oxford: Clarendon Press)
- De la Maza, A.; Coderch, L.; Manich, A.M.; Martí, M.; Parra, J.L. & Serra, S. (1998). Optimizing a Wool Dyeing Process with an Azoic 1:2 Metal Complex Dye Using Commercial Available Liposomes. *Textile Res. J.* Vol. 68, No. 9, pp. 635-642, ISSN 1746-7748.
- Dauvermann-Gotsche, C.; Evans, D.J.; Corino, J.L. & Korner, A. (2000). Labelling of 18-Methyleicosanoic Acid Containing Proteo-lipids of Wool with Monomaleimido Nanogold. *Proceedings 10th Int. Wool Text. Res. Conf.* Aachen, German Wool Research Institute, Vol. St-10, pp. 1-10, ISBN 3-00-007905-X.
- Elias, P.M. (1981). Lipids and the Epidermal Permeability Barrier. *Arch. Dermatol. Res.* Vol. 270, pp. 95-117, ISSN 0340-3696.
- El-Zawahry, M. M.; Ibrahim, N. A. & Eid, M. A. (2006). The Impact of Nitrogen Plasma Treatment upon the Physicochemical and Dyeing Properties of Wool Fabric, *Polym. Plast. Technol. Eng.* Vol. 45, No. 10, pp. 1123-1132, ISSN 0360-2559.
- Erra, P.; Jovancic, P.; Molina, R.; Jovic, D. & Julia, M. R. (2002). Study of Surface Modification of Wool Fibres by Means of SEM, AFM and Light Microscopy, in "Science, Technology and Education of Microscopy: an Overview," Vol. II, pp. 549-556, Formatex: Badajoz, Spain.
- Fonollosa, J.; Campos, L.; Martí, M.; de la Maza, A.; Parra, J.L. & Coderch, L. (2004). X-ray diffraction analysis of internal wool lipids. *Chem. Phys. Lipids*, Vol. 130, 159-166, ISSN 0009-3084.
- Fonollosa, J.; Martí, M.; de la Maza, A.; Sabés, M.; Parra, J.L. & Coderch, L. (2000). Thermodynamic and Structural Aspects of Internal Wool Lipids. *Langmuir*, Vol. 16, No. 11, pp. 4808-4812, ISSN 0743-7463.
- Haly A.H.; Snaith, J.W. (1967). Differential Thermal Analysis of Wool -The Phase-Transition Endotherm Under Various Conditions 1. *Textile Res. J.* Vol. 37, No. 10, pp. 898-907, ISSN 1746-7748.

- Hampton, G.M. & Rattee, I.D. (1979). Surface Barrier Effects in Wool Dyeing Part I –The Location of the Surface Barrier. *J. Soc. Dyers Colour.* Vol.95, No. 11, pp. 396-399, ISSN 0037-9859.
- Hearle, J.W.S (1991). Understanding and control of textile fiber. *J. Appl. Polym. Symp.*; ISSN 0271-9460.
- Höcker, H.; Thomas, H.; Küsters, A., and Herrling, J. & Färben von Plasmabehandelte Wolle. (1994). Dyeing of plasma treated wool. *Melliand Textilber.* Vol. 75, pp. 506–512.
- Jocic, D.; Vilchez, S.; Topalovic, T.; Molina, R.; Navarro, A.; Jovancic, P.; Julia, M. R. & Erra, P. (2005). Effect of Low-temperature Plasma and Chitosan Treatment on Wool Dyeing with Acid Red 27. *J. Appl. Polym. Sci.* Vol. 97, pp. 2204–2214, ISSN 1097-4628.
- Joko, K.; Koga, J. & Nuroki, N. (1985). The Interaction of Dyes with Wool Keratin – The Effect of Solvent Treatment of Dyeing Behavior. *Proceedings 7th Int. Wool Text. Res. Conf.*, Tokyo, Vol.5, pp.23-32.
- Kalkbrenner, U.; Körner, A.; Höcker, H. & Rivett, D.E. (1990). Studies on the Lipid Composition of the Wool Cuticle. *Proceedings 8th Int. Wool Text. Res. Conf.* Christchurch, Wool Research Organization of New Zealand, Vol. 1, pp. 398-407.
- Kan, C.W.; Chan, K. & Yuen, C.W.M. (2004). Surface Characterization of Low Temperature Plasma Treated Wool Fiber – The Effect of the Nature of Gas. *Fibers Polymers.* Vol. 5, No. 1; pp. 52-58, ISSN 1229-9197.
- Kan, C. W.; Chan, K.; Yuen, C. W. M. & Miao, M. H. (1998). Plasma Modification on Wool Fibre: Effect on the Dyeing Properties, *J. Soc. Dyers Colour.* Vol. 114, pp. 61–65, ISSN 0037-9859.
- Kan, C. W. (2006). Dyeing Behavior of Low Temperature Plasma Treated Wool, *Fibers Polym.* Vol. 7, No. 3, pp. 262–269, ISSN 1229-9197.
- Kan, C. W. & Yuen, C. W. M. (2008). *Plasma Technology in Wool*, (Textile Progress). CRC Press, Vol. 39, pp. 121–187 ISBN: 9780415467452, United States.
- Kerscher, M.,Korting, H.C. & Scharfer-Korting, M. (1991). Skin Ceramides: Structure and Function. *Eur. J. Dermatol.*, Vol. 1, pp. 1-25, ISSN 1167-1122.
- Klausen, T.; Thomas, H. & Höcker, H. (1995). Influence of Oxygen Plasma Treatment in the Chemical and Morphological Changes of the Wool Fiber Surface. *Proceedings 9th Int. Wool Text. Res. Conf.* Biella, International Wool Textile Organization, Vol. 2, pp. 241-248.
- Körner, A. & Wortmann, G. (2005). Isolation of 18-MEA Containing Proteolipids from Wool Fiber Cuticle, *Proceedings 11th Int. Wool Text. Res. Conf.* Leeds, University of Leeds, Vol. 92FWSA, ISBN 0-9553154-0-9.
- Körner, A.; Petrovic, S. & Höcker, H. (1995). Cell Membrane lipids of Wool and Human Hair Form Liposomes. *Textile Res. J.*, Vol. 65, No. 1, pp. 56-58, ISSN 1746-7748.
- Lasic D.D. (1993). *Liposomes: From Physics to Application*, Elsevier, Amsterdam, ISSN 978-0444895486
- Lee, M.; Wakida, T.; Lee, M. S.; Pak, P. K. & Chen, J. (2001). Dyeing Transition Temperature of Wools Treated with Low Temperature Plasma, Liquid Ammonia, and High-

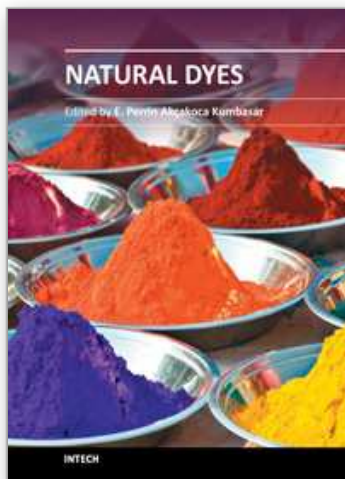
- pressure Steam in Dyeing with Acid and Disperse Dyes. *J. Appl. Polym. Sci.* Vol. 80, pp. 1058-1062, ISSN 1097-4628.
- Leeder J.D. (1999). Comments on "Pathways for Aqueous Diffusion in Keratin Fibers", *Textile Res. J.*, Vol. 69, No.3, pp. 229, ISSN 1746-7748.
- Leeder, J.D.; Holt, L.A.; Rippon, J.A. & Stapleton, I. W. (1990). Diffusion of Dyes and Other Reagents into the Wool Fibre. *Proceedings 8th Int. Wool Text. Res. Conf.*, Christchurch, Vol. 4, pp. 227-238.
- Leeder, J.D. & Rippon, J.A. (1982). Histological Differentiation of Wool Fibres in Formic Acid. *J. Textile Institute.*, Vol. 73, No.3, pp. 149-151, ISSN 0040-5000.
- Leeder, J.D.; Rippon, J.A. & Rivett, D.E. (1985a). Modification of the Surface Properties of Wool by Treatment with Anhydrous Alkali. *Proceedings 7th Int. Wool Text. Res. Conf.*, Tokyo, Vol.4, pp.312-321.
- Leeder, J.D.; Rippon, J.A.; Rothery, F.E. & Stapleton, I.W. (1985b). Use of the Transmission Electron Microscope to study Dyeing and Diffusion Processes. *Proceedings 7th Int. Wool Text. Res. Conf.*, Tokyo, Vol.5, pp.99-108.
- Lindberg, J.; Mercer, E.H.; Philip, B. & Gralén, N. (1949). The Fine Hystology of the Keratin Fibers. *Textile Res J.*, Vol. 19, No. 11, pp. 673-678, ISSN 1746-7748.
- Lindberg, J. (1953). Relationship between Various Surface Properties of Wool Fibers: Part III: Sorption of Dyes and Acids in Wool Fibers. *Textile Res J.*, Vol. 23, pp. 573-584, ISSN 1746-7748.
- Makinson, K. R. (1968). Some New Observations on the Effects of Mild Shrinkproofing Treatments on Wool Fibers. *Textile Res J.*, Vol. 38, No. 8, pp. 831-842, ISSN 1746-7748.
- Manich, A.M.; Carilla, J.; Vilchez, S.; de Castellar, M.D.; Oller, P. & Erra, P. (2005). Thermomechanical Analysis of Merino Wool Yarns. *J. Therm. Anal. Calorim.* Vol. 82, No.1, pp.119-123, ISSN: 1388-6150.
- Martí, M.; Serra, S.; de la Maza, A.; Parra, J.L. & Coderch, L. (2001). Dyeing Wool at Low Temperatures: New Method Using Liposomes. *Textile Res. J.*, Vol. 71, No.8, pp. 678-682 ISSN 1746-7748.
- Martí, M.; Coderch, L.; de la Maza, A.; Manich, A.M. & Parra J.L. (1998). Phosphatidilcholine Liposomes as Vehicles for Disperse Dyes for dyeing Polyester/Wool Blends. *Textile Res. J.*, Vol.68, No. 3, pp. 209218, ISSN 1746-7748.
- Martí, M.; Barsukov, L.I.; Fonollosa, J.; Parra, J.L.; Sukhanov, S.V. & Coderch, L. (2004). Physicochemical Aspects of the Liposome-Wool Interaction in Wool Dyeing. *Langmuir.* Vol. 20, pp. 3068-3073, ISSN 0743-7463.
- Martí, M.; Ramírez, R.; Manich, A.M.; Coderch, L. & Parra J.L. (2007). Thermal Analysis of Merino Fibers without Internal Lipids. *J. of App. Polym. Sci.*, Vol. 104, No. 1, pp. 545-551, ISSN 1097-4628.
- Martí, M.; Ramirez, R.; Barba, C.; Coderch, L. & Parra, J.L. (2010). Influence of Internal Lipid on Dyeing of Wool Fibers. *Textile Res. J.* Vol. 80, No. 4, pp. 365-373, ISSN 1746-7748.
- Martí, M.; Manich, A.M.; Oller, P.; Coderch, L.; Parra, J.L. (2005). Calorimetric Study of Lipid Extracted Wool Fibers. *Proceedings 11th Int. Wool Res. Conf.*, Leeds. Fi 5S-3, ISBN 0-9553154-0-9.

- Martí, M.; de la Maza, A.; Parra, J.L. & Coderch, L. (2001). Dyeing wool at low temperatures: new method using liposomes. *Textile Res J.*, Vol. 71, No. 8, pp. 678-682, ISSN 1746-7748.
- Medley, J.A. & Andrews, M.W. (1959). The Effect a Surface Barrier on Uptake Rates of Dyes into Wool Fiber. *Textile Res. J.* Vol.29, No. 5, pp. 398-403, ISSN 1746-7748.
- Méndez, S.; Martí, M.; Barba, C.; Parra, J.L. & Coderch, L. (2007). Thermotropic behavior of ceramides and their isolation from wool. *Langmuir*, Vol. 23, No. 3, pp. 1359-1364, ISSN 0743-7463.
- Millson, H.E. & Turl, L.H. (1950). *Amer. Dyestuff Reprtr.* Vol.93, pp. 647.
- Montazer, M.; Validi, M. & Toliyat, T. (2006). Influence of temperature on stability of multilamellar liposomes in wool dyeing. *J. Liposome Res.* Vol 16, No.1, pp. 81-89, ISSN 0898-2104.
- Montazer, M.; Taghavi, F.A.; Toliyat, T. & Bameni Moghadam, M. (2007). Optimizing of Dyeing of Wool with Madder and Liposomes by Central Composite Design. *J. of Appl. Polym. Sci.*, Vol. 106, No. 4, pp.1614-1621, ISSN 1097-4628.
- Naebe, M.; Cooksoon, P.G.; Rippon, J.; Brady, R.P. & Wang, X. (2010). Effects of Plasma Treatment of Wool on the Uptake of Sulfonated Dyes with Different Hydrophobic Properties. *Textile Res. J.* Vol. 80, No. 4, pp. 312-324, ISSN 1746-7748
- Negri, A.P.; Cornell, H.J. & Rivett, D.E. (1993). The modification of the Surface Diffusion Barrier Wool. *J. Soc. Dyers Colour.* Vol. 109, No. 9, pp.296-301, ISSN 0037-9859.
- Petersen, R.D. (1992). Ceramides: Key Components for Skin Protection. *Cosmet. Toiletries.* Vol. 107, pp. 45-49, ISSN 0361-4387.
- Ramírez, R.; Garay, I.; Álvarez, J.; Martí, M.; Parra, J.L. & Coderch, L. (2008a). Supercritical fluid extraction to obtain ceramides from wool fibers. *Sep. Purif. Technol.* Vol.63, pp. 552-557, ISSN 1383-5866.
- Ramírez, R.; Martí, M.; Manich, A.M.; Parra, J.L. & Coderch, L. (2008b). Ceramides extracted from wool: pilot plant solvent extraction. *Textile Res. J.* Vol.78, No. 1, pp. 73-80, ISSN 1746-7748.
- Ramírez, R.; Martí, M.; Garay, I.; Manich, A.M.; Parra, J.L. & Coderch, L. (2009b). Ceramides extracted from wool: Supercritical Extraction Processes. *Textile Res. J.* Vol.79, No. 8, pp. 721-727, ISSN 1746-7748.
- Ramirez, R.; Martí, M.; Cavaco-Paulo, A.; Silva, R.; de la Maza, A.; Parra, J.L. & Coderch, L. (2009a). Liposome formation with wool lipid extracts rich in ceramides, *J. Liposome Res.*, Vol. 19, pp. 77-83, ISSN 0898-2104.
- Rippon, J. A. (1992). The Structure of Wool, in "Wool Dyeing," Lewis, D. M., (Ed.), Society of Dyers and Colourists, Bradford, England, pp. 1-51, ISBN 0 901956 53 8.
- Rippon J.A. (1999). Comments on "Pathways for Dye Diffusion in Wool Fibers", *Textile Res. J.* Vol. 69, No. 4, pp. 307-308, ISSN 1746-7748.
- Rippon, J.A. & Leeder, J.D. (1986). The Effect of Treatment with Perchloroethylene on the Abrasion Resistance of Wool Fabric. *J. Soc. Dyers Colour.* Vol. 102, pp. 171-176, ISSN 0037-9859.
- Rivett, D.E. (1991). Structural Lipids of the Wool Fibre. *Wool Sci. Rev.*, 67, 1-25

- Rocha Gomes, J.I.N.; Genovez, M.C. & Hrdina, R. (1997). Controlling exhaustion of reactive dyes on wool by microencapsulation with liposomes. *Textile Res J.*, Vol. 67, pp. 537-541, ISSN 1746-7748.
- Schaefer, H. & Redelmeier, T.E. (1996). Skin Barrier: Principles in Percutaneous Penetration pp. 55-58, Karger, ISBN 3-8055-6326, Basel, Switzerland.
- Schürer, N.Y.; Plewing, G.; & Elias P.M. (1991). Stratum Corneum Lipid Function. *Dermatologica*. Vol.183, No. 2, pp. 77-94, ISSN 1018-8665.
- Simmonds, D.H. (1955). *Aust. J. Biol. Sci.* Vol.8, pp. 537.
- Simonova, T.N.; Sukhanov, S.V.; Barsukova, O.V. & Barsukov, L.I. (2000). Liposomes as a Tool in studies of Wool dyeing. *Proceedings of the 10th International Wool Textile Research Conference*, Deutsches Wollforschungsinstitut: Aachen, Germany, 2000, DY-8, pp.121, ISBN 3-00-007905-X.
- Spei, M. & Holzem, R. (1987). Thermoanalytical Investigations of Extended and Annealed Keratins. *Colloid & Polym. Sci.* Vol. 265, pp.965-970, ISSN 0303-402X.
- Swift J.A. (1999). Pathways for Aqueous Diffusion in Keratin Fibers. *Textile Res. J.* Vol. 69, No. 2, pp. 152, ISSN 1746-7748.
- Thomas, H.; Lehmann, G.; Höcker, H.; Möller, M.; Thode, C. & Lindmayer, M. (2005). Plasma Pre-Treatment at Atmospheric Conditions for Improved Processing and Performance Characteristics of Wool Fabrics. *Proceedings 11th Int. Wool Text. Res. Conf.* Leeds, University of Leeds, 86 FWS, ISBN 0-9553154-0-9.
- Thomas, H. (2007). Plasma Modification of Wool, In: *Plasma Technologies for Textiles*, Shishoo, R., (Ed.), pp. 228-246, Woodhead Publishing Limited, Cambridge, England.
- Wakida, T.; Tokino, S.; Niu, S.; Kawamura, H.; Sato, Y.; Lee, M.; Uchiyama, H. & Inagaki, H. (1993). Surface Characteristics of Wool and Poly(ethylene Terephthalate) Fabrics and Film Treated with Low Temperature Plasma Under Atmospheric Pressure, *Textile Res. J.* Vol.63, No. 8, pp.433-438, ISSN 1746-7748.
- Wakida, T.; Lee, M.; Sato, Y.; Ogasawara, S.; Ge, Y. & Niu, S. (1996). Dyeing Properties of Oxygen Low-temperature Plasmatreated Wool and Nylon 6 Fibres with Acid and Basic Dyes. *J. Soc. Dyers Colour.* Vol. 112, pp.233-236, ISSN 0037-9859.
- Wakida, T.; Lee, M.; Niu, S.; Kobayashi, S. & Ogasawara, S. (1994). Microscopic Observation of Cross-section of Dyed Wool and Nylon 6 Fibres after Treatment with Low-temperature Plasma. *Seni Gakkaishi* Vol. 50, pp. 421-423.
- Ward, R.J.; Willis, H.A.; George, G.A.; Guise, G.B.; Denning, R.J.; Evans, D.J. & Short, R.D. (1993). Surface Analysis of Wool by X-Ray Photoelectron Spectroscopy and Static Secondary Ion Mass Spectrometry. *Textile Res J.*, Vol. 63, No. 6, pp. 362-368, ISSN 1746-7748.
- Wortmann, F.J.; Wortmann, G. & Zahn, H. (1997). Pathways for Dye Diffusion in Wool Fibers, *Textile Res. J.*, Vol. 67, pp. 720-724, ISSN 1746-7748.
- Wortmann, F.J. & Deutz, H.J. (1998). Thermal Analysis of Ortho- and Para-cortical Cells Isolated from Wool Fibers. *J. Appl. Polym. Sci.* Vol. 68, No. 12, pp. 1991-1995, ISSN:1097-4628.
- Wortmann, F.J. (2005). Facets of the Structure and Physical Properties of Keratin Fibres. *Proceedings of the 11th Intern. Wool Res. Conf.* Leeds, September 2005, 19 KN, ISBN 0-9553154-0-9.

- Wortmann, F.J. & Deutz, H.J. (1993). Characterizing Keratin Using High-pressure Differential Scanning Calorimetry (HPDSC). *J. Appl. Polym. Sci.* Vol. 48, No. 1 pp. 137-150, ISSN 1097-4628.
- Yoon, N. S.; Lim, Y. J.; Tahara, M. & Takagishi, T. (1996). Mechanical and Dyeing Properties of Wool and Cotton Fabrics Treated with Low Temperature Plasma and Enzymes, *Textile Res. J.* Vol. 66, No. 5, pp. 329-336, ISSN 1746-7748.
- Zarubina, N.P.; Belokurova, O.A. & Telegin, F.Y. (2000). Thermal Transition in Wool Evaluated by Sorption of Acid Dyes. *Proceedings 10th Int. Wool Text. Res. Conf.* Aachen, German Wool Research Institute, Vol. ST-P9, pp. 1-8, ISBN 3-00-007905-X
- Zhan, H. (1980). Plenary Lecture, 6th *Intern. Wool Res. Conf.* Pretoria, Vol. 1

IntechOpen



Natural Dyes

Edited by Dr. Emriye Akcakoca Kumbasar

ISBN 978-953-307-783-3

Hard cover, 124 pages

Publisher InTech

Published online 14, November, 2011

Published in print edition November, 2011

Textile materials without colorants cannot be imagined and according to archaeological evidence dyeing has been widely used for over 5000 years. With the development of chemical industry all finishing processes of textile materials are developing continuously and, ecological and sustainable production methods are very important nowadays. In this book you can be find the results about the latest researches on natural dyeing.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Meritxell Martí, José Luis Parra and Luisa Coderch (2011). Lipid Role in Wool Dyeing, Natural Dyes, Dr. Emriye Akcakoca Kumbasar (Ed.), ISBN: 978-953-307-783-3, InTech, Available from: <http://www.intechopen.com/books/natural-dyes/lipid-role-in-wool-dyeing>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen