

## Article

# Bio-Innovative Pretreatment of Coarse Wool Fibers

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**Abstract:** From the textile manufacturers' point of view, coarse and medullated fibers are undesirable in the production of fine woolen materials, but highly desirable in the production of textiles and yarns with special effects, especially in carpet production. For sustainability, the entire sheep fleece should be used, including the coarse and medullated fibers. The raw wool must be scoured to obtain clean wool fibers without damage or excessive fiber entanglement, with a certain moisture content, low dirt content and residual grease for further processing, and proper color. In order to remove the impurities in raw wool with maximum efficiency, save energy and minimize the environmental impact, this study investigated the changes in some fiber properties during the scouring process due to the effect of the enzyme complex on coarse wool fibers. The effects were studied through the amount of clean wool fibers and impurities within the fleece, the fiber diameter and color. Conventional and enzyme scoured coarse wool were bleached with an unconventional bleaching agent, percarbonate, and compared to bleaching with hydrogen peroxide to achieve higher whiteness and brilliant color with minimal fiber property changes. The changes after the bleaching process were determined based on the sorption of moisture and dyes and the color parameters. The bio-innovative pretreatment with enzyme complex scouring and percarbonate bleaching resulted in excellent fiber properties even for coarse wool. SEM analysis was performed to confirm these results. Taking into account the sustainability of the process and environmental protection, enzyme complex scouring and percarbonate bleaching are recommended as pretreatment processes for raw coarse wool.

**Keywords:** coarse wool; enzyme scouring; percarbonate bleaching; swelling; whiteness; dye exhaustion; color strength



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## 1. Introduction

Wool is an important raw material for the textile industry. Interest in the processing of domestic wool has increased in the last decade, mainly due to its renewability [1]. However, it is a useful technological resource or may pose a significant environmental hazard due to improper disposal of wool (whole fleece) and/or uncontrolled release of effluents from the scouring process. The sheep fleece is a mixture of fine and coarse fibers, grease (lipids, high fatty acids and their ethers, ethers, alcohols, sterols and lanolin), suint (sweat: ammonium salts, urea, amino acids and K, Mg, Ca, Fe, Cu, Zn, Mn sulphates, oxalates and phosphates) and contaminants as dander, vegetable matter, dirt, sand, urine and microorganisms [2–7].

Wool fiber is a natural fiber composed mainly of the protein keratin (approx. 82%), formed by biosynthesis of  $\alpha$ -amino acids. The main components of the wool fiber structure are the cuticle, subcuticle, cortex and in some cases medulla. The outer layer of the fiber, the cuticle, differs in fine and coarse fibers. The cuticle of fine wool fibers is composed of plate-like or ring-like scales, partially superimposed so that each upper part is inserted into the lower, covering two-thirds of the scale and one-third of the protruding fiber. Coarse fibers are covered with irregular plate-like scales on the surface, so that the fiber has a large number of scales on top of each other and the surface is very rough. The coarse fibers

differ from the ordinary cuticle-cortex fibers in a way that they have medulla (continuous or discontinuous) in the core of the fiber, i.e., cuticle-cortex-medulla fibers. The cuticle cells, i.e., scales, are responsible for important fiber properties such as wettability, hand and felting [2,5,8–12].

From the perspective of textile manufacturers, coarse and medullated fibers are undesirable in the production of fine wool textiles, but highly desirable in wool for the production of textiles and yarns with special effects, especially in carpet production. Medullated fibers are coarse hollow fibers usually found on skirtings' (the edges of the sheep fleece). They cause serious problems in dyeing as they are dyed in lighter shades than non-medullated fibers, but give a hairy appearance, increase volume and have higher resistance to bending and compression. The term "medullation" refers to the percentage of medullated fibers in a wool sample. The presence of medullated fibers in the fleeces of today's sheep is a legacy of the past and genetic traits and is exacerbated by harsh climatic conditions, inadequate nutrition and sheep breeding. For sustainability, the entire sheep fleece should be used, including coarse fibers and medullated fibers [9–12].

To remove all wool impurities with maximum efficiency, efficient use of energy and minimum environmental impact, the raw wool must be scoured. This process is performed to obtain clean wool without damage or excessive fiber entanglement, with a certain moisture content, low dirt content (i.e., vegetable matter) and residual grease for further processing, and proper color [13–15]. The most common methods of wool scouring are scouring in the suint, and emulsion scouring with soaps or surfactants in an alkaline medium [6–9]. For many years, wool scouring and finishing were considered the most environmentally unfavorable processes in the textile industry. Alternation was found in application of enzymes and enzyme complexes due to their ecological premises, special activity on certain substance and the possibility of improving the primary properties of the fibers [16–25]. Additionally, other sustainable techniques for raw wool cleaning and functionalization have been explored, such as low-plasma and air-plasma treatment [25–27], ultrasound treatment [28], chitosan coating [29], etc.

Enzymes are natural proteins that act as biocatalysts. Great advances in biotechnology have enabled the development of enzymes with specific activity that are produced for commercial purposes. Most of the enzymes used in textiles are hydrolases that catalyze cleavage reactions by hydrolysis, i.e., proteases, lipases, and cellulases [24]. The enzymes that can be used in wool processing are proteases (peptidases and proteinases) that cleave polypeptide chains into amino acids, amines and minor peptides; lipases that cleave lipids into fatty acids and glycerol, especially triglycerides and other fatty acids; and lipoprotein lipases that hydrolyze the lipoprotein bonds of lipoproteins [16–25].

Mechanical agitation in the scouring bath moves the fibers in the direction of least friction, they bend and stretch, the product thickens, shrinks and deforms, likely forming a wool felt. The felting of wool depends directly on the specific structure of wool, i.e., its scaly surface and the bilateral asymmetry of the cortex, friction, hydrolysis of ionic bonds and destruction of disulfide bonds. If any of them is absent, the felting does not take place [11]. Due to the action of the enzyme complex in the scouring bath, the primary properties of the wool, such as yield, fineness and strength, are preserved, while color, luster and resistance to felting, as well as dimensional stability are increased [19–23].

This research is focused on coarse wool enzyme scouring and subsequently innovated bleaching. As the scoured wool still retains natural pigments, the process of bleaching is necessary, especially for coarse wool due to demands for palette of light and pastel shades. Another problem is yellowing, which can easily occur, especially when the wet wool is exposed to sunlight. The bleaching process can be done solely by oxidation, reduction or the combination of oxidation/reduction and dyeing. Most reductive wool bleaching processes are carried out with stabilized dithionite, but it is possible to use sodium borohydride as well. Hydrogen peroxide (HP) is usually used as the oxidizing agent [8,14,30–40]. However, the HP solutions require a bleach activator, usually in alkali conditions. Such treatment at pH 9 leads to damage of wool fibers due to progressive oxidation of disulfide bonds.

Peroxide bleaching of wool can be carried out under slightly acidic conditions (pH 5–6) if a buffer such as Prestogen W (BASF) [31] or citric acid is used. Peroxyacetic acid (PAA) can also be used but can cause fiber damage. Sodium perborate or sodium percarbonate (PC) are bleach used in the detergent, with the addition of TAED as an activator that they can bleach at lower temperatures and lower pH [37,38]. Perborate and percarbonate have an advantage over HP in detergency because they do not change during storage due to their stability in powder form. Sodium percarbonate has been found to be a good bleaching agent for cashmere [39] and virgin wool [37]. Therefore, in this research, conventional and enzyme scoured coarse wool was chemically bleached in a PC oxidizing system and compared with HP bleaching to achieve higher whiteness and brilliant color with minimal fiber damage.

The concept of this research involves the processing of coarse wool fibers from an autochthon sheep breed by alternative scouring and bleaching with the intention to achieve higher whiteness and brilliant color with minimal structural changes. Enzymatic processes for so-called fine wool (with fibers below 30 microns) have been widely studied [17–19], but the different structure and morphology of coarse wool (majority of fibers above 30 microns) results in different fiber properties [8,15,41]. Therefore, for the selected coarse wool, the morphology, moisture content and dyeability were determined after bleaching and dyeing with acid dyes.

## 2. Materials and Methods

### 2.1. Materials

The fleece of an autochthon sheep breeds of southern Mediterranean, Comisana (having fine and coarse fibers with overall share of 15% medullated fibers in the fleece) was used in this research.

Sodium hydroxide p.a. (NaOH), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), hydrogen peroxide (35%,  $\text{H}_2\text{O}_2$ ), tetra acetyl ethylene diamine (TAED), acetic acid ( $\text{CH}_3\text{COOH}$ ), urea, ammonia ( $\text{NH}_3$ ), potassium hydroxide p.a. (KOH) and bromine water solution were purchased from Kemika, Croatia. Sodium bisulfite ( $\text{NaHSO}_3$ ) and Acid Red 111 were purchased from Sigma-Aldrich. Bactosol WO, a biocatalyst based on selected enzymes, based on hydrolase enzymes, with specific action on protein, i.e., wool fibers, Sandoclean PC, a nonionic surfactant (fatty alcohol ethoxylate), from Clariant, Switzerland were used. Lanaset Navy R, mixture of dyes: anthraquinone (Acid Blue 225) and 1:2 azo metal-complex (Acid Blue 317) was purchased from Huntsman, Hungary. Prestogen W, a buffer/stabilizer that consists of a combination of organic and inorganic salts which enables hydrogen peroxide solutions to be used at neutral or acid pH, from BASF, Germany was used. Sodium percarbonate ( $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ ) was donated from Labud, Croatia; and Felosan NOF, a nonionic surfactant, Contavan ALR, an organic stabilizing agent and Cotoblanc SEL, an anionic surfactant, were donated from CHT-Bezema, Switzerland.

### 2.2. Pretreatment Procedures

Scouring of wool was performed in three different processes: (1) conventional scouring (CS), (2) bio-scouring (ES) and (3) conventional scouring with enzymatic after treatment (CS-E). Processes were performed in AHIBA–universal turbomat TM 6 II, BR 1:30, at pH 8.5, at 60 °C for 60 min. Bath for (1) CS contained: 0.5 g/L Sandoclean PC and 5 g/L  $\text{Na}_2\text{CO}_3$ ; and for (2) ES contained: 0.5 g/L Sandoclean PC and 3.5% owf (over weight of fiber) Bactosol WO. For scouring process (3) CS-E, first the conventional scouring process was performed (same bath) and then after-treatment with 3.5% owf Bactosol WO at the same conditions was done.

Bleaching was carried out in Linitest (Original Hanau) at 60 °C for 1 h in different oxidizing baths containing hydrogen peroxide (HP) or percarbonate (PC). As wool is a protein fiber, it was necessary to adjust the conditions of bleaching in slightly alkaline to acidic medium. Prestogen W and TAED were used as activators. HP bleaching was performed at pH 5.5 in a bath containing: 15 g/L  $\text{H}_2\text{O}_2$  (35%), 5 g/L Prestogen W and

1 g/L Felosan NOF. PC bleaching was performed at pH 8 in a bath containing: 15 g/L  $2\text{Na}_2\text{CO}_3 \times 3\text{H}_2\text{O}_2$ , 1.5 g/L TAED, 2 g/L Contavan ALR and 1 g/L Felosan NOF.

After pretreatments, scouring and bleaching, fibers were rinsed in warm and cold distilled water, neutralized if necessary with 5% acetic acid, and again rinsed with distilled water to neutral.

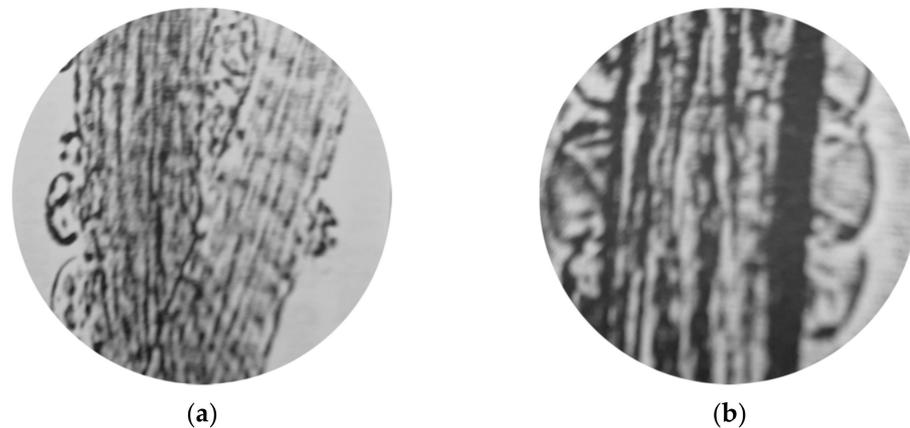
### 2.3. Dyeing

For dyeing, 3% owf of acid dyes: a dark shade Lanaset Navy R, mixture of dyes: antraquinone (Acid Blue 225) and 1:2 azo metal-complex (Acid Blue 317), and a brilliant shade Acid Red 111 were used. Dyeing of all pretreated fibers was performed in AHIBA–universal turbomat TM 6 II, BR 1:30, at pH 5 (adjusted with  $\text{CH}_3\text{COOH}$ ), for 75 min (30 min heating, 45 min at 90 °C). After dyeing, fibers were soaped with Cotoblanc SEL and rinsed. For control of dye exhaustion, a bath aliquot was taken at the end of the dyeing process (75 min).

### 2.4. Characterization Methods

The effect of cleaning fibers in scouring was examined by determination of loss in mass of raw wool, the mass fraction of clean wool fiber, extracted grease and dirt in fleece, fiber diameter and color. For that purpose, 100 g from the 20 different areas on fleece were sampled and mixed, resulting in 2 kg of raw wool for investigation. The loss of raw wool mass in scouring (scouring yield) was done by gravimetric determination of mass before and after the process using an analytical balance, model ALJ 220-5DNM (KERN & Sohn GmbH, Balingen, Germany). Extraction of grease after scouring was done according to ISO 3074:2014. Dirt was separated manually. All weightings were done on absolutely dry mass.

Qualitative and quantitative tests were done in order to determine the changes in fiber properties, and fiber damages in scouring process, if any. The solubility in alkali (AS) and in urea bisulphite (UBS) were determined according to the standard methods. Alkali solubility was determined in 0.1 M NaOH solution according to ISO 3072:1975. The solubility in solution containing 50% urea and 3% bisulphite was determined according to BS 3584:1989, respectively. The solubility was calculated as the value of the loss in mass of difference in the mass of the dry sample before and after treatment. For determination chemical damage, the time of characteristic swelling reactions in the Kraiss–Markert–Viertel and Allworden reagents was measured [5,42,43]. Kraiss–Markert–Viertel reagent is a mixture of  $\text{NH}_3$  and KOH used to determine acid damage to wool. Combed and parallelized fibers are placed on a microscope slide and the swelling time is measured after dropping Kraiss–Markert–Viertel reagent under the lens of Olympus CX22 Binocular LED microscope at 100× magnification. The swelling responses at room temperature are next: 1–2 min for acid-damaged, >20 min for alkali-damaged and 6–10 min for undamaged fibers. Testing with Allworden reagent is similar. Allworden reagent is a mixture of bromide water solution and water in a 1:1 ratio. The swelling reaction in Allworden reagent is very specific—epicuticle opens and detaches from fiber, resulting in visible bubbles. At room temperature, the swelling times are as follows: 1 min for acid-damaged, >30 min for alkali-damaged fibers and 2 min for undamaged fibers. The swelling reactions of wool in Kraiss–Markert–Viertel and Allworden reagent are shown in Figure 1.



**Figure 1.** The swelling reaction of wool in (a) Krais–Markert–Viertel and (b) Allworden reagent.

Fiber diameter,  $d$  ( $\mu\text{m}$ ) was measured on 1000 fibers using Lanameter, Carl Zeiss-Jena, a special projection microscope for measuring the diameter of wool fibers [44]. Measurements were performed in cedar oil and in water. For the purpose of swelling calculation, fiber diameter was measured before and after 24 h in water. Considering that fibers represent wool from the whole fleece, which contains fine, coarse and medullated wool, a detailed analysis was made depending on the ratio of particular fiber diameter range. For each 100 fibers by diameter increase, i.e., 10%, the analysis was performed, and the swelling values were compared for every such 10% of fiber diameter ranges in the representative sample. Since medulla is a morphological characteristic of the breed, moreover, of each sheep, it should not change with pretreatment. Therefore, during the determination of fiber diameter in cedar oil, the share of medullated fibers with continuous and discontinuous medulla, was simultaneously determined according to the IWTO-8 method [44].

The wool moisture content at different ambient relative humidity (RH 30, 65, 72, and 100%) was determined using standard method for testing textiles and oven-drying (ASTM D2654-22). Results are represented as regain,  $R$  (%).

The surface morphology of fibers after selected pretreatments was analyzed from micrographs taken on a scanning electron microscope (SEM) FE-SEM, Mira II, LMU (Tescan, Brno, Czech Republic) with a magnification of  $1000\times$ . The fabrics were coated with a thin layer of chromium for 120 s in a sputter coater Quorum-Q150T ES.

From the reflectance/remission ( $R$ ) measured on remission spectrophotometer Spectraflash SF 300 (Datacolor), spectral characteristics were calculated and analyzed. The measurement was made under the standard light source D65–Xenon lamp,  $8^\circ$  standard observer illuminance, excluding the specular component and including UV specular component. For the purpose of measurement, scoured wool was mechanically combed and parallelized into a strand, superimposed in different directions to avoid voids/air spaces and to create a homogeneous sample for measurement and fixed in a cardboard frame for easy handling so that the sample could be measured on random locations. The measurement was performed using the Datacolor Tools computer program and the “Measuring until tolerance” command, which requires at least 5 measurements, and the results are accepted if the total color difference is less than 0.1 ( $\Delta E^* < 0.1$ ). CIE whiteness degree ( $W_{\text{CIE}}$ ) according to ISO 105-J02:1997 and Yellowing Index (YI) according to DIN 6167:1980 were calculated automatically. CIE  $L^*$ ,  $C^*$ ,  $h^\circ$  values and color strength (K/S) were calculated on acid dyed fibers as well. The analysis of dye bath was performed on the UV/VIS spectrophotometer Cary 50 Solascreen, Varian, Australia. The dyestuff exhaustion was calculated from the bath aliquots taken at the end of the dyeing process using the initial dyestuff concentration,  $D_0$  (g/L) in the bath and the concentration of the dyestuff remaining in the bath  $D_B$  (g/L). Dye exhaustion,  $D_{ex}$  (%) was calculated according to the following equation:

$$D_{ex} = ((D_0 - D_B) / D_0) \cdot 100 \quad (1)$$

The results of exhausted dye, and color strength are analyzed and compared. For the analysis of color strength, the highest K/S value was determined at 460 nm for Acid Red 111 and at 600 nm for Lanaset Navy R.

### 3. Results and Discussion

#### 3.1. Coarse Wool Changes in Scouring Process

Raw wool (RW) contains suint, greases and dirt (vegetable impurities, soil, sand, etc.), which depend on the sheep breed and its cultivation. Therefore, before any finishing, i.e., dyeing, printing, functionalizing, it must be scoured/washed to remove the natural and added impurities. During the scouring process, the loss of mass occurs depending on wool type (fine-coarse), chemicals used and process conditions. Considering more prevalent ecological aspects in general, three different scouring process were performed: conventional scouring (CS); enzymatic, bio-scouring (ES); and a two phase process (CS-E): conventional scouring and enzymatic after-treatment.

In Table 1. the loss of raw wool mass in scouring, mass of clean wool, extracted grease and dirt are given.

**Table 1.** The loss of raw wool mass in scouring ( $\Delta m_{scouring}$ ), and absolutely dry clean wool ( $m_{clean\ wool}$ ), extracted grease ( $m_{grease}$ ) and dirt ( $m_{dirt}$ ) present in wool.

Wool	$\Delta m_{scouring}$ [%]	$m_{clean\ wool}$ [%]	$m_{grease}$ [%]	$m_{dirt}$ [%]
RW	-	-	4.91	14.20
CS	30.13	69.87	0.99 <sup>a</sup>	12.90 <sup>b</sup>
ES	27.27	72.73	0.84 <sup>a</sup>	13.10 <sup>b</sup>
CS-E	29.15	70.85	0.75 <sup>a</sup>	13.80 <sup>b</sup>

<sup>a</sup> residual grease; <sup>b</sup> residual dirt.

After scouring, dirt and emulsified grease remain in the bath, while some impurities must be removed mechanically to obtain a clean wool fiber. From the results in Table 1, the loss of raw wool mass is highest in conventional scouring (approx. 30%) and lowest in enzymatic bio-scouring (approx. 27%). However, the mass of dirt removed mechanically is higher. One of the direct indicators of scouring efficiency is the amount of residual grease. Raw wool contains 4.91% grease, and after scouring it was 0.75% to 0.99%. The reason for the lowest value of 0.75% is due to two phase processes. Since the grease content in bio-scoured wool of 0.84% is also lower than in conventional scoured one, it can be concluded that the enzyme complex acts more strongly on grease.

Whether the scouring process was appropriate can be indirectly assessed from the changes in fiber properties. The results of alkali solubility, the solubility in urea bisulphite, reaction time in Krais–Markert–Vierteil reagent and in Allworden reagent are presented in Table 2.

**Table 2.** The alkali solubility (AS), the solubility in urea bisulphite (UBS), reaction time in Krais–Markert–Vierteil reagent ( $t_{KMV}$ ) and in Allworden reagent ( $t_A$ ) of raw and scoured wool.

Wool	AS [%]	UBS [%]	$t_{KMV}$ [min]	$t_A$ [min]
RW	18.60	48.20	-	-
CS	9.00	32.65	6–9	2
ES	10.75	33.15	7–8	2
CS-E	11.05	32.70	7–8	2

Microscopic examination in Krais–Markert–Vierteil reagent shows that all samples (CS, ES and CS-E) react in a period of 6 to 9 min, which confirms that no alkali or acid damage occurred to the fibers. In all wool samples fibers starts to swell in 2–3 min, scales become less visible, cross stripes occur and in 5 min the edges get characteristic knots. The full reaction occurs after 6 min on fine, and in 9 min on coarse fibers in conventionally scoured

wool. In enzyme scoured wool (ES, CS-E), the reaction occurs after 7 min on fine, and in 8 min on coarse fibers. Characteristic knots (Figure 1) can be seen, whilst the scales not, the stripes can be observed in the middle of the fiber and reagent bubbles inside medulla.

The same was confirmed by microscopy in the Allworden reagent, where all samples reacted within 2 min, which is characteristic of undamaged samples (Figure 1).

Measurement of alkali solubility (AS) gave values within the limits for undamaged fibers (9–12%), while for raw wool (RW) the value is slightly higher, since alkalis dilute part of the impurities present in raw wool. The solubility in urea bisulfite (UBS) for raw wool (RW) is about 50%, while the samples washed in an alkaline medium have a urea bisulfite content of about 30%, which corresponds to the recommendation of the standard.

Wool fibers have a high affinity for water, which at first glance is in contrast to their water repellency. However, due to the specific composition of wool fibers, water affinity depends not only on the interior of the fiber (which is generally held responsible for liquid absorption and swelling), but also on the nature of the fiber surface, which is structurally quite different from the interior of the wool fiber [1,8,41]. The sorption properties of wool fibers depend on physical and chemical factors. Physical factors originate in the morphological composition of the fiber in question and are explained by the capillary activity of the intermolecular and especially interfibrillar parts of the fiber. Chemical factors originate in the chemical composition of the fiber and are explained by the presence of some active hydrophilic groups (in wool these are the groups  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{COO}$ ,  $-\text{CONH}-$ ), which have the ability to bind water molecules and enable the fiber to react with water, dyes or other reagents. During the formation of keratin polymer molecules, crystalline and amorphous areas are formed and only the groups in the side chains remain free and active. When water penetrates a fiber, the water molecules combine with the free hydrophilic groups of the amorphous region to the point where there is an excess of water molecules, causing the keratin parts to move apart. Considerable structural changes occur, manifested by an increase in fiber diameter, usually referred to as fiber swelling [41]. However, there is a limit to dimensional changes, defined crystalline areas in the fiber, because the intermolecular bonds in these areas are so strong that no water can penetrate them. Since swelling is one of the most important indicators of the sorption properties of fibers, fiber diameter was measured on raw and scoured wool before (in cedar oil) and after swelling in water. The results are collected in Table 3 and in Figure 2.

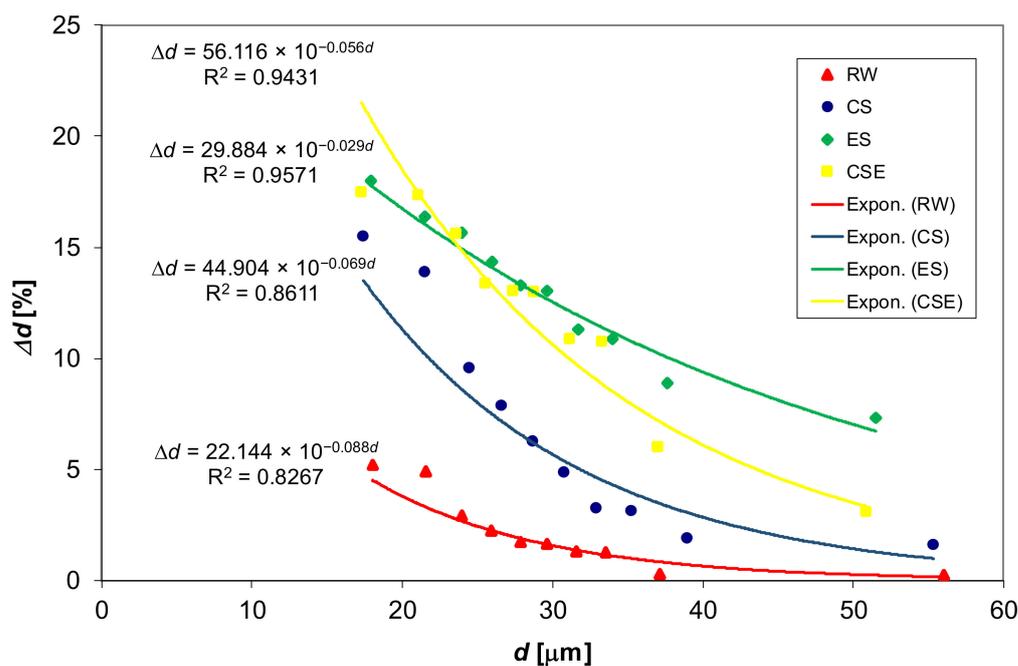


Figure 2. Degree of swelling raw and scoured wool in water.

**Table 3.** Fiber diameter ( $d$ ) of raw and scoured wool before (in cedar oil,  $d_1$ ) and after 24 h swelling in water ( $d_2$ ).

Wool/Group		RW		CS		ES		CS-E	
		$d_1$	$d_2$	$d_1$	$d_2$	$d_1$	$d_2$	$d_1$	$d_2$
Average $n = 1000$	$d_{range}$ [ $\mu\text{m}$ ]	10–132	10–138	10–118	12–124	10–132	12–136	10–112	12–136
	$d$ [ $\mu\text{m}$ ]	30.33	31.09	31.18	32.82	30.17	33.80	29.61	32.74
	CV [%]	40.75	38.79	37.62	32.81	34.17	31.75	33.72	30.15
Group 1 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	10–20	10–20	10–20	12–22	10–20	12–24	10–20	12–22
	$d$ [ $\mu\text{m}$ ]	18.02	18.96	17.42	20.12	17.90	21.12	17.30	20.12
	CV [%]	12.57	12.41	14.25	11.11	12.24	11.91	21.97	11.96
Group 2 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	20–22	22–24	20–24	22–26	20–22	24–26	20–22	22–26
	$d$ [ $\mu\text{m}$ ]	21.58	22.64	21.48	24.46	21.52	25.04	21.06	24.78
	CV [%]	3.79	4.14	4.31	4.17	3.99	4.01	4.76	4.66
Group 3 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	22–24	24–26	24–26	26–28	22–24	26–28	22–24	26–28
	$d$ [ $\mu\text{m}$ ]	23.94	24.64	24.46	26.8	23.98	27.74	23.58	27.26
	CV [%]	1.43	3.80	3.46	3.67	0.83	2.44	3.47	3.56
Group 4 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	24–26	26–28	26–28	28–30	24–26	28–30	24–26	28–30
	$d$ [ $\mu\text{m}$ ]	25.94	26.52	26.62	28.72	25.96	29.68	25.54	28.96
	CV [%]	1.31	3.32	3.49	3.36	1.09	2.48	3.31	3.47
Group 5 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	26–28	28–30	28–30	30–32	26–28	30–32	26–28	30–32
	$d$ [ $\mu\text{m}$ ]	27.90	28.36	28.66	30.46	27.90	31.66	27.34	30.90
	CV [%]	1.57	2.72	3.29	2.77	1.57	2.38	3.48	3.24
Group 6 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	28–30	30–32	30–32	32–34	28–30	32–34	28–30	32–34
	$d$ [ $\mu\text{m}$ ]	29.62	30.14	30.74	32.24	29.64	33.50	28.78	32.52
	CV [%]	2.66	1.70	3.16	2.03	2.61	2.59	3.41	2.71
Group 7 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	30–32	32–32	32–34	34–34	30–32	34–36	30–32	34–36
	$d$ [ $\mu\text{m}$ ]	31.58	32.00	32.92	34.00	31.70	35.28	31.12	34.50
	CV [%]	2.59	0	3.04	0	2.26	2.73	3.21	2.52
Group 8 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	32–34	32–36	34–36	36–38	32–36	36–40	32–34	36–38
	$d$ [ $\mu\text{m}$ ]	33.52	33.94	35.22	36.32	33.98	37.66	33.26	36.84
	CV [%]	2.56	1.56	2.78	2.03	3.50	2.62	2.92	2.69
Group 9 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	36–40	36–40	36–42	38–44	36–40	40–44	34–40	38–42
	$d$ [ $\mu\text{m}$ ]	37.12	37.20	38.94	39.68	37.62	40.96	37.02	39.24
	CV [%]	4.57	4.04	3.21	5.13	3.83	2.81	4.03	2.88
Group 10 $n = 100$	$d_{range}$ [ $\mu\text{m}$ ]	40–132	40–138	42–118	44–124	40–132	44–136	40–112	42–136
	$d$ [ $\mu\text{m}$ ]	56.06	56.22	55.34	56.22	51.50	55.28	50.86	52.92
	CV [%]	10.12	39.60	32.89	28.52	30.32	32.27	25.71	29.72

Note: Each group represents 10% of tested fibers; Group 1 is 10% of the finest fibers (fibers with the smallest diameter) while Group 10 is 10% of the coarsest fibers (fibers with the largest diameter).

The lower swelling of the raw wool compared to the scoured one is the result of the less available and more hydrophobic surface of a raw and greasy wool fiber. Swelling confirmed the influence of the scouring process to sorption properties, i.e., better sorption and higher swelling of the enzyme scoured wool (ES and CS-E) compared to the conventionally scoured one (CS). Enzyme scoured wool (ES and CS-E) swell significantly more than conventional scoured wool (CS) or raw wool (RW).

Since not all fibers swell uniformly because they do not have the same diameter (range from 10 to 132  $\mu\text{m}$ ) and finer fibers swell more, a detailed analysis of the swelling was performed. The swelling difference in fiber diameter ( $\Delta d$ ) were compared for each 10% of fibers in the sample (range of 100 fibers). The measuring of fiber diameter ( $d$ ) in cedar oil and after 24 h in water (Table 3), showed that the extent of swelling in each sample, regardless of the scouring process, depends exponentially on the fineness of the fiber (Figure 2). For fine fibers ( $d < 30 \mu\text{m}$ ), CS-E swells more or the same as ES. However, for coarser fibers ( $d > 30 \mu\text{m}$ ), sample ES is shown to swell significantly more than CS-E. A

slightly lower value of swelling may be due to partial damage of the CS-E, since the enzyme complex is applied on almost clean fibers, while in the case of a single bath the enzyme is acting on impurities.

During the determination of fiber diameter in cedar oil, the share of medullated fibers was determined. For the raw wool sample, it was expected to be about 15%, but there was only 6.7% (continuous medulla, con. 3.5%; discontinuous medulla, discon. 3.2%). In wool sample CS there was only 4% (con. 2.0%, discon. 2.1%). After bio-scouring sample ES, there was 9% (con. 5.8%, discon. 3.2%), and in the two-phase scouring process CS-E only 3.9% (con. 1.7%, discon. 2.2%) confirming that it depends not only on sheep, but on sampling as well.

From the results of tested wool properties, it can be seen that different scouring processes did not result in noticeable fiber damage or morphological changes. However, for most applications, scoured wool needs to be bleached to achieve brilliant whiteness or color. Therefore, after the scouring process, wool was bleached with an unconventional bleaching agent, percarbonate (PC), to achieve good whiteness with minimum damage in comparison to hydrogen peroxide (HP) bleaching.

### 3.2. Coarse Wool Changes in Bleaching and Dyeing Process

The changes after the bleaching process were monitored by sorption of moisture and dyestuff. The results of moisture content, expressed as regain, R, at different RH (30, 65, 72 and 100%), and degree of whiteness (W) and yellowing index (YI) are shown in Table 4.

**Table 4.** The moisture content (regain, R) at different RH (30, 65, 72 and 100%), degree of whiteness (W) and yellowing index (YI) of raw, scoured and bleached wool.

Wool	$R_{RH30}$ [%]	$R_{RH65}$ [%]	$R_{RH72}$ [%]	$R_{RH100}$ [%]	W	YI
RW	-	-	-	-	-2.5	25.9
CS	6.56	13.53	13.62	27.23	2.1	17.4
ES	6.77	14.15	14.64	29.53	10.3	14.3
CS-E	6.62	13.83	13.91	27.64	4.7	16.4
CS-HP <sup>1</sup>	8.12	15.42	15.22	30.34	12.7	13.7
CS-PC <sup>2</sup>	7.98	14.88	14.77	28.12	11.8	12.5
ES-HP <sup>1</sup>	8.11	15.74	15.66	32.33	17.6	10.3
ES-PC <sup>2</sup>	8.08	15.15	15.29	30.94	15.3	11.2
CS-E-HP <sup>1</sup>	8.14	15.51	15.74	32.45	14.7	12.0
CS-E-PC <sup>2</sup>	8.05	15.23	15.41	31.04	14.3	12.4

<sup>1</sup> Wool samples bleached with HP; <sup>2</sup> Wool samples bleached with PC.

In general, wool is characterized by high hygroscopicity, which means that it has a high ability to absorb and release moisture until an equilibrium is reached between the moisture in the surrounding area and in the fiber. Any change in the moisture content of the ambient air will result in a corresponding change in the fibers, which may lead to a change in the fiber properties [8,41]. From the results, it can be seen that the moisture content of the fibers increased with higher relative humidity, regardless of the scouring or bleaching process indicating good cleanup process. Although the moisture content differences between the samples are small at first glance, the trends can be identified. By comparing the scoured samples, it was found that the CS wool fibers absorb the least amount of moisture, while the moisture content in enzymatic treated wools (ES, CS-E) is higher. This correlates with fiber swelling results. After the bleaching process, the fiber surface opens and wool can absorb more moisture. Comparing the bleaching process, it can be seen that results achieved with PC are similar to the HP bleaching, which is considered the conventional one. This points out that bleaching of enzyme scoured wool results in better moisture sorption properties.

From the results of whiteness degree (W) and yellowing index (YI), it can be seen that the whiteness obtained by the enzyme treatment is significantly higher than that

obtained by conventional scouring (Table 4). The enzyme scoured wool (ES) exhibits the highest degree of whiteness. Since both enzymatic scoured wools have higher whiteness, it can be assumed that the enzymes also act as bleaching agents. After bleaching, better whiteness was obtained regardless of the bleaching agent used. The yellowing index is significantly lower, indicating that the pigments in natural wool are better degraded and the disulfide bonds are not affected. Again, bleaching of enzyme scoured wool results in better properties. It should be noted that PC bleaching of enzyme scoured wool (ES-PC) results in better whiteness, than when HP bleach is applied to conventional scoured wool (CS-HP). Comparing the whiteness degree of enzyme scoured wools it can be seen that better results were obtained in the single bath process (ES – W = 10.3, CS-E – W = 4.7). Oxidative bleaching reduces this difference, but ES still shows higher whiteness.

The removal of impurities and the whiteness obtained proved that the enzyme complex has an additional activity, removing the greasy hydrophobic layer. The Bactosol complex, a mixture of enzymes based on hydrolase enzymes, could cause the degradation and softening of scales on the wool fiber surface [20]. When the thin epicuticle layer is softened or removed, the barrier to dye diffusion and moisture and bleach is also removed. However, achieved results might be attributed to possible oxidative damage, so an SEM analysis was performed on selected fibers. The SEM micrographs are shown in Figure 3.

Using the SEM micrographs, the fiber surface was characterized. The morphology of wool fibers after conventional scouring (Figure 3a) resembles that of raw wool; the fibers have pronounced scales that are raised at the edges. Certain morphological changes are observed in the enzyme scoured fibers (Figure 3d), the scales are more adherent, the fiber is smoother and the edges are more closed. This is the reason why the wool was much easier to clean mechanically after enzyme scouring, as there were no fiber tangles (no felting). The fiber surface of wool scoured in the two-step process (CS-E) has scales that are more adherent (Figure 3g), but less than in the one-step process. After PC bleaching (Figure 3c,f,h) there are no morphological changes related to the scouring process. Although Prestogen W was used as buffer, after HP bleaching changes are observed—some scales detach. This is more pronounced on the conventional scoured wool fiber, indicating that enzyme scouring also contributes to the HP bleaching. This points out that more adherent scales and smoother fiber surface, as stated above, lead to low friction and an anti-felting property in the textile care processes [11,41,43].

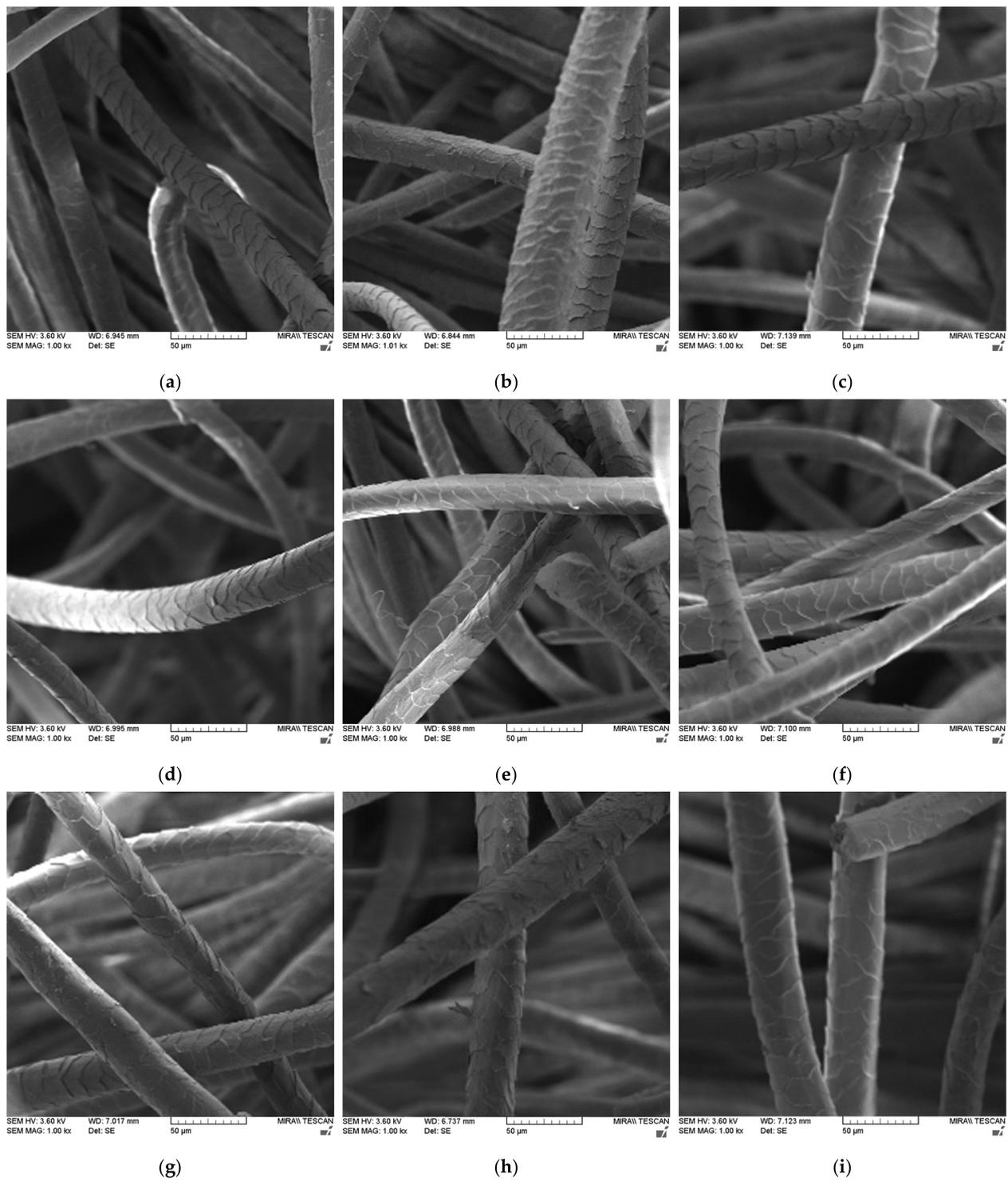
To determine adsorption, dyeing was performed with acid dyes Acid Red 111 and Lanaset Navy R (mixture of Acid Blue 225 and Acid Blue 317). Spectral analysis was performed using the results of spectrophotometric measurement of the dyed fibers, and the color strength (K/S) was calculated. The calibration curve was used for the calculation of the exhaustion of acid dyes after the dyeing process. Therefore, the different dyestuff concentrations were prepared and the absorbance was measured on UV/VIS spectrophotometer. The absorbance of dye solution before and after the dyeing process was measured and the concentration was calculated based on Lambert–Beer’s law.

The equations for calibration curve in regard to absorbance used for calculation are:

$$y = 0.0858x - 0.00459 \text{ for Acid Red 111}$$

$$y = 0.1263x - 0.00052 \text{ for Lanaset Navy R.}$$

The results of dye exhaustion expressed in % as well as spectral characteristics are shown in Tables 5 and 6.



**Figure 3.** SEM micrographs of scoured and bleached wool. (a) CS; (b) CS-HP; (c) CS-PC; (d) ES; (e) ES-HP; (f) ES-PC; (g) CS-E; (h) CS-E-HP; (i) CS-E-PC.

**Table 5.** Color parameters ( $L^*$ ,  $C^*$ ,  $h^\circ$ ), dye exhaustion ( $D_{ex}$ ) and color strength at 450 nm (K/S) of scoured and bleached wool fibers dyed with 3% owf Acid Red 111.

Wool	$L^*$	$C^*$	$h^\circ$	$D_{ex}$ [%]	K/S
CS	45.05	74.12	38.26	77.2	6.72
ES	45.53	76.93	38.54	82.4	7.34
CS-E	45.40	76.11	38.76	80.9	6.88
CS-HP	46.11	76.39	38.30	79.8	7.75
CS-PC	44.36	75.81	38.96	78.7	7.87
ES-HP	45.43	76.42	38.77	84.9	8.24
ES-PC	46.69	76.17	38.42	83.8	8.68
CS-E-HP	45.52	76.36	38.88	82.1	8.04
CS-E-PC	46.04	76.14	38.79	82.0	8.01

**Table 6.** Color parameters ( $L^*$ ,  $C^*$ ,  $h^\circ$ ), dye exhaustion ( $D_{ex}$ ) and color strength at 600 nm (K/S) of scoured and bleached wool fibers dyed with 3% owf Lanaset Navy R.

Wool	$L^*$	$C^*$	$h^\circ$	$D_{ex}$ [%]	K/S
CS	18.12	12.27	277.12	82.8	3.67
ES	17.96	11.98	277.07	86.5	4.21
CS-E	18.05	12.04	277.31	85.0	3.97
CS-HP	19.03	12.19	276.67	85.5	4.33
CS-PC	18.61	12.60	277.36	84.9	4.07
ES-HP	19.07	13.65	276.05	88.0	5.54
ES-PC	18.43	12.57	277.19	87.6	4.97
CS-E-HP	18.54	12.87	277.30	87.8	5.28
CS-E-PC	18.71	12.62	277.26	87.6	4.93

The results of the color parameters presented in Tables 4 and 5 show a color analysis of the wool fibers pretreated with different agents and procedures, dyed with acid dyes. The fibers dyed with the Acid Red 111 have similar lightness ( $L^*$ ) and hue ( $h^\circ$ ), but differ in chromaticity (Table 5). Although chromaticity ( $C^*$ ) does not correspond to the percentage of dye on the material, it increases as the amount of dye on the fiber increases. Therefore, it can be considered an indirect measure of the dye adsorbed on the fiber. The fibers dyed with metal-complex acid dye Lanaset Navy R results in dark shade ( $L^* > 18$ ), so the chromaticity and hue are similar (Table 6). The result of color strength (K/S) show that enzyme scoured wool (ES and CS-E) generally has higher chromaticity (for Acid Red 111) and color strength (for both dyes) than conventionally scoured wool (CS). This confirms the findings of other authors [45,46] that enzyme action removes the barrier to dye diffusion. It also allows better activity of bleach, so additional bleaching with HP and PC not only removes pigments, but also opens the structure, resulting in higher chromaticity and color strength. The results of dye exhaustion confirm these findings.

#### 4. Conclusions

Enzyme scouring of coarse medullated wool resulted in better fiber properties—higher adsorption and whiteness, better dyeability and less tendency to felt without causing negative morphological changes or chemical damage to the fibers. The results of enzyme application in a single bath process are even better than in two phase processes. The properties obtained are maintained even after the bleaching process. It should be noted that percarbonate bleaching offers additional environmental advantages, as the medium is slightly alkaline. It does not cause fiber damage, but improves whiteness and opens the fiber structure, resulting in higher sorption and better dyeability.

Considering the sustainability of the processes and environmental protection, one-bath enzyme scouring and percarbonate bleaching should be recommended as pretreatments for coarse wool.

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