

5930 words

## **Hide unhairing: Achieving lower pollution loads, decreased wastewater toxicity and solid waste reduction**

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### **Abstract**

This study aims to diminish the pollution being discharged into wastewaters through changes in the unhairing process. To this aim, we are replacing a reductive hair degrading process with a process which combines a reductive hair degrading process with an oxidative hair degrading process. Hydrogen peroxide is used to decrease the supply of sulfide as unhairing chemical. As a result, commercially acceptable leather regarding both costs and quality is obtained and significant reductions in the contaminant load of the wastewater being discharged are observed. Results indicate that wastewater conductivity is

23 cut by 26%, suspended solids decrease by 75%, observable sulfide disappears, while the  
24 amount of chromium being absorbed by the hides is increased. This leads to considerable  
25 savings in the chromium salt offer in hide tanning and, consequently, a decrease in the  
26 amount chromium in the wastewater.

28 *Keywords: Unhairing; Tanning; Leather; Hydrogen peroxide; Pollution reduction*

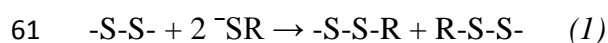
## 30 **1. Introduction**

32 Chemically speaking, tanning means stabilizing a protein called collagen, which is  
33 the main constituent of the skin. The tanning process may be divided into several stages.  
34 The beamhouse procedures are cleaning operations that prepare the hides for the  
35 subsequent leather making process. Beamhouse involves high water consumption and is  
36 considered as highly polluting. Actually, this is the stage that generates the most polluted  
37 wastewaters (Saravanabhan et al., 2006) and most solid waste (Kanagaraj et al., 2015).  
38 According to data published by the International Union of Leather Technologists and  
39 Chemists Societies (IULTCS, 2008), the beamhouse stage uses about 60% of all the water  
40 consumed in the whole tanning process and generates about 75% of the chemical oxygen  
41 demand (COD), 80% of suspended solids (SS), and 100% of sulfide ( $S^{2-}$ ).

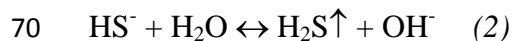
42 These data are an average assuming good practices in working conditions.  
43 According to the Food and Agriculture Organization of the United Nations (FAO, 2013),  
44 yearly world production of cattle hides, expressed in wet salted weight, approaches 6.5 Mt.  
45 This means that each year beamhouse operations worldwide approximately consume 104

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4 46 Mm<sup>3</sup> of water. Likewise, approximately 0.91 Mt of COD, 0.036 Mt SS and 0.62 Mt of S<sup>2-</sup>  
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6 47 are generated. These figures are actually lower than the real ones especially for two  
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8 48 reasons. First, numerous tanneries are located in countries where environmental laws are  
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10 49 practically nonexistent, which suggests that the import figures are actually higher. Second,  
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12 50 besides tanned cowhides, also other types of skins are being tanned worldwide (sheep, pigs,  
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14 51 reptiles, etc.), although to a much lesser extent. In fact, cowhides account for approximately  
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16 52 75% of total world leather. All in all, the figures above suggest that the pollution generated  
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18 53 during the beamhouse stage may be considered a major environmental problem.  
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23 54 Unhairing, one of the operations during the beamhouse stage, consists in removing  
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25 55 the hair or wool off the hides and skins. The reagents conventionally being used during this  
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27 56 operation are sodium sulfide and/or sodium hydrosulfide and lime. After a reductive  
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29 57 reaction, the joint action of hydrosulfide (HS<sup>-</sup>) and hydroxyl (OH<sup>-</sup>) ions causes the  
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31 58 disruption of the disulfide bridges of hair cystine, thus transforming it into cysteine and  
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33 59 obtaining the subsequent hydrolysis of keratin (hair protein). *Eq. (1)* shows one of the  
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35 60 possible mechanisms of this reaction.  
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43 62 The hydrolysis of keratin influences the characteristics of the effluent resulting from  
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45 63 the unhairing process, and therefore its COD and Total Kjeldahl Nitrogen (TKN) values are  
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47 64 considerably high. The presence of hydrosulfide and sulfide ions is also a major challenge,  
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49 65 especially due to the possibility of transformation into hydrogen sulfide (Black et al.,  
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51 66 2013). Over the years there have been numerous poisonings and even fatalities due to  
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53 67 inhalation of hydrogen sulfide. Theoretically, hydrogen sulfide production should be  
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55 68 avoided by maintaining the pH of the float at a certain level, as the chemical reaction below  
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57 69 shows in *Eq. (2)*.  
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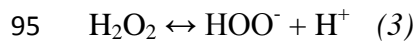
7 71 Unfortunately though, production of hydrogen sulfide has not always been avoided.

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9 72 Besides, sulfide and hydrosulfide ions are not completely removed from the hides,  
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11 73 which is also major drawback. The next step after unhairing is the fleshing operation, in  
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13 74 which a large amount of solid waste is generated. The fleshings contain sulfides and this  
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15 75 increases the difficulty and cost of their recovery for glue, gelatin or cosmetic production  
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17 76 (Bayramoglu et al., 2014).  
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21 77 In the last decades numerous studies (Vidal et al., 2004; Sengil et al., 2009; Haydar  
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23 78 and Aziz, 2009) have been carried out to try to minimize the environmental impact of  
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25 79 unhairing. One of the systems to reduce pollutant loads from residual floats and thus  
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27 80 facilitate their subsequent treatment is to implement the hair recovery process (Frendrup,  
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29 81 2000; Valeika et al., 2009; Galarza et al., 2010). This process consists of two parts: First the  
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31 82 shaft of the hair is protected with lime against the attack of sodium sulfide. This operation  
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33 83 is called immunization and involves the formation of compounds such as lanthionine (see  
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35 84 Fig. 1) and other similar compounds. As a result, only the hair root undergoes  
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37 85 hydrolyzation, whereas the shaft of the hair separates from the hide without hydrolyzing,  
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39 86 and COD and TKN values are significantly reduced in the wastewater float. Subsequently,  
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41 87 the hair root must be hydrolyzed by adding more sodium sulfide. This system is used on an  
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43 88 industrial scale and its main problem is the presence of sulfides in waste floats and in  
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45 89 unhaired hides.  
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53 90 Another line of research is based on the use of hydrogen peroxide as an unhairing  
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55 91 agent instead of sodium sulfide/hydrosulfide (Bronco et al., 2005; Morera et al., 2008;  
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57 92 Andrioli and Gutterres, 2014). Hydrogen peroxide, at pH values close to 13, is capable of  
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4 93 hydrolyzing the hair through an oxidative reaction. The oxidative attack of the S-S bond is  
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6 94 due to the formation of peroxy anion from hydrogen peroxide (*Eq. (3)*).



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11 96 Research has also been conducted to explore the possibility of performing this type  
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14 97 of unhairing by immunizing the hair first in order to minimize the pollution load from  
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16 98 wastewater floats. The environmental impact of this practice has been evaluated by  
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18 99 performing a life cycle assessment (LCA) (Castiello et al., 2006). This system reduces the  
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21 100 pollution discharged and eliminates sulfides in the wastewater. However, further research is  
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23 101 needed to implement it in the industry.

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26 102 The use of enzyme products to replace sodium sulfide as an unhairing agent is an  
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28 103 old practice (Heidemann, 1993). The problem is that the enzymes used to date, besides  
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30 104 attacking the hair, do also attack the collagen, thus damaging the surface of the hides. Of  
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33 105 course, this considerably diminishes the commercial value of hides and therefore is an  
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36 106 impediment to the industrial application of this system. However, numerous researchers are  
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38 107 currently exploring the behavior of various unhairing enzymes on the hides under different  
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40 108 conditions of pH, temperature, concentration, etc. (Thangam et al., 2001; Jian et al., 2011;  
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42 109 Dettmer et al., 2012).

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45 110 In short, there are various lines of research open to explore the replacement of  
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48 111 sodium sulfide as unhairing agent. So far though, an effective, inexpensive product that  
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50 112 may be applied at an industrial scale has not yet been found.

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53 113 Our work has studied the possibility of modifying the reductive unhairing process  
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55 114 with hair recovery (using lime, sodium sulfide and sodium hydrosulfide), combining it with  
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57 115 an oxidative unhairing (using hydrogen peroxide) to obtain less polluted wastewater.  
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59 116 Moreover, the new process is less toxic due to sulfide removal.  
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4 117 Specifically our studies aim to eliminate the use of sodium sulfide to hydrolyze the  
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6 118 hair root, replacing it with hydrogen peroxide, as well as examine the consequences of this  
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9 119 change in the discharged wastewater. The anticipated improvement in wastewater quality  
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11 120 should not compromise the physical properties of the leather required for the manufacture  
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14 121 of consumer goods.

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## 17 18 19 123 **2. Materials and methods**

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### 23 24 125 **2.1. Materials**

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29 127 Part of the laboratory tests were carried out using 0.40 m in diameter and 0.15 m  
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32 128 wide stainless steel drums, Inoxvic brand. The rest of the laboratory tests and the pilot plan  
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34 129 tests were carried out using 1 m in diameter and 0.4 m wide stainless steel drums, Olcina  
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36 130 brand. Drums are cylindrical vessels that rotate around an axle (Fig. 2).

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39 131 The chemicals and the machinery used in the beamhouse operations were those  
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41 132 normally used in the leather industry: Sodium hydroxide (50% w/w), lime (95% w/w),  
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44 133 sodium hydrosulfide (70% w/w), sodium sulfide (60% w/w), formic acid (85% w/w) and  
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46 134 ammonium sulfate (99% w/w). The bating agent is a commercial product based on proteatic  
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49 135 enzymes. Provided by TFL its name is Oropon OR. The unhairing auxiliary is a  
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51 136 commercial product that is based on secondary amines and has unhairing properties.  
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54 137 Provided by Cromogenia Units S.A. its name is Ribersal PLE BASE. For laboratory  
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56 138 analysis grade chemicals were used.

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59 139 Soaked and fleshed bovine hides were used in order to perform the tests.  
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141 **2.2. Methodology**

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143 All tests were conducted in triplicate.

144 The experimentation was performed in two stages, namely laboratory and pilot  
145 plant, which will be detailed below.

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147 *2.2.1. Laboratory tests.*148 The objective of these tests was to determine the amount of hydrogen peroxide  
149 required to remove the hair roots with the same efficiency as the traditional method, based  
150 on the use of sodium sulfide and / or hydrosulfide.151 Three soaked and fleshed bovine salted hides were used to perform the tests. The  
152 first part of the reductive unhairing was performed following the traditional formula (Table  
153 1).

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**Table 1**

Laboratory tests: Reductive unhairing formula (first part)

100% Water	T = 30 °C
0.5% Sodium hydroxide (50%)	Rotate 10 min.
1% Amine product	Rotate 1 h. pH = 10
0.8% Lime	Rotate 30 min.
1% Sodium hydrosulfide	Rotate 30 min.
1% Sodium sulfide	Rotate 8 h. Overnight rest
	Rotate 2h.
Wash twice	

Rest 24 h. on a horse

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157 Subsequently, five pieces of approximately 0.1 m × 0.5 m were cut from each hide.

158 The pieces were cut from the center of the hide to establish comparative tests. The pieces

159 were then subjected to treatment with hydrogen peroxide (oxidative unhairing) to remove

160 hair roots that remained in the skin. Each piece was processed separately, thus varying the

161 offers of hydrogen peroxide. Offers of sodium hydroxide and formic acid were also varied

162 to maintain the appropriate pH of the skin at all times. Table 2 shows the formula of

163 oxidative unhairing, while Table 3 outlines the various offers tested on the chemicals.

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**Table 2**

Laboratory tests: Oxidative unhairing formula

30% Water	T = 25 °C
0.5% Sodium hydroxide (50%)	Rotate 15 min.; pH =13
X/2% Hydrogen peroxide (50%)	Rotate 15 min.
Y% Sodium hydroxide	Rotate 15 min.
X/2% Hydrogen peroxide (50%)	Rotate 2 h.
Z% Formic acid	In three times. Rotate 45 min.
170% Water	Rotate 3.5h. Night: Rotate 5 min. per hour. pH = 8.7

Drain and wash the hide

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**Table 3**

Offer of chemicals for each laboratory test

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Test	Hydrogen peroxide (X%)	Sodium hydroxide (Y%)	Formic acid (Z%)
1	4.5	4	2
2	3	2	1.5
3	2.5	1.67	1.4
4	2	1.33	1.3
5	1	0	0.5

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169 After completing all the oxidative unhairing tests, cuts were made in each piece of  
 170 hide and the pieces were cut in halves. The cross section of each piece was observed and  
 171 photographed by a Leica Stereomicroscope MZ12.5. The amount of root hairs that  
 172 remained unhydrolyzed in each of the pieces of hide determined the amount of hydrogen  
 173 peroxide to be used in the formulations of the pilot plant tests.

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### 175 2.2.2. Pilot plant tests

176 When hydrogen peroxide is in contact with the hide at high pH values, both the hair  
 177 and the collagen get hydrolyzed. This hydrolysis decreases the values of the physical  
 178 properties of the leather while it increases its capacity for absorbing chromium (Morera et  
 179 al., 2006).

180 First, laboratory tests determined the amount of hydrogen peroxide needed for  
 181 conducting an effective unhairing (Section 2.2.1.). Our objective was then to find out the  
 182 influence of the length of the oxidative unhairing on the physical properties and chrome  
 183 absorption of the final leather as well as the values of certain parameters in wastewater  
 184 floats resulting from unhairing and tanning. We must consider that not all leathers are

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4 185 expected have the same properties. These depend on the final leather goods intended to be  
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6 186 manufactured. It is by all means important to determine the minimum time possible for the  
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9 187 oxidative unhairing to work, since the greater the hydrolysis of hair and hide, the higher the  
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11 188 pollutant loads in the effluents. This parameter is also extremely significant because it will  
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14 189 determine the amount of chromium salt to be added in subsequent tanning operations.  
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16 190 Adding too much chromium salt leads to higher concentrations of chromium in  
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19 191 wastewaters, which is not only detrimental to the environment, but also raises water  
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21 192 treatment costs.

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23 193 To perform the test a first reductive unhairing was performed on three soaked and  
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26 194 fleshed hides, following the formulation shown in Table 1. Subsequently, each hide was  
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29 195 divided in four symmetric pieces.

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31 196 Then one piece was separated from each hide. An oxidative unhairing, with an offer  
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33 197 of 3% hydrogen peroxide, was carried out for each of the remaining pieces. This amount  
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36 198 was chosen based on the results of the laboratory tests (Section 2.2.1.). The rotating time  
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38 199 was different for each of the tests performed: 2 hours, 4 hours and 6 hours respectively.

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41 200 The formula being used is shown in Table 4, which includes the chemical operation  
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43 201 performed immediately afterwards, known as bating. The aim of bating is to hydrolyze the  
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45 202 proteins called elastins to get softer hides. In our case the bating was very soft (because the  
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48 203 hydrogen peroxide hydrolyzes the collagen more that the sodium sulfide does).

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**Table 4**

Pilot plant tests: Oxidative unhairing formula

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30% Water

T = 25 °C

1% Sodium hydroxide (50%)

Rotate 30 min.; pH =13

1.5% Hydrogen peroxide (50%)	Rotate 15 min.
2% Sodium hydroxide (50%)	Rotate 15 min.
1.5% Hydrogen peroxide (50%)	Rotate 2 h., 4 h. or 6 h.; pH =11.2-11.4
1.5% Formic acid	In three times. Rotate 45 min.
170% Water	Rotate 6h. Night: Rotate 5 min. per hour. pH = 7.8
	Drain
200% Water	T = 30°C
	Rotate 20 min.
	Drain
150% Water	T = 37°C
0.1% Bating agent	Rotate 20 min.; pH = 8.5
Drain and wash	

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206 To quantify improvements in the reductive-oxidative system versus the reductive  
207 system (already implemented on an industrial scale), the unhairing of the fourth piece of  
208 each hide was completed with a traditional reductive unhairing. The formula we used is  
209 shown in Table 5, which includes the chemical operations performed immediately  
210 afterwards: deliming and bating. Deliming was carried out in order to remove lime and  
211 alkaline products from within the skins or hides.

212 After bating, all the tested hides were collected, placed in the same drum and the  
213 process continued.

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**Table 5**

 Pilot plant tests: Reductive unhairing formula (second part)
 

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200% Water	T = 30°C
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1% Sodium sulfide	
2% Lime	Rotate 6 h. Overnight rest
	Drain
200% Water	T = 30°C
	Rotate 20 min.
	Drain
150% Water	T = 37°C
0.3% Sodium metabisulfite	
1.5% Ammonium sulfate	Rotate 30 min.; pH = 8.5
1% Bating agent	Rotate 1 h.
Drain and wash	

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217           The wastewaters resulting from all the unhairings were analyzed. We focused only  
218 on the effluents resulting from the second part of the unhairing, in which the hair root had  
219 been hydrolyzed, since the first unhairing stage is common for both systems under  
220 examination. Subsequently, the hides continued to be processed until they underwent the  
221 tannage with chromium salt. We then performed physical and chemical tests on the  
222 resulting leathers and final effluents to quantify the differences between the two systems.

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### 224 *2.2.3. Physical testing and chemical analysis*

225           The parameters analyzed in the wastewaters from the unhairing operation were  
226 Chemical Oxygen Demand (COD), Suspended Solids (SS), Conductivity and sulfide  
227 content ( $S^{2-}$ ).

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228 Analyses of COD, SS and Conductivity were carried out according to the Standard  
229 Methods (APHA, 1998).

230 Sulfide content was determined through the Sulfide Test Kit, reference 114779,  
231 Merck brand, which is a photometric method.

232 Chromium oxide content in the tanning effluents was analyzed following the ASTM  
233 D-3898-93 standard, which is a test method for chromic oxide in basic chromium tanning  
234 liquors (ASTM, 2009).

235 The Official IUP and IUC methods specified below were followed to analyze the  
236 leather: *IUP 6 (ISO 3376:2011). Determination of tensile strength and percentage*  
237 *extension (IUP 6, 2011); IUP 8 (ISO 3377-2:2002). Determination of tear load - Part 2:*  
238 *Double edge tear (IUP 8, 2002); IUP 9 (ISO 3379:2015). Determination of distension and*  
239 *strength of surface (Ball burst method) (IUP 9, 2015); IUP 16 (ISO 3380:2015).*  
240 *Determination of shrinkage temperature up to 100 °C (IUP 16, 2015) and IUC 8-1 (ISO*  
241 *5398-1:2007). Chemical determination of chromic oxide content. Part I: Quantification by titration*  
242 *(IUC 8-1, 2007).*

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### 244 **3. Results and discussion**

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#### 246 **3.1. Laboratory tests**

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248 Fig. 3 shows the cross section of the hide after the reductive unhairing was  
249 performed. Numerous remains of hair were clearly visible. The addition of hydrogen  
250 peroxide led to the removal of these hair remains. It was necessary to add 3% hydrogen

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4 251 peroxide to virtually achieve complete removal. Likewise, it was observed that the  
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6 252 hydrogen peroxide bleaches the hair before hydrolyzing it completely. This actually  
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9 253 constitutes an advantage for the tanner because even if traces of hair remain, if they are  
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11 254 colorless, they do not detract from the quality of the leather as the final color of the product  
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14 255 is not affected. However, if the hair remains are black, which sometimes occurs when  
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16 256 applying traditional reductive unhairing, small black spots usually appear, resulting in  
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19 257 leather that may lack the desired evenness and color brightness. Figs. 4 and 5 show cross  
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21 258 sections of two hides unhaird with 1% and 3% hydrogen peroxide. The hide unhaird with  
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23 259 1% hydrogen peroxide clearly shows remains of hair that are yet to be hydrolyzed, while  
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26 260 the hide unhaird with 3% hydrogen peroxide shows that hydrolysis is almost complete.  
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29 261 Only tiny remains may be appreciated in the form of different colors dots.

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31 262         Considering that hydrogen peroxide hydrolyzes not only keratin but also collagen, it  
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33 263 was concluded that the 3% hydrogen peroxide offer was most fit for the types of hides used  
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36 264 in the tests. This offer enabled a sufficient degree of unhairing of the hides, while  
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38 265 sustaining a minimal degradation of the collagen, that is to say, it preserved the physical  
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41 266 properties of the hide. It is important to note that this amount was valid for the hides used in  
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43 267 the experiments described, but may vary depending on the type of hides. The more similar  
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46 268 the hides being used are to the ones being used in the tests, the more the ideal offer will  
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48 269 approach 3%. It stands to reason that if one wants to unhair cattle hides the ideal percentage  
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51 270 of hydrogen peroxide will be closer to 3% than if one intends to unhair goatskins, for  
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53 271 example. Nor should we forget that the offer of unhairing chemicals is traditionally  
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55 272 measured on hide weight but should really be measured in relation to hide yield, since what  
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58 273 really matters is the amount of hair contained in the hide, not the total amount of hair and  
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60 274 collagen. It is also commonly known that black hair is harder to remove than white hair, for  
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275 example. Therefore, within cattle hides, the ideal percentage of hydrogen peroxide may  
 276 vary depending on factors including animal breed and hair color.

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### 278 **3.2 Pilot plant tests**

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280 After performing the different unhairings, the cross sections of the hides were  
 281 observed through the lens. Fig. 6 shows the appearance of the hide after the second  
 282 unhairing, in this case using sodium sulfide to hydrolyze the hair. Figs. 7, 8, and 9 show the  
 283 appearance of the skin after the second unhairing, using in this case hydrogen peroxide as  
 284 unhairing agent with different rotating times (2 hours, 4 hours and 6 hours). The second  
 285 reductive unhairing hydrolyzes virtually all the hair but in Fig. 6 remains of black hair are  
 286 still observed. These remains may damage the final appearance of the leather, especially if  
 287 the desired item requires light color unfinished leather. Fig. 7, 8 and 9 outline two  
 288 conclusions. The first is that with 3% hydrogen peroxide and after 2 hours of unhairing, the  
 289 hair remains are already decolored, evolving from black to yellow. The second is that the  
 290 longer the unhairing time, the more the hair remains are effectively hydrolyzed.

291 The results of the analyses of unhairing and tanning effluents as well as the physical  
 292 and chemical tests of the final leather are shown in Table 6.

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**Table 6**

Pilot plant tests: Results of comparative analyses

Type of unhairing (second part)	Oxidative		Reductive	
Time (h)	6	4	2	
<i>Wastewater analyses</i>				
Conductivity (mS/cm)	6.85±0.34	6.66±0.33	7.33±0.37	9.86±0.49

SS (kg/t hide)	2.35±0.12	1.56±0.07	1.89±0.10	6.36±0.32
COD (kg/t hide)	16.97±0.34	12.83±0.23	11.00±0.23	11.28±0.21
Sulfide (kg HS <sup>-</sup> /t hide)	0	0	0	1.0±0.1

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*Leather analyses*

Chromium of leather (% Cr <sub>2</sub> O <sub>3</sub> )	3.45±0.02	3.38±0.02	3.28±0.02	3.14±0.02
Shrinkage temperature (°C)	112±1	113±1	112±1	107±1
Tensile strength (N/mm <sup>2</sup> )	1313±28	1502±30	1882±41	2323±44
% Elongation	63.2±2.4	63.7±2.6	66.2±2.5	69.4±2.8
Tearing Load (N/mm)	99.3±6.0	113.3±6.8	127.9±7.7	146.8±8.8
Grain Crack Load (N)	57±3	57±3	49±3	40±2
Grain Crack Distension (mm)	12.03±0.30	11.55±0.29	11.86±0.30	12.55±0.31

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The results of the analyses of the unhairing effluents suggest the conclusions set out

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below. The conductivity of the unhairing effluent decreases dramatically (between 26% and

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32%) when replacing sodium sulfide and calcium hydroxide with hydrogen peroxide and

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sodium hydroxide. This is reasonable since in the first case (sodium sulfide and calcium

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hydroxide unhairing) more salts are formed than in the second case (hydrogen peroxide and

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sodium hydroxide unhairing), in which hydrogen peroxide is transformed into water.

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Suspended solids show a similar behavior towards conductivity, decreasing between 63%

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and 75% when using oxidative unhairing versus reductive unhairing. The presence of

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excess calcium hydroxide (very insoluble) in the reductive unhairing may explain this

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decline. The rise in suspended solids when increasing unhairing time using hydrogen

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peroxide is probably due to a greater partial hydrolysis of the hair and the collagen.

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Regarding the chemical oxygen demand, it is found that when the oxidative unhairing takes

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2 hours, the results are practically the same as those obtained through reductive unhairing.

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4 309 By increasing the time of the oxidative unhairing, COD rises up to 50%. This increase is  
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6 310 due to a greater hydrolysis of collagen, which raises the organic matter in the float. It is also  
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9 311 noteworthy that in oxidative unhairing, sulfide content is not detected, which is reasonable,  
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11 312 as no sodium sulfide has been used in the process. In contrast, in reductive unhairing  
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14 313 sulfide does indeed appear in the effluents. The presence of sulfide involves increased risks  
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16 314 to workers due to its toxicity. Also, it raises the toxicity parameter of wastewaters, which in  
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19 315 turn increments treatment costs. During wastewater treatment sulfides are oxidized to  
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21 316 sulfates, a new source of problems within the treatment process. Finally, it is interesting to  
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24 317 note that in the oxidative unhairing the role of acid formic is not only to decrease pH of  
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26 318 medium. It also acts as a deliming chemical. Therefore the addition of ammonium  
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29 319 compounds is avoided, which is very good from environmental point of view.

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31 320 The results of the chemical and physical analyses to which the final leather was  
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33 321 subjected enable us to reach the conclusions set out below. The hides that underwent  
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36 322 oxidative unhairing absorbed higher amounts of chrome (between 4% and 10% rises) than  
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38 323 those that underwent reductive unhairing. According to some authors (Shi et al., 2003) this  
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41 324 is probably due to increase of carboxyl groups derived from oxidation of aminoacid  
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43 325 residues containing hydroxyl groups thus serine and threonine residues. Chromium mainly  
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46 326 coordinates with collagen by forming links with carboxylic groups. When the duration of  
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48 327 the oxidative unhairing increases, the oxidative effect is boosted; thus the number of  
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51 328 carboxylic groups rise and, consequently, more chrome is absorbed. The chromium content  
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53 329 in the leather affects its physical properties. Actually, if the leather absorbs an excess of  
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55 330 chromium its overall quality may even be damaged. In oxidative unhairing a smaller offer  
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58 331 of chromium salt is needed to get the same amount of chromium absorption as in reductive  
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60 332 unhairing, which implies that the chromium content of the effluent, and therefore its  
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4 333 pollution load, will be smaller. This constitutes an economic advantage because it involves  
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6 334 both less spending on the chromium salt needed for tanning and less spending on  
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8 335 wastewater treatment. The shrinkage temperature depends on the amount of chromium  
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10 336 coordinated with the collagen. Leathers unhaired through oxidative unhairing show higher  
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12 337 shrinkage temperatures than those unhaired through reductive unhairing. It must be noted  
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14 338 that the three pieces of leathers unhaired with hydrogen peroxide show exactly the same  
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16 339 shrinkage temperatures, which suggests that once a certain point has been reached more  
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18 340 absorption of chromium does not contribute to increasing the degree of tanning (resistance  
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20 341 to collagen degradation) of the leather. Tensile strength, elongation and tear strength follow  
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22 342 the trends described above. The values obtained by the leathers unhaired using hydrogen  
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24 343 peroxide are lower than those obtained by the leathers unhaired using sodium sulfide. The  
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26 344 longer the oxidative unhairing, the lower the tensile strength values. The most significant  
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28 345 changes occur in the tensile strength values, with decreases ranging from 19% to 43%. Tear  
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30 346 strength values show more moderate falls, between 13% and 33%. The decrease in  
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32 347 elongation values is even more moderate, between 4% and 9%. The greater hydrolysis of  
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34 348 collagen is probably the main reason for the decrease in these physical properties. The  
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36 349 measurement of the distension and strength of the grain by the ball burst test shows that a  
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38 350 stronger force (between 21% and 42%) must be applied to break the grain (the upper and  
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40 351 most valued part of the hide) in hides subjected to oxidative unhairing versus those  
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42 352 subjected to reductive unhairing. Besides, the longer the oxidative process, the greater the  
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44 353 strength to be applied in order to break the grain. In contrast, the distension is slightly  
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46 354 higher in the hides subjected to reductive unhairing (between 4% and 5%). This shows that  
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48 355 the longer the oxidative process, the greater the distension.  
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4 356 From the overall results, it can be concluded that with a two-hour oxidative unhairing  
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6 357 the leathers obtained show similar chemical and physical characteristics to the leathers  
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9 358 unhairied through reductive unhairing. Besides, much less contamination is generated in the  
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11 359 wastewater, especially in conductivity (26% decrease), suspended solids (75% decrease)  
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14 360 and sulfides (100% decrease). If the time of oxidative unhairing increases, the physical  
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16 361 properties of the leather deteriorate, the COD increases, and conductivity and SS in  
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18 362 wastewater decrease. Also, the amount of chromium contained in the leather increases 4%.  
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21 363 Therefore, chromium salt offer in the tannage may be reduced and, consequently, the  
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23 364 amount of chromium present in the effluents resulting from the tannage may also decrease.

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26 365 Therefore, our research suggests that oxidative unhairing enables to obtain similar  
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28 366 quality leathers while significantly decreasing the pollution being discharged into  
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30 367 wastewaters. Oxidative unhairing also allows for an easier use of the solid waste generated  
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33 368 (sulfide-free fleshings).

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### 37 38 370 **3.3. Economic considerations**

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43 372 As it is less pollutant, oxidative unhairing presents economic advantages in terms of  
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45 373 cost of wastewater treatment (unhairing and tanning) and solid waste management  
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48 374 (fleshings without the presence of sulfides). From the commercial viewpoint, no problems  
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50 375 are observed, since the final leather shows similar or even better quality (depending on the  
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52 376 final product) than the final leather obtained following the traditional unhairing process.

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55 377 At this point though, it is imperative to compare the costs of the two unhairing  
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58 378 systems to ensure that the proposed system is feasible on an industrial scale. This may be  
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60 379 calculated by simply comparing the costs of the reagents used in each process, since the  
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380 other factors (water consumption, rotating time, among others) are virtually the same in  
 381 both systems. This comparison is shown in Table 7. The costs in the calculations were  
 382 supplied by a distributor of chemicals and are representative of those currently being  
 383 applied in Spain.  
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**Table 7**

Economic viability study

Unhairing type	Chemical	t chemical /t hide	Price (€/t chemical)	Cost (€/t hide)
	Sodium sulfide	0.1	870	87
	Lime	0.2	150	30
Reductive	Sodium hydrogen sulfite	0.03	480	14.4
	Ammonium sulfate	0.18	310	55.8
	Bating agent	0.1	900	90
	<b>TOTAL COST</b>			<b>277.2</b>
	Sodium hydroxide	0.3	240	72
	Hydrogen peroxide	0.3	360	108
Oxidative	Formic acid	0.15	620	93
	Bating agent	0.01	900	9
	<b>TOTAL COST</b>			<b>282</b>

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387 The cost difference in the chemicals of both unhairing processes is 0.48 € / t of hide,  
 388 that is, 1.73%. The calculation includes the chemicals used in the delimiting and bating

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4 389 operations, which are both post-unhairing. After these operations the hides, regardless of  
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6 390 the type of unhairing employed, undergo the same process. The calculation does not  
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9 391 include the hypothetical chromium salt savings in oxidative unhairing, as these have not  
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11 392 been experimentally tested.  
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14 393 This minimal difference in cost is more than offset by the savings in treatment costs  
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16 394 involved in decreasing the pollution load of the resulting wastewater. Therefore, we can  
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18 395 state that the process is economically viable. Even in countries where the discharge of  
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21 396 highly polluted wastewater is not penalized, the cost difference is so small that it should not  
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23 397 prevent the implementation of the new unhairing system.  
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#### 27 28 399 **4. Conclusions** 29 30

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34 401 Traditional unhairing has been significantly modified, replacing part of the sodium  
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36 402 sulfide with hydrogen peroxide as unhairing agent. This change is economically viable and  
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38 403 has allowed a significant reduction of the pollution load and toxicity of the wastewater as  
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41 404 well as a minimization of the solid waste resulting from the unhairing process. Actually, the  
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43 405 sustainability of the whole process has not only been improved environmentally but also  
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45 406 from the perspective of the safety and health of workers, as the possibility of producing  
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48 407 hydrogen sulfide during the process is eliminated with the new system.  
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#### 53 409 **References** 54 55

56 410  
57  
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- 1  
2  
3  
4 411 Andrioli, E., Gutterres, M., 2014. Associated use of enzymes and hydrogen peroxide for  
5  
6 412 cowhide hair removal. J. Am. Leather Chem. As. 109, 41-48.  
7  
8  
9 413 APHA, 1998. Standard Methods for the Examination of Water and Wastewater, 18th. ed.  
10  
11 414 American Public Health Association, Washington DC.  
12  
13  
14 415 ASTM, 2009. ASTM D3898-93: Standard test method for chromic oxide in basic  
15  
16 416 chromium tanning liquors, ASTM International Database. <http://www.astm.org> (accessed  
17  
18 417 January 2015)  
19  
20  
21 418 Bayramoglu, E.E., Yorgancioglu, A., Yeldiyar, G., Onez, E., 2014. Extraction of keratin  
22  
23 419 from unhairing wastes of goatskin and creating new emulsion formulation containing  
24  
25 420 keratin and calendula flower (*calendula officinalis L.*). J. Am. Leather Chem. As. 109, 49-  
26  
27 421 55.  
28  
29  
30  
31 422 Black, M., Canova, M., Rydin, S., Scalet, B.M., S. Roudier, S., Sancho, L.D., 2013. Best  
32  
33 423 Available Techniques (BAT) Reference Document on for the Tanning of Hides and Skin, p.  
34  
35 424 46. European Commission Database.  
36  
37 425 [http://eippcb.jrc.ec.europa.eu/reference/BREF/TAN\\_Published\\_def.pdf](http://eippcb.jrc.ec.europa.eu/reference/BREF/TAN_Published_def.pdf) (accessed January  
38  
39 426 2015).  
40  
41  
42  
43 427 Bronco, S., Castiello, D., d'Elia, G., Salvadori, M., Seggiani, M. Vitolo, S., 2005.  
44  
45 428 Oxidative unhairing with hydrogen peroxide: development of an industrial scale process for  
46  
47 429 high-quality upper leather. J. Am. Leather Chem. As. 100, 45–53.  
48  
49  
50 430 Castiello, D., Puccinu, M., Seggiani, M., Vitolo, S., Zammori, F., 2008. Life cycle  
51  
52 431 assessment (LCA) of the oxidative unhairing process by hydrogen peroxide. J. Am. Leather  
53  
54 432 Chem. As. 103, 1–6.  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

- 1  
2  
3  
4 433 Dettmer, A., Cavalli, E., Ayub, M.A.Z., Gutterres, M., 2012. Optimization of the unhairing  
5  
6 434 leather processing with enzymes and the evaluation of inter-fibrillary proteins removal: an  
7  
8  
9 435 environment-friendly alternative. *Bioprocess Biosyst. Eng.* 35, 1317–1324.  
10  
11 436 FAO, 2013. Market and Policy Analyses of Raw Materials, Horticulture and Tropical  
12  
13  
14 437 Products Team. World Statistical Compendium for raw hides and skins, leather and leather  
15  
16 438 footwear 1993-2012. Food and Agricultural Organization (FAO) Database.  
17  
18  
19 439 [http://www.fao.org/fileadmin/templates/est/COMM\\_MARKETS\\_MONITORING/Hides\\_S](http://www.fao.org/fileadmin/templates/est/COMM_MARKETS_MONITORING/Hides_Skins/Documents/COMPENDIUM2013.pdf)  
20  
21 440 [kins/Documents/COMPENDIUM2013.pdf](http://www.fao.org/fileadmin/templates/est/COMM_MARKETS_MONITORING/Hides_Skins/Documents/COMPENDIUM2013.pdf) (accessed January 2015).  
22  
23  
24 441 Frentrup, W., 2000. United Nations Industrial Development Organization Database.  
25  
26 442 [http://www.unido.org/fileadmin/user\\_media/Publications/Pub\\_free/Hair\\_save\\_unhairing\\_m](http://www.unido.org/fileadmin/user_media/Publications/Pub_free/Hair_save_unhairing_methods_in_leather_processing.pdf)  
27  
28 443 [ethods in leather processing.pdf](http://www.unido.org/fileadmin/user_media/Publications/Pub_free/Hair_save_unhairing_methods_in_leather_processing.pdf) (accessed January 2015).  
29  
30  
31 444 Galarza, B.C., Cabello, I., Greco, C.A., Hours, R., Schuldt, M.M., Cantera, C.S., 2010.  
32  
33 445 Alternative technologies for adding value to bovine hair waste. *J. Soc. Leather Tech. Ch.*  
34  
35 446 94, 26-32.  
36  
37  
38 447 Haydar, S., Aziz, J.A., 2009. Characterization and treatability studies of tannery wastewater  
39  
40 448 using chemically enhanced primary treatment (CEPT) – A case study of Saddiq Leather  
41  
42 449 Works. *J. Hazard. Mater.* 163, 1076-1083.  
43  
44  
45 450 Heidemann, E., 1993. *Fundamentals of Leather Manufacturing*, first ed. Eduard Roether,  
46  
47 451 K.G., Darmstadt (Germany), p. 189.  
48  
49  
50 452 IUC 8-1, 2007. ISO 5398-1:2007. Leather - Chemical determination of chromic oxide  
51  
52 453 content - Part 1: Quantification by titration.  
53  
54  
55 454 IULTCS, 2008. IUE- 6: Pollution values from tannery processes under conditions of good  
56  
57 455 practice. International Union of Leather Technologists and Chemists (IULTCS) Database.  
58  
59  
60 456 [http://www.iultcs.org/pdf/IUE6\\_2008.pdf](http://www.iultcs.org/pdf/IUE6_2008.pdf) (accessed January 2015).  
61  
62  
63  
64  
65

- 1  
2  
3  
4 457 IUP 6, 2011. ISO 3376:2011. Leather - Physical and mechanical tests - Determination of  
5  
6 458 tensile strength and percentage extension.  
7  
8  
9 459 IUP 8, 2002. ISO 3377-2:2002. Leather - Physical and mechanical tests - Determination of  
10  
11 460 tear load - Part 2: Double edge tear.  
12  
13  
14 461 IUP 9, 2015. ISO 3379: 2015. Leather - Determination of distension and strength of surface  
15  
16 462 (Ball burst method).  
17  
18  
19 463 IUP 16, 2015. ISO 3380:2015. Leather - Physical and mechanical tests - Determination of  
20  
21 464 shrinkage temperature up to 100 °C.  
22  
23  
24 465 Jian, S., Wenyi, T., Wuyong, C., 2011. Kinetics of enzymatic unhairing by protease in  
25  
26 466 leather industry. *J. Clean. Prod.* 19, 325–331.  
27  
28  
29 467 Kanagaraj, J., Senthilvelan, T., Panda, R.C., Kavitha, S., 2015. Eco-friendly waste  
30  
31 468 management strategies for greener environment towards sustainable development in  
32  
33 469 leather. *J. Clean. Prod.* 89, 1-17.  
34  
35  
36 470 Morera, J.M., Bartolí, E., Borrás, M.D., Banaszak, S., 2006. Oxidative unhairing of  
37  
38 471 leathers: influence of several process parameters and environmental improvements. *J. Am.*  
39  
40 472 *Leather Chem. As.* 101, 347–354.  
41  
42  
43 473 Morera, J.M., Bacardit, A., Ollé, L., Bartolí, E., Borrás, M.D., 2008. Minimization of the  
44  
45 474 environmental impact in the unhairing of bovine hides. *Chemosphere* 72, 1681–1686.  
46  
47  
48 475 Saravanabhan, S., Thanikaivelan, P., Rao, J.R., Nair, B.U., Ramasami, T., 2006. Reversing  
49  
50 476 the conventional leather processing sequence for cleaner leather production. *Environ. Sci.*  
51  
52 477 *Technol.* 40, 1069–1075.  
53  
54  
55 478 Sengil, A., Kulaç, S., Özakar, M., 2009. Treatment of tannery liming drum wastewater by  
56  
57 479 electrocoagulation, *J. Hazard. Mater.* 167, 940-946.  
58  
59  
60  
61  
62  
63  
64  
65



- 1  
2  
3  
4 480 Shi, B., Lu, X., Sun, D., 2003. Further investigations of oxidative unhairing using hydrogen  
5  
6 481 peroxide, J. Am. Leather Chem. As. 98, 185–192.  
7  
8  
9 482 Thangam, E.B., Nagarajan, T., Rajkumar, G.S., Chandrababu, N.K., 2001. Application of  
10  
11 483 alkaline protease isolated from *Alcaligenes faecalis* for enzymatic unhairing in tanneries. J.  
12  
13  
14 484 Am. Leather Chem. As. 96, 127–132.  
15  
16 485 Valeika, V., Baleska, K., Valeikiene, V., Kolodzeiskis, V., 2009. An approach to cleaner  
17  
18 486 production: from hair burning to hair saving using a lime-free unhairing system, J. Clean.  
19  
20  
21 487 Prod. 17, 214-221.  
22  
23 488 Vidal, G., Nieto, J., Cooman, K., Gajardo, M., Bornhardt, C., 2004. Unhairing effluents  
24  
25  
26 489 treated by an activated sludge system. J. Hazard. Mater. 112, 143-149.  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
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Dear Sir,

The paper deals with the environmental concerns generated by the tanning industry and focuses on the beamhouse, the most polluting part of the process. This operation consists in cleaning and preparing the hides for tanning and involves using large quantities of clean water that will end up being transformed into highly contaminant wastewater. In order to provide an idea of the quantity of the pollution load we are talking about here we can state that the latest studies by official organisms estimate that in the world 6.5Mt of bovine raw hides are tanned yearly. This means generating about 104 Mm<sup>3</sup> of contaminated water, 0.91Mt of COD, 0.036Mt of SS, 0.62Mt of sulphides among others.

The use of sodium sulfide as unhairing agent is of special concern for the tanning industry. It poses a great danger for workers since the sulfide may turn into hydrogen sulfide resulting in intoxications that may even be fatal. Unfortunately, the measures taken to prevent this type of accidents have failed on more than one occasion. This is even more so in countries with more permissive labour safety legislation and it is precisely in these countries where the tanning industry has boomed in the recent years.

Although several paths towards a change in working processes have been explored, the classical unhairing system has not yet been replaced.

One of the most radical alternatives for change lately has been the replacement of sodium sulfide by hydrogen peroxide as unhairing agent. We have developed a new process taking this proposal into account and incorporating hair recovery as a new corrective action in order to minimize pollution. Results have shown that leather quality is not affected by the implementation of the new process and that several parameters are reduced significantly. These include wastewater conductivity (38%), Suspended Solids (75%) and sulfides (100%). Also, the risk associated with the production of hydrogen sulfide is eliminated, which signifies a dramatic improvement in safety for the workers. Given the large amounts of water and chemical pollution discharged in the process, the reductions in absolute values represent a significant improvement.

The system has been tested on a pilot plant scale. So far the characteristics of the system indicate that no major complications should arise when the process is implemented on an industrial scale.

**Highlights:**

- A new unhairing process is developed.
- Hydrogen peroxide is used to decrease the supply of sulfide as unhairing chemical.
- Pollution load and toxicity of wastewater and solid waste decrease considerably.
- Less chromium in tanning wastewater and sulfide-free solid waste are achieved.

Figure 1

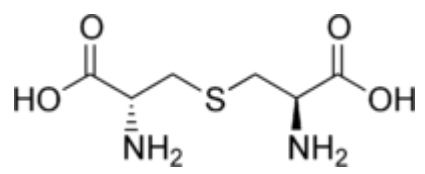


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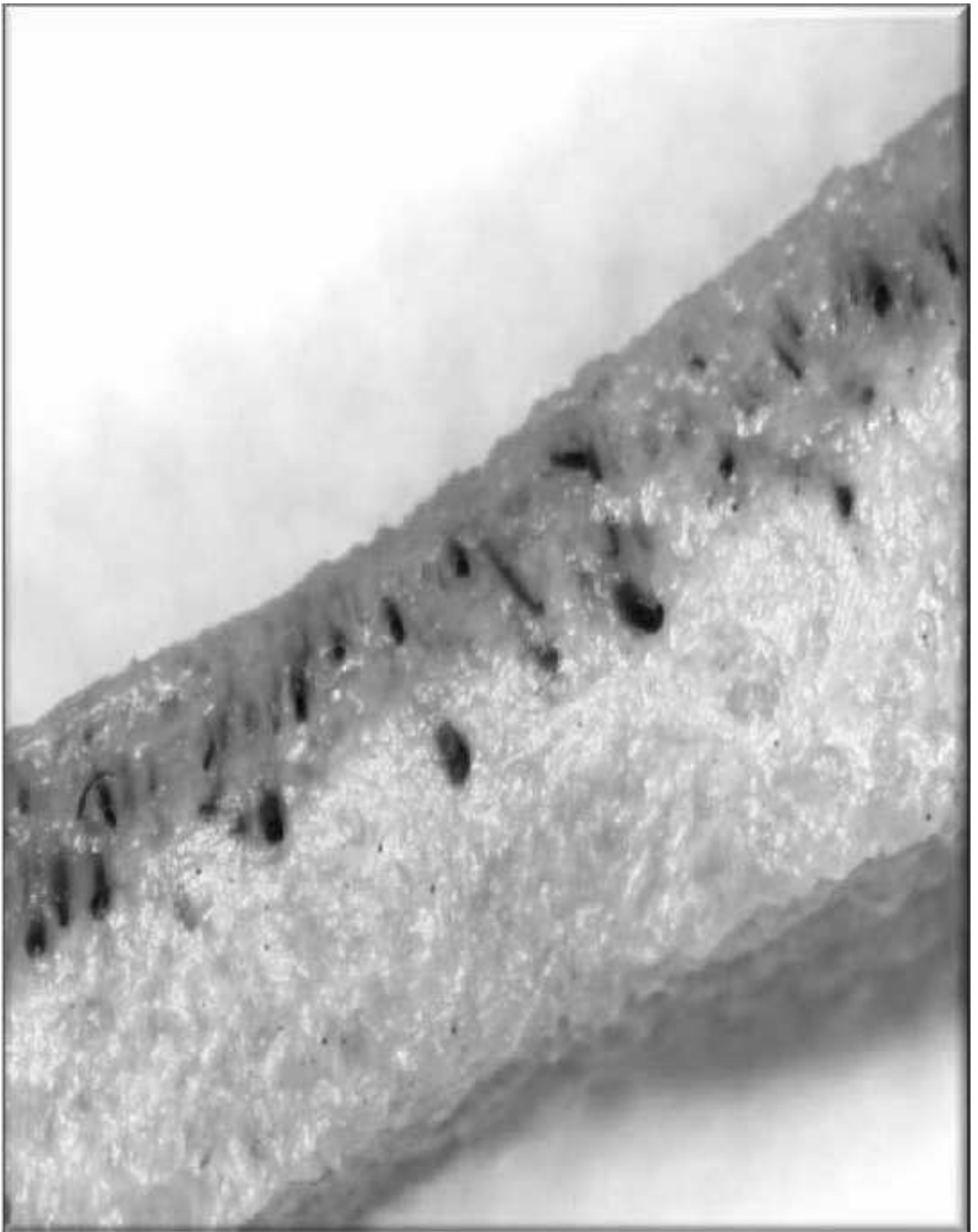




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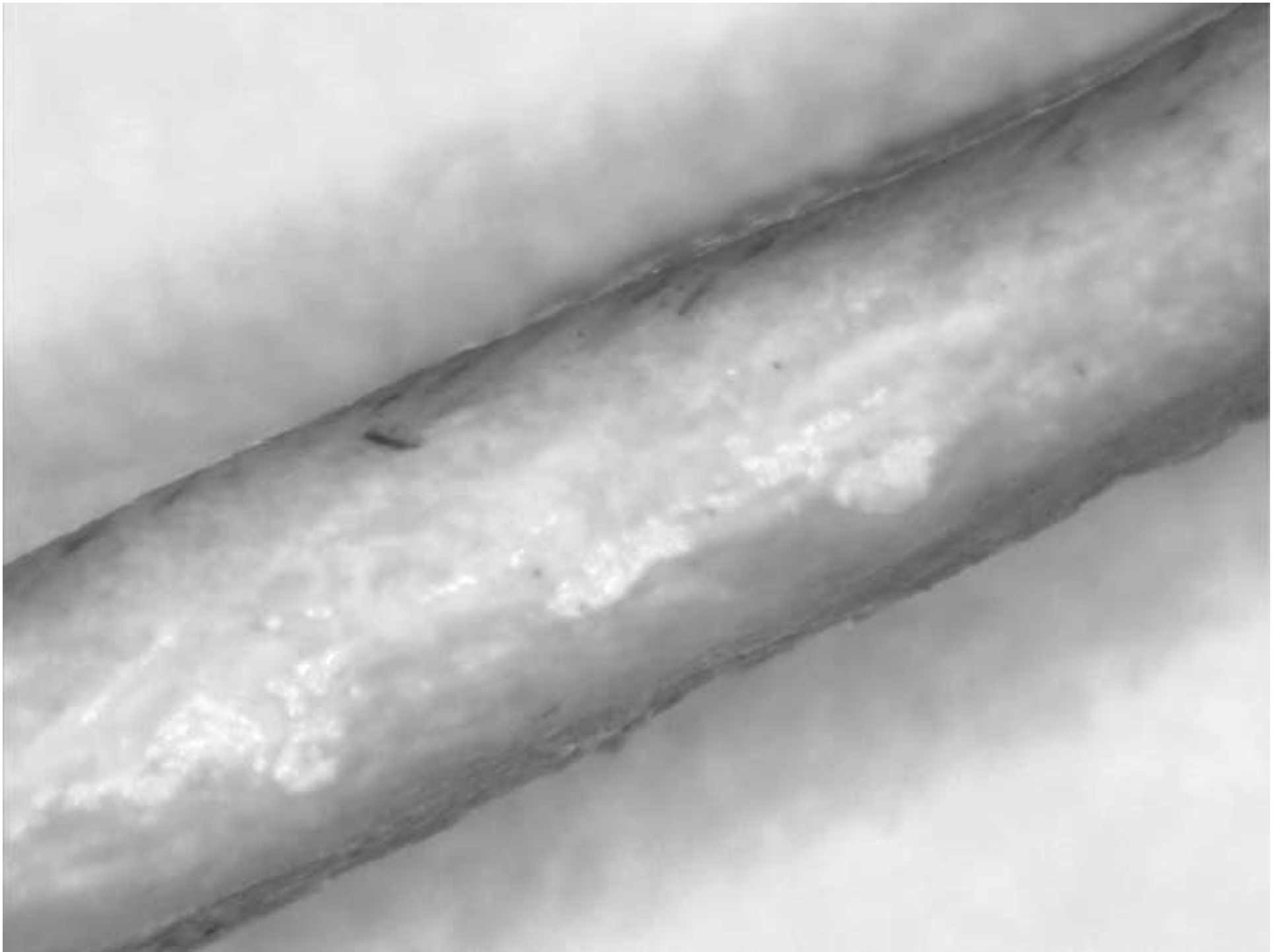


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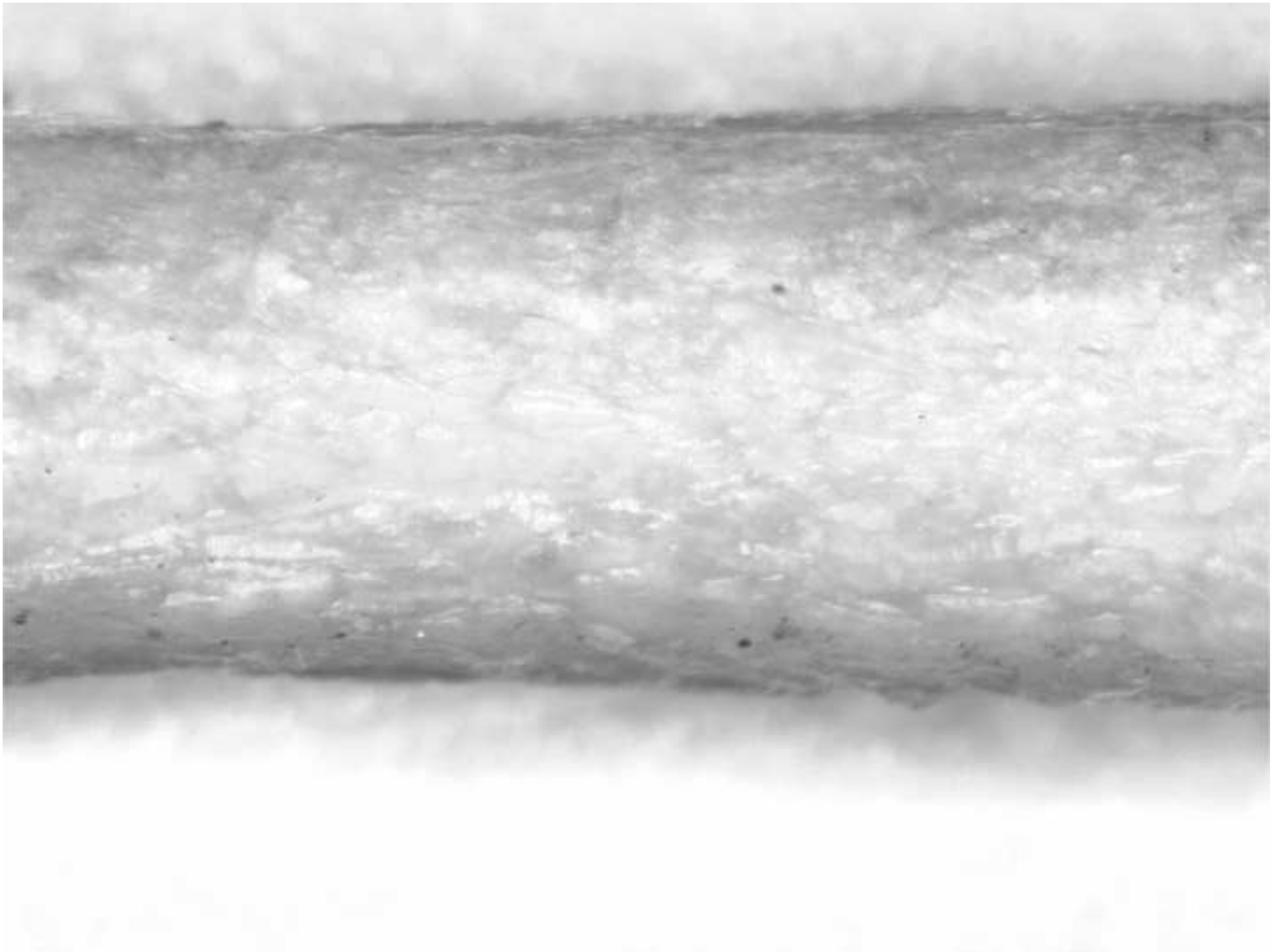


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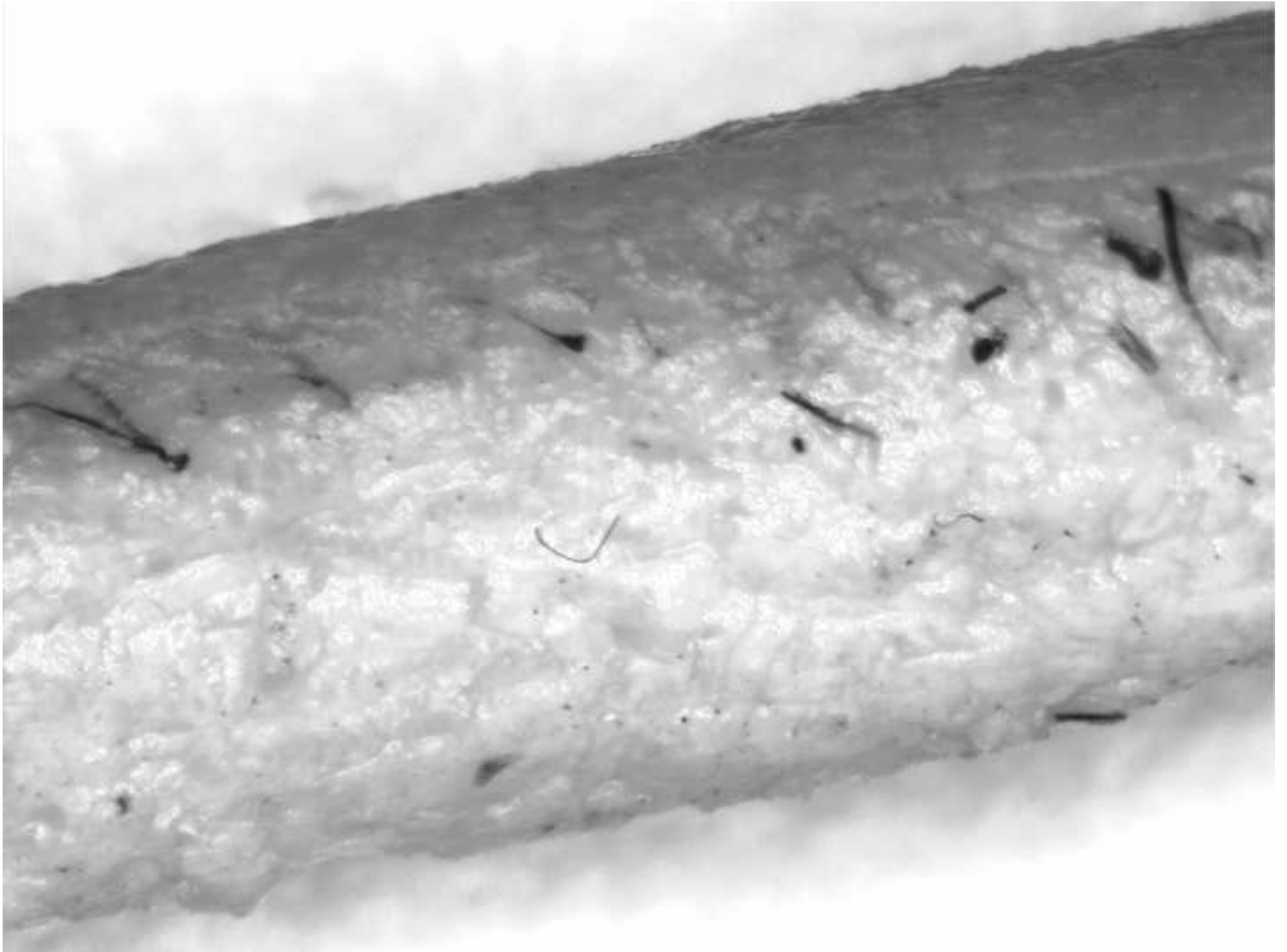
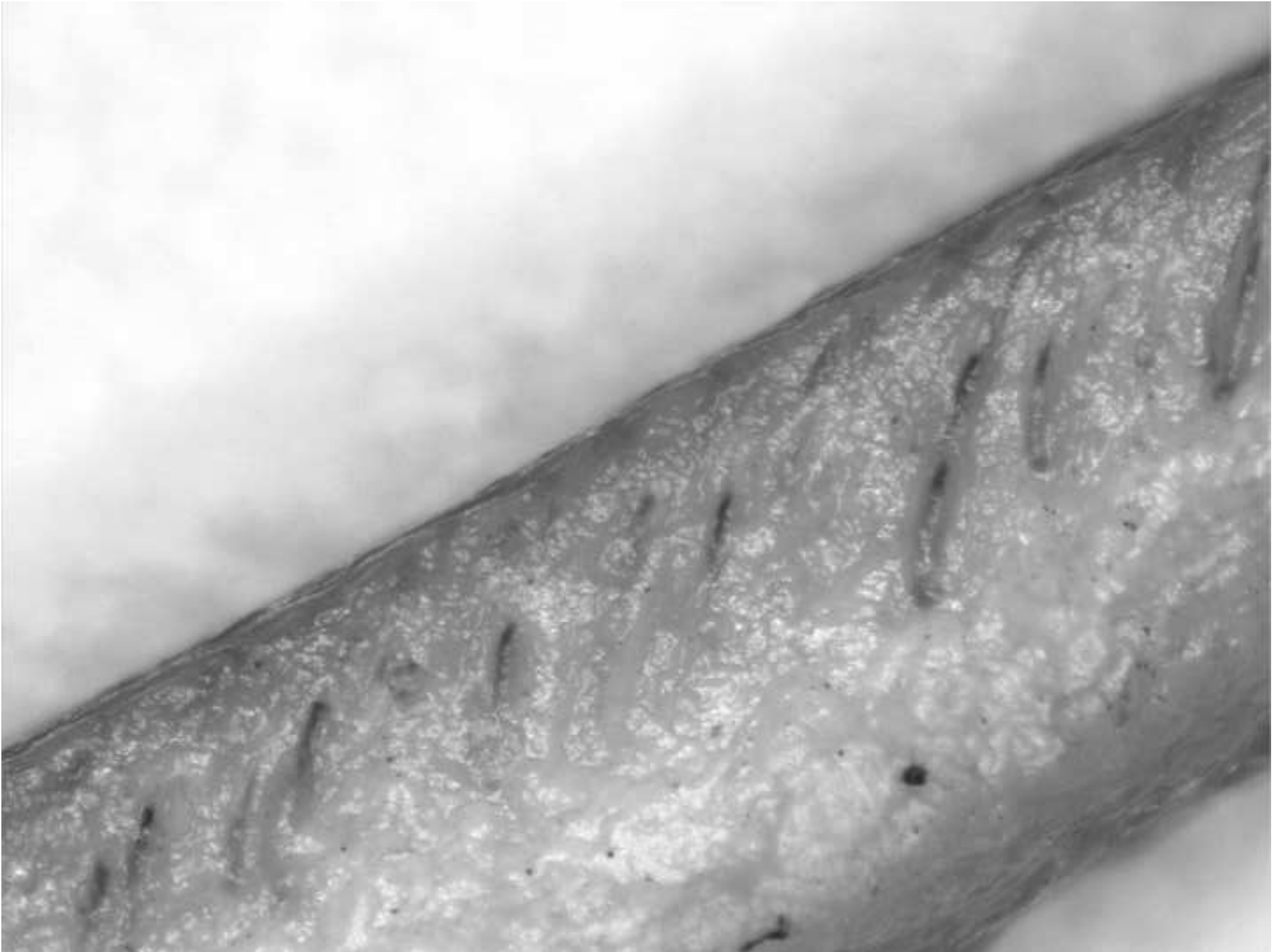


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**Figure 8 Color**  
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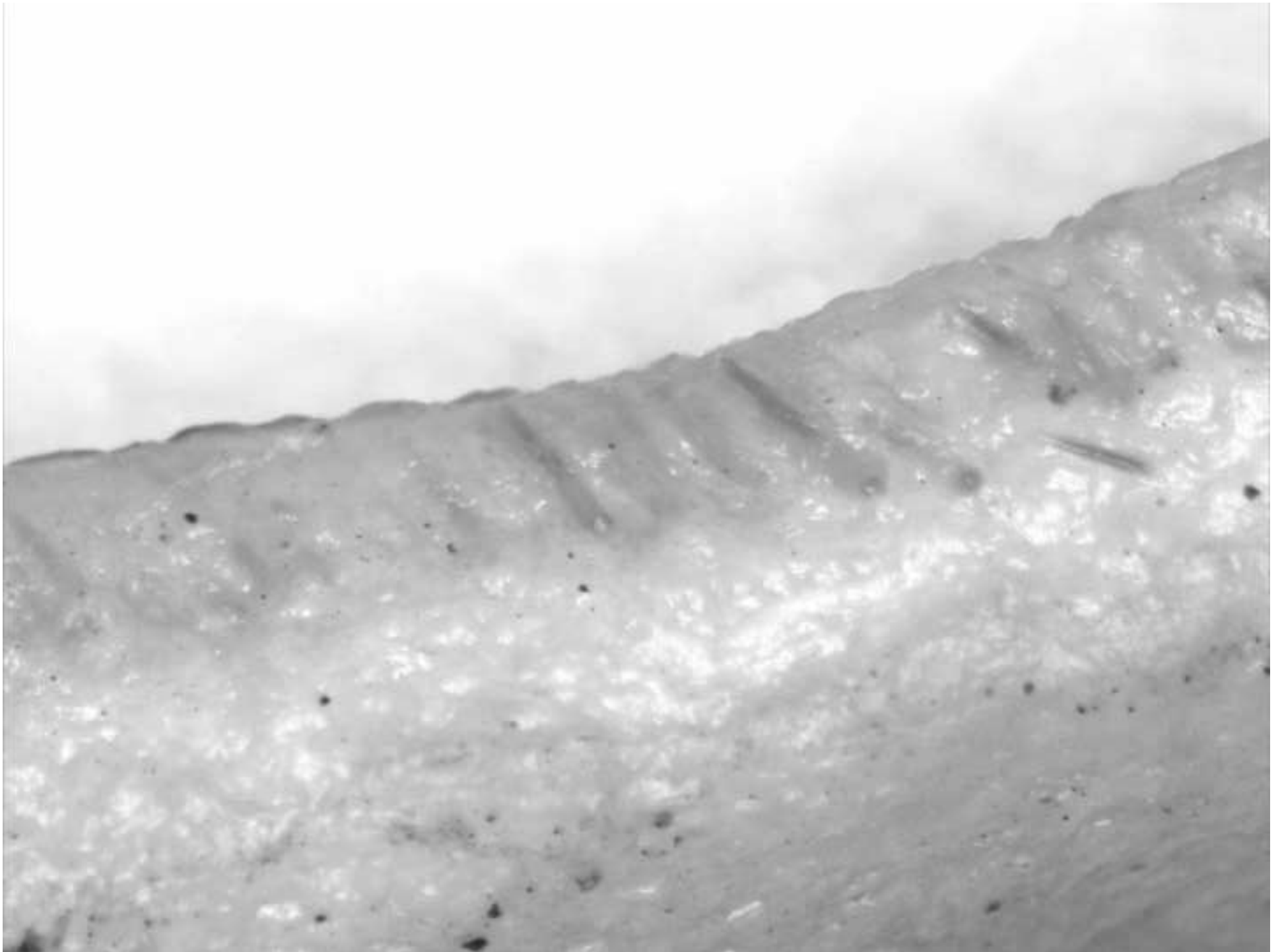


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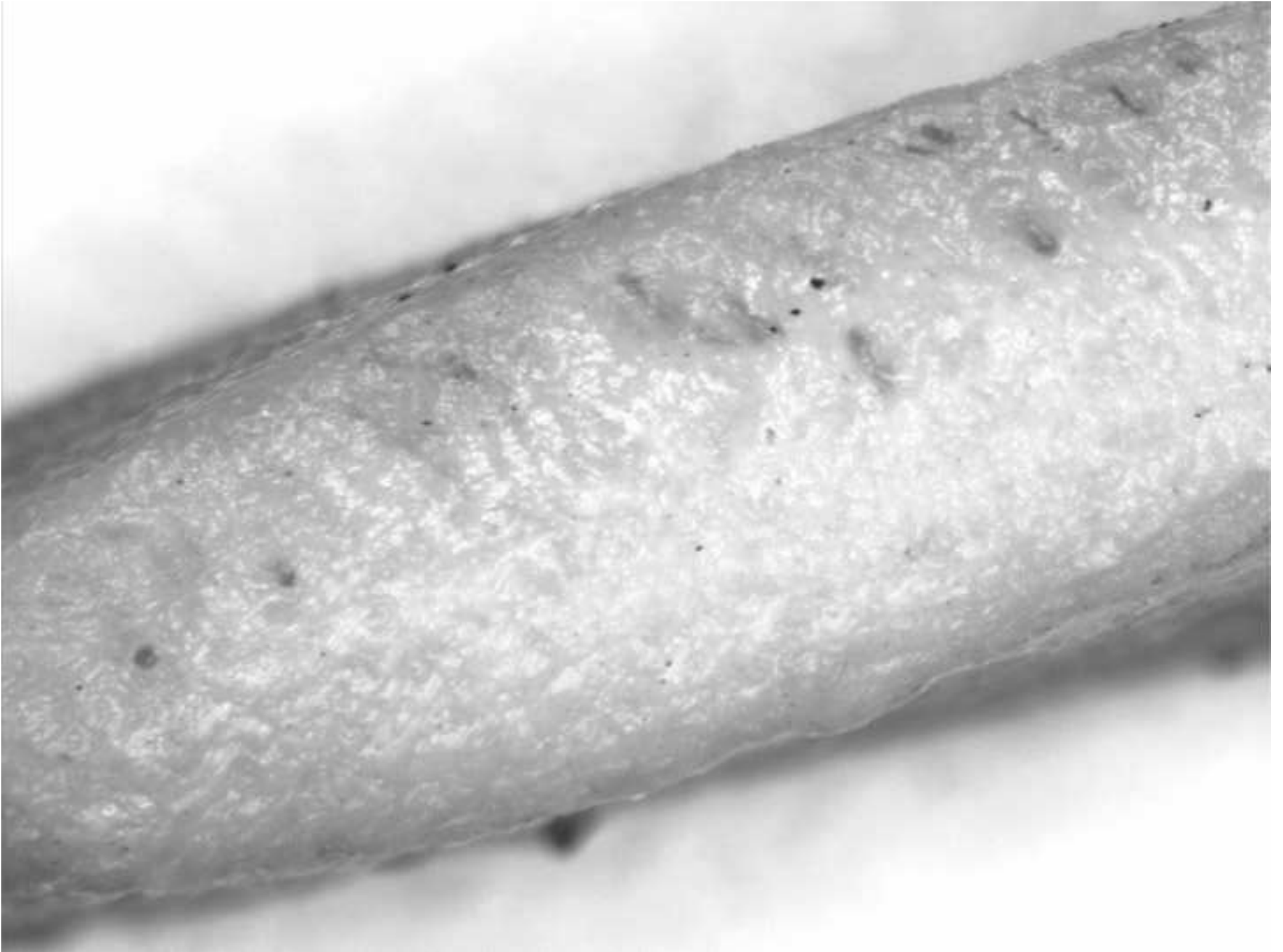


Fig. 1. Lanthionine structure.

Fig. 2. Pilot plant drum.

Fig. 3. Laboratory tests. Enlarged view (12.5x) of the cross section of the hide after reductive unhairing.

Fig. 4. Laboratory tests. Enlarged view (12.5x) of the cross section of the hide unhaired with 1% hydrogen peroxide.

Fig. 5. Laboratory tests. Enlarged view (12.5x) of the cross section of the hide unhaired with 3% hydrogen peroxide.

Fig. 6. Pilot plant tests. Enlarged view (12.5x) of the cross section of the hide unhaired with sodium sulfide and lime.

Fig. 7. Pilot plant tests. Enlarged view (12.5x) of the cross section of the hide unhaired with hydrogen peroxide for 2 hours.

Fig. 8. Pilot plant tests. Enlarged view (12.5x) of the cross section of the hide unhaired with hydrogen peroxide for 4 hours.

Fig. 9. Pilot plant tests. Enlarged view (12.5x) of the cross section of the hide unhaired with hydrogen peroxide for 6 hours.

**ABSTRACT**

This study aims to diminish the pollution being discharged into wastewaters through changes in the unhairing process. To this aim, we are replacing a reductive hair degrading process with a process which combines a reductive hair degrading process with an oxidative hair degrading process. Hydrogen peroxide is used to decrease the supply of sulfide as unhairing chemical. As a result, commercially acceptable leather regarding both costs and quality is obtained and significant reductions in the contaminant load of the wastewater being discharged are observed. Results indicate that wastewater conductivity is cut by 26%, suspended solids decrease by 75%, observable sulfide disappears, while the amount of chromium being absorbed by the hides is increased. This leads to considerable savings in the chromium salt offer in hide tanning and, consequently, a decrease in the amount chromium in the wastewater.