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Immunization Effect of Sodium Aluminate on Wool

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Abstract

Since the environmental requirements for leather manufacture as well as for other industry branches are becoming stricter, investigations of unhairing have been directed towards conditions of the process which allow the saving of hair: enzymatic unhairing or unhairing with hair immunization conventionally achieved by using lime and sodium sulphide. The problem is that lime forms a big quantity of liquid waste which contains lime sludge polluted by sulphides and protein degradation products. The research is devoted to the replacement of $Ca(OH)_2$ as hair immunization material with some other soluble non-hazardous material with a similar immunization effect. The preliminary tests showed that alkaline sodium aluminate suits this purpose very well. Its immunisation efficiency increases with prolonged treatment duration and increased concentration of the treatment solution. Treatment with 20 g/l of sodium silicate solution for 3 h allows to reach a high immunization ability almost the same as that of calcium hydroxide under the same conditions. The immunisation effect lasts when the pH is approx. 13.

Key words: *immunization, wool, keratin, sodium aluminate, sodium sulphide.*

Introduction

A major contributor to pollution from the tanning industry is the conventional unhairing-liming process using sodium sulphide and lime. Bovine and ovine hair is obtained as a by-product from tanneries during the hair-saving unhairing process, and it is estimated that about 5% of dry hair is recovered based on the raw hide weight [1]. However, most tanneries still follow the hair-burning process, which destroys hair completely and contributes a high amount of COD, BOD, TDS etc. to waste water [2]. Accordingly there are two most important reasons to develop hair- saving unhairing: i) the products of hair degradation complicate the cleaning of the unhairing solutions used, and ii) the saved hair can be used as a raw material for other applications [3].

A major part of hair-saving unhairing process investigations is devoted to enzymatic unhairing [4, 5]. Despite the fact that the enzymatic process has a serious advantage from an environmental point of view, i.e. wastewaters after the process are free from sulphides and hair degradation products, pure enzymatic unhairing is not widely used in the industry. The first reason for this is that often after the enzymatic unhairing – separate hair, some epidermis and scud stay on the hide, and the second that there is a too weak or too strong opening up of the derma structure [6]. For the final removal of such remnants on grain, and for the sufficient opening up of thederma structure, treatment with sulphides or oxidizers [7] must be carried out.

The alternative way to save hair is to perform the unhairing process with hair immunization using lime and sulphide [8].

The immunisation phenomenon of hair is explainable by the formation of a lanthionic bond when keratin is treated with alkalizing substances [9] under particular conditions. The increasing of the solution pH has a special role in decreasing the solubility of all hair components [10]. In his review of hair immunisation investigations, Cantera [11] concluded that a pH range of 12.5-13.0 is appropriate for hair protection purposes.

Heideman et al. [10] proposed that hair treated with any alkali of sufficient strength can become immune to solubilisation by reducing agents like sodium sulphide.

Castiello et al. summarized that the exposure of hair to divalent cations, unlike monovalent cations, induces the formation of new cross-links in the keratin structure and promotes immunization [12]. The possible mechanism of divalent cation action can be shown through the reactions [11] (see ***Figure 1***).

Unfortunately huge amounts of lime sludge and total solids formation are the main drawbacks of lime [13]. Herewith the wastes are toxic and characterised by a high concentration of sulphur, mineral compounds as well as a high alkalinity and organic load. The cleaning process of the solid wastes is expensive, complicated and lingering [14].

Soluble alkalis such as sodium alkali [13] or sodium silicate [15] seem more attractive for this purpose. Unfortunately sodium alkali does not have an immunization effect on hair keratin [11].

Investigation using sodium silicate showed that immunization can be reached at relatively high pH values when the immunizing agent does not contain a divalent cation [16, 17].

Sodium metasilicate produces NaOH due to hydrolysis [18] when it dissolves in water, thus giving high alkalinity of solution (pH of 5% Na_2SiO_3 solution reaches 13.4). The NaOH obtained is the main player in the process of unhairing, where NaOH degrades hair and (or) opens up the derma structure. Therefore differences which appear when sodium silicate is used in comparison with the case where pure sodium hydroxide is used depend on the other products of sodium metasilicate hydrolysis [16].

There is another class of salts similar to silicates, which are soluble, from NaOH whose solutions have high pH values: sodium aluminates.

The main aim of the present research was an evaluation of the dependence of the immunization capability of sodium aluminate on the concentration and exposure time.

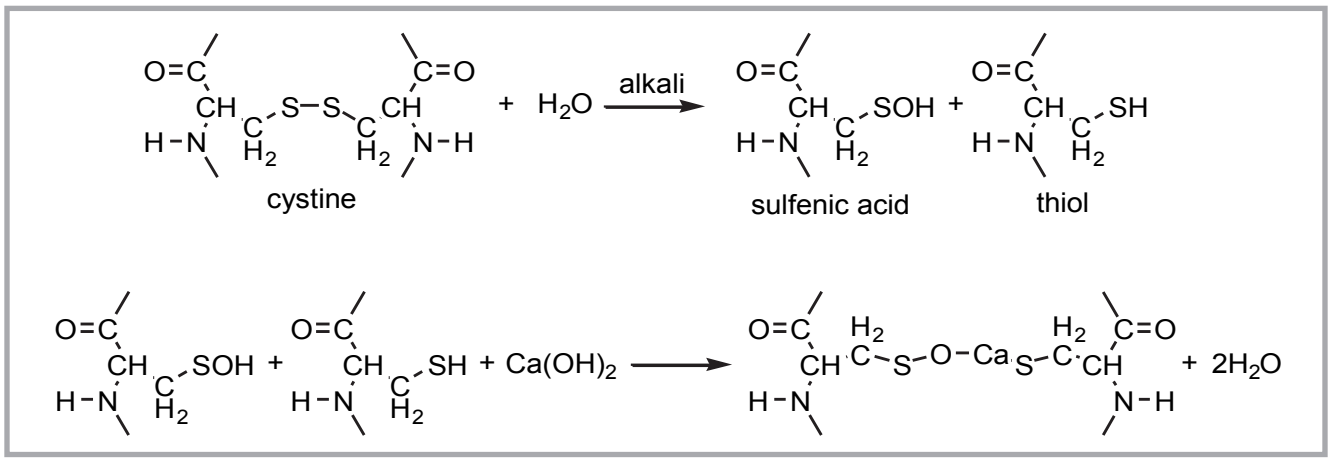

Figure 1. *Scheme of formation of the link between keratin and non-ionized divalent metal atom.*

Materials and methods

Four pieces (20x20 cm) were cut from four merino sheep skins (with medium wool) preserved by salting. The pieces were soaked under the following conditions: H_2O 1000%, sodium fluorosilicate 1 g/l, temperature 30 °C, duration 6 h, run continuously, with draining. The samples soaked were degreased: H_2O 1000%, sodium alkansulphonate "Volgonat" (Chimprom, Russia) 7 g/l, alkyl sulphate "Novost" (Chimprom, Russia) 5 g/l, temperature 42 °C, duration 1 h, run continuously (draining in the end of process) and washed three times: H_2O 1000%, temperature 42 °C, duration 20 min. Afterwards the wool was cut from the samples, dried and used for experiments, with wool moisture content 8-9% and the total nitrogen content 16.2% (dry weight).

Wool treatment by alkali solutions was carried out by pouring 100 ml of alkali solution on 1 g of wool and shaking with agitation at 120 rpm and 20-22 °C.

The immunization effect was estimated based on changes in the wool mass loss and content of nitrogen in the treatment solution.

Evaluation of the wool mass treated by alkalis was carried out as follows: the treated wool was washed with distilled water, the amount of which was 100 times bigger than the mass of the dry wool sample before treatment. The temperature of the water was 20-22 °C, and washing was carried out three times in a shaker with agitation at 120 rpm for a duration of 20 min. After that the sample was washed in 0.05 mol/l HCl solution (with the aim of completely removing possible absorbed alkalis) and again in distilled water at the temperature, duration and agitation as described above. The treated wool was separated from the solution using sieve with mesh size 0.1 mm. Therewith the wool sample was dried and weighed.

The total amount of nitrogen in the treatment solutions was estimated by employing Kjeldahl's method [19].

Scanning electron microscopy (SEM) was carried out using a scanning microscope *JSM–840A* (*Joel,* USA). SEM parameters were as follows: 150 and 1200 times, accelerating voltage 25 kV, detector SE, high vacuum regime. The samples were coated with gold-palladium using *JFC–1110 FINE COAT ION SPUTTER* equipment (*Joel,* USA).

Reflectance infrared spectra of the wool samples were obtained using a Perkin-Elmer FTIR Frontier (USA) spectrometer with a Universal ATR Sampling Accessory. The resolution was 1 cm^{-1}, scan rate 0.2 cm/s and scan number – 4 times. "Spectrum 5.0.1" software was used for calculation of the area of the peaks in the spectra ΔS ($A \cdot cm^{-1}$).

All data were expressed as the average value of triplicate measurements. Confidence limits were set at $P < 0.05$, and standard deviations did not exceed 5% for the values obtained.

Results and discussion

For evaluation of the immunisation ability of such alkalis as $Ca(OH)_2$ and KOH, samples containing 1 g of dry wool were treated with 100 ml of solution of the alkalis. The solutions contained 20 g/l $Ca(OH)_2$ or 34 g/l KOH, respectively.

Two methods of wool treatment were used:

1. Initially the wool was treated with alkali for 1, 2, 3 or 5 h, afterwards 10 g/l of Na_2S was added and treatment was prolonged for an additional 2 h.
2. Simultaneous treatment with both alkali and Na_2S for 2 or 5 h.

The effect of treatment on the wool was estimated by determining the nitrogen concentration in the solution and the wool mass after treatment (***Table 1***).

Table 1. *Effect of treatment with solution of alkali and sodium sulphide on wool degradation level.* ***Note:*** *After complete dissolving of 1 g of wool in 100 ml solution containing 100 g/l of NaOH, the nitrogen concentration was 1.47 g/l.*

Alkali, concentration and pH of solution	Index	Duration of treatment with alkali solution before adding Na_2S, h				Duration of treatment by alkali and Na_2S, h	
		1	2	3	5	2	5
$Ca(OH)_2$ 20 g/l, pH 12.5	Wool mass decrease, %	17.4	15.5	13.8	6.9	56.3	69.2
	Nitrogen concentration, g/l	0.19	0.15	0.11	0.04	0.58	0.96
KOH 34 g/l, pH 13.5	Wool mass decrease, %	21.9	35.6	39.8	44.0	80.2	94.0
	Nitrogen concentration, g/l	0.24	0.43	0.55	0.60	0.97	1.29

Table 2. *Effect of wool treatment with sodium aluminate on nitrogen content in solution.*

$NaAlO_2$ concentration and pH of solution	Nitrogen content in solution (g/l) when					
	duration of treatment with $NaAlO_2$ solution before adding of Na_2S is				duration of treatment by $NaAlO_2$ and Na_2S is	
	1 h	2 h	3 h	5 h	2 h	5 h
5 g/l, pH 12.0	0.50	0.50	0.35	0.20	0.45	0.70
10 g/l, pH 12.3	0.29	0.22	0.15	0.09	0.46	0.75
20 g/l, pH 12.6	0.15	0.08	0.07	0.05	0.44	0.70
30 g/l, pH 12.8	0.10	0.05	0.05	0.04	0.38	0.75
50 g/l, pH 12.9	0.05	0.03	0.05	0.06	0.35	0.63

Table 3. *Effect of treatment by sodium aluminate on wool mass loss.*

$NaAlO_2$ concentration	Wool mas loss (%) when					
	duration of treatment with $NaAlO_2$ solution before adding of Na_2S is				duration of treatment by $NaAlO_2$ and Na_2S is	
	1 h	2 h	3 h	5 h	2 h	5 h
5 g/l	54.3	50.5	36.4	23.8	40.0	54.0
10 g/l	34.1	28.4	14.8	11.0	40.0	60.5
20 g/l	20.2	12.2	6.9	7.2	45.6	64.3
30 g/l	10.6	8.7	6.6	5.4	38.9	67.4
50 g/l	9.8	4.7	6.6	5.9	40.7	65.6

Table 4. *Wool degradation during 24 h treatment with alkalis.*

Alkali solution concentration	Index	24 h treatment only with alkali	24 h treatment with alkali alone + 2h together with Na_2S
$Ca(OH)_2$ 20 g/l	Wool mass decrease, %	2.4	3.4
	Nitrogen concentration, g/l	0.01	0.05
Na_2SiO_3 20 g/l [16]	Wool mass decrease, %	7.3	10.8
	Nitrogen concentration, g/l	0.06	0.09
$NaAlO_2$ 20 g/l	Wool mass decrease, %	7.2	8.4
	Nitrogen concentration, g/l	0.05	0.07
$NaAlO_2$ 30 g/l	Wool mass decrease, %	3.4	4.6
	Nitrogen concentration, g/l	0.04	0.05

Table 5*. Data of IR-spectrum quantitative analysis.*

Functional group or bond to which the vibration is attributed	Alkali used for wool treatment					
	not treated		$Ca(OH)_2$		$NaAlO_2$	
	ν, cm^{-1}	S, $A \cdot cm^{-1}$	ν, cm^{-1}	S, $A \cdot cm^{-1}$	ν, cm^{-1}	S, $A \cdot cm^{-1}$
N–H; O–H [20]	3280	236	3282	228	3275	213
C–H [21]	2921	68	2921	62	2921	52
=C=O "amide band I" [22]	1630	130	1630	132	1630	129
"amide band II" [22]	1512	101	1512	101	1512	103
CH_2; CH_3 [23]	1452	44	1453	45	1452	45
$–COO^-$ [24]	1386	25	1384	26	1385	25
"amide band III" [25]	1231	57	1231	58	1231	56

As seen from the data obtained, $Ca(OH)_2$ has an evident wool immunisation effect. Prolongation of the treatment with $Ca(OH)_2$ decreases the degradation level of the wool significantly for both indexes of nitrogen concentration in the treatment solution, as well as the wool mass loss.

The results of the investigation of the treatment with KOH show that this alkali also somewhat cuts the level of wool degradation. Of course, in comparison with $Ca(OH)_2$ the effect is significantly lower, but it is noticeable. The wool degradation slowing effect of both alkalis becomes evident while comparing the treatment, where pure alkali acts for a certain time before the addition of Na_2S to the treatment, where alkali and sodium sulphide act together from the beginning of the process.

A further experiment was carried out by treating wool with sodium aluminate solutions of various concentrations and estimating wool degradation via determination of the nitrogen content in the treatment solution and the wool mass loss after the treatment.

The data obtained and presented in ***Tables 2*** and ***3*** show that $NaAlO_2$ is capable of immunising wool when a specific combination of treatment conditions: concentration and treatment duration, is achieved. When the concentration is 10 g/l, a significant immunisation effect is attained during a time not shorter than 5 h. When the concentration is 30 g/l, 2 hours of treatment is enough to achieve the effective blocking of hair dissolution. A further increase in concentration up to 50 g/l leads to a shortening of the treatment duration (when the most effective immunisation is achieved) down to 1 h.

On the other hand, the immunization effects obtained are very close in the case of both treatments (30 g/l and 50 g/l) described above. Therefore it is more effective to prolong the treatment duration till 2 h than to use almost two times higher concentration of sodium aluminate.

In summary, it can be stated that 2 hour treatment with 20-30 g/l $NaAlO_2$ solution effectively immunises wool.

The treatment only with alkali for 24 h (***Table 4***) leads to a different effect on the treated wool, depending on the alkali used. After treatment with $Ca(OH)_2$, almost unaffected wool was obtained. When Na_2S was further added into the solution of $Ca(OH)_2$, the effect was very weak, the aggregate effect being significantly lower than that obtained during 5 h treatment with $Ca(OH)_2$ + 2 h with added Na_2S (***Table 1***); fact of which once again confirms the strong immunisation action of this alkali.

The data for the 24 hour action of $NaAlO_2$ solutions on wool (***Table 4***) indicate that these solutions affect wool almost as much as $Ca(OH)_2$, despite the fact that the solution of $NaAlO_2$ is of high alkalinity (pH 12.6-12.8) and divalent cation is absent, contrary to the case of treatments with $Ca(OH)_2$ [12]. When comparing the action of $NaAlO_2$ and Na_2SiO_3 [16], the effect of both salts is very close as well.

SEM images (***Figure 2***) indicate that the outcome of the treatment with sodium aluminate is very similar to that of sodium silicate. Only a slightly affected surface of wool is seen in both cases, be-

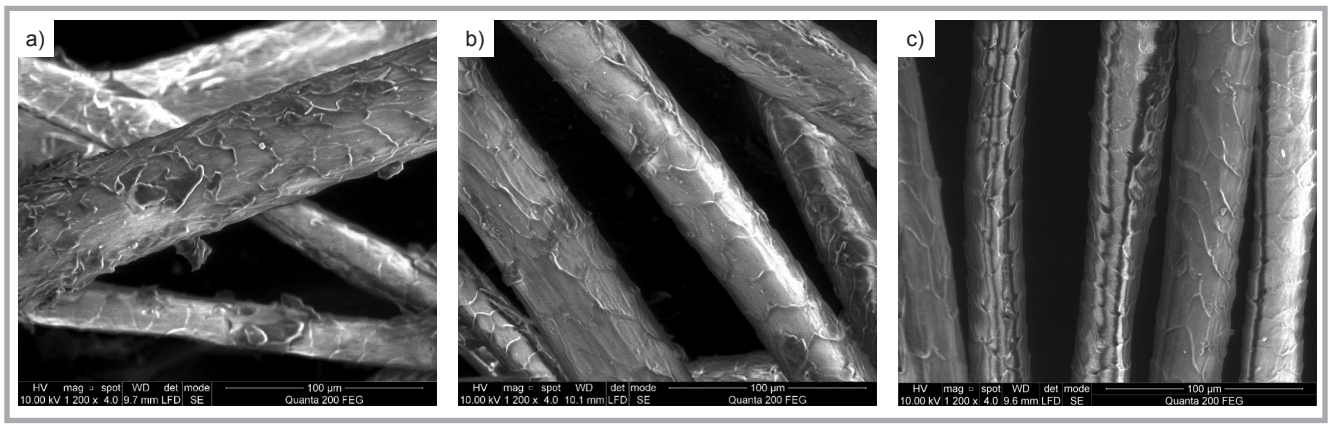

Figure 2. *SEM photographs: a) native wool, b) wool treated 24 hours with $Ca(OH)_2$, c) wool treated 24 hours with $NaAlO_2$ (magnification: – 1200 times).*

ing simply cleaner and no injuries can be observed. Overall the appearance of wool treated with sodium silicate or sodium aluminate practically does not differ from that of non-treated wool. This, once again, leads to the assumption of the high immunization ability of sodium aluminate.

Analysis of the IR spectrum (***Figure 3***) reveals that only usual peaks are observable in all spectra of non-treated wool or in that treated with calcium hydroxide or sodium aluminate. Peaks in range of 3500-3200 cm^{-1} are attributed to N–H and O–H valence vibrations [20]. The intensity of peaks (***Table 5***) in this range depends on the wool treatment method. It can be supposed that a decrease in the intensity of this peak is proportional to the amount of broken hydrogen bonds. Accordingly the peak in the spectrum for non-treated wool has the highest intensity and that in the spectrum for wool treated with sodium aluminate has the lowest .

Various CH bands are reflected by peaks in the range of 3000-2800 cm^{-1} [21]. Here a very similar situation as described for the above-mentioned peak can be observed: a stronger affect leads to a lower peak intensity.

In the amide I region (1700-1600 cm^{-1}), each type of secondary structure gives rise to a somewhat different C = O stretching frequency due to the unique molecular geometry and hydrogen bonding pattern [22]. Amide II is found in the 1510 and 1580 cm^{-1} region and the peak is labelled as C-N stretching and N–H bending vibration [22]. The amide III band occurs in the range of 1220-1300 cm^{-1} [25], and it can be concluded that no differences are visible in the peaks in the ranges mentioned.

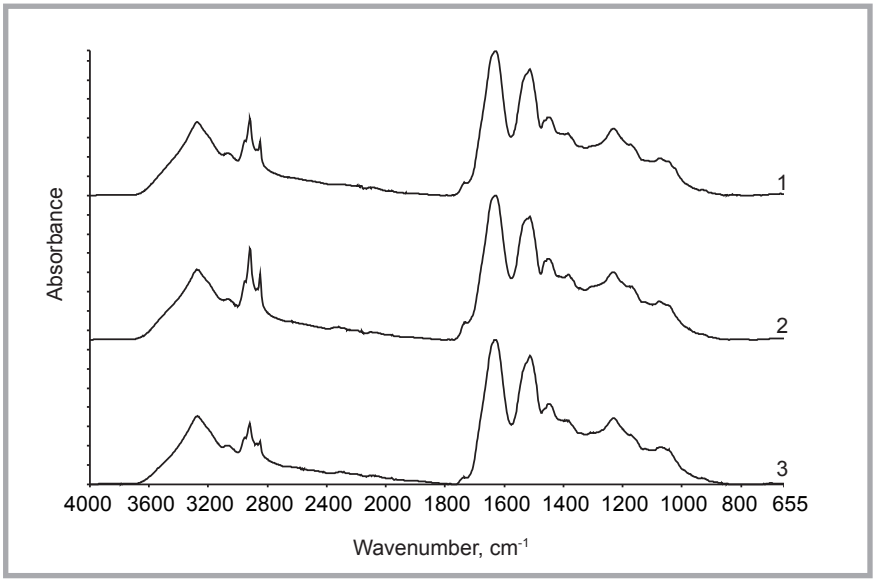

Figure 3*. IR spectra of not treated wool (1) and 24 h treated wool with $Ca(OH)_2$ (2) and with $NaAlO_2$ (3).*

There are two intense peaks in the spectra of all samples at 1452 cm^{-1} and 1386 cm^{-1}. Espinoza et al [23] attributed the first peak to the vibration of groups CH_2 and CH_3. The next peak can be attributed to COO^- vibration [24]. It should be mentioned that there are no differences in these peak intensities.

In summary, we can state that treatment with calcium hydroxide or sodium aluminate does not lead to serious changes in the wool structure which can be reflected in its spectra.

Conslusions

The wool immunization ability of such alkalis as calcium and potassium hydroxides, and sodium aluminate was investigated by evaluating the degradation level of the wool after treatment. Sodium aluminate has been confirmed as an effective immunization agent.

Sodium aluminate immunisation efficiency increases while prolonging the treatment duration and increasing the treatment solution concentration. Treatment with 20 g/l of sodium silicate solution for 3 h allows to reach a high immunization ability almost the same as that for calcium hydroxide under the conditions presented. The immunization effect lasts when the pH is about 13.

The divalent cation is absent in sodium aluminate, contrary to calcium hydroxide, which leads to the assumption that the immunization mechanism is different in this case. Research work is in progress in order to clarify the mechanism of hair

immunization by sodium aluminate because, despite the various experiments carried out, it is still not absolutely clear.

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