An Innovative New Application of Oxidizing Agents to Accelerate Chamois Leather Tanning

Part I: the effects of oxidizing agents on chamois leather quality

by

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Abstract

A disadvantage of chamois leather tanning practiced nowadays is that its oxidation process takes relatively long time, i.e. 9 to 14 days. The use of an oxidizing agent, such as sodium percarbonate was reported to shorten the tanning oxidation process. However, the price of this oxidizing agent is relatively high; a constraint in its application. Other oxidizing agents, such as hydrogen peroxide, may have the same function of accelerating the process. The objectives of this study were to investigate the effects of type and concentration of oxidizing agents in order to obtain the optimum combination of process acceleration and chamois leather characteristics. This study consisted of the leather tanning with rubber seed oil with oil oxidation comparing two types of oxidizing agents at three concentrations of each oxidizing agents; testing of physical, chemical, and organoleptic properties of the leathers, and microscopic studies of the leathers. The results of this study indicate that hydrogen peroxide could be used as oxidizing agents for the chamois leather manufacture, since the chamois leather produced met the quality standards. The best treatment of this trial was hydrogen peroxide at 6% (w/w based on of the weight of rubber seed oil applied). The use of hydrogen peroxide could shorten the oxidation process from 9-14 days to about three days.

Resumen

Una de las desventajas de la curtición de cuero al aceite (chamois) tal cómo se produce hoy en día, es que la oxidación es muy demorada v. y g. de 9 a 14 días. El empleo de un agente oxidante cómo percarbonato sódico fue reportado para acortar el proceso curtiente oxidativo. Desafortunadamente el precio de este agente oxidante es relativamente alto; lo que restringe su uso. Otros agentes, tal cómo Peróxido de Hidrógeno, podrían tener la propiedad de acelerar el proceso. Los objetivos de esta investigación fueron determinar los efectos causados por tipos y concentraciones de los agentes oxidantes para lograr la óptima combinación de la aceleración del proceso así cómo también las mejores características del chamois. Este estudio consistió en curtición de cuero con aceite proveniente de la semilla del caucho por medio de la oxidación comparativa ocasionada por dos agentes oxidantes distintos, ofrecidos a tres concentraciones diferentes; la investigación de las propiedades físicas, químicas, y organolépticas del cuero, así cómo evaluaciones microscópicas fueron efectuadas. Los resultados de esta investigación indican que peróxido de hidrógeno podría utilizarse cómo agente oxidante en la fabricación de chamois ya que el cuero resultante cumple con las normas de calidad. El óptimo tratamiento en este ensayo fue de ofrecer peróxido de hidrógeno al 6% (peso/peso basado en el aceite de semilla de caucho ofrecido). El uso de peróxido de hidrógeno podría acortar el proceso de oxidación de 9-14 días a unos tres días.

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Introduction

Chamois leather is one of the popular leather products in the market. The use of the leather in the human life becomes more spread and diverse. The leather has specific properties, such as it has low density, excellent softness and comfortable.[1] It has specific uses in high quality gasoline filtration and cleaning of optical equipment, such as windows, glasses, and body of the vehicle. Besides that, it can be used as gloves, jewelery wrapping and orthopaedic leather. Oil tanning used in the production of chamois leather practiced today has a disadvantage, i.e. the oxidation stage taking relatively long time, 9 to 14 days.[2,3,4] This causes the production of chamois leather need a relatively long time and increase the production cost.

The use of sodium percarbonate ($2Na_2CO_3{\cdot}3H_2O_2$) could accelerate the process of oil tanning.[3,4] Sodium percarbonate is a white crystalline and water-soluble chemical. It contains sodium carbonate (Na_2CO_3) and hydrogen peroxide (H_2O_2), a strong oxidizing agent. However, sodium percarbonate is relatively expensive, so its use in chamois leather industry will face obstacles of the production cost. Use of one of the sodium percarbonate elements separately, i.e. hydrogen peroxide, might be able to accelerate the process. Price of the compound is much lower than that of sodium percarbonate, so it will be profitable if the material can be used in the chamois leather production. The objectives of this study were to investigate the effects of type and concentration of oxidizing agents on the chamois leather quality and to obtain the best combination of type and concentration of the oxidizing agents to accelerate the oxidation process.

Experimental

Materials and Equipment

Materials used in this study were goat skin pickled pelt, rubber seed oil, sodium chloride, glutaraldehyde (Relugan® GT50), sodium formate, sodium carbonate, and Eusapon® S. Pickled goatskins were used in this trial, as the price of pickled goatskins in Indonesia was cheaper than that of pickled sheepskins. Oxidizing agents used were sodium percarbonate and hydrogen peroxide. Equipment used were tannery/rotary drum, stacking, sammying machine, shaving machine, toggle, buffing machine, thickness gauge, pH meter, shaker, grinder, oven, burner, tensile strength tester (Instron), Kubelka glass apparatus, and JSM-5000 scanning electron microscope (SEM). The rubber seed oil used in the experiment was a liquid material extracted from rubber (*Hevea brasiliensis*) seeds. Relugan® GT 50 is 50% solutions of glutaraldehyde used as pretanning, self-tanning and retanning agent for all types of leather. Eusapon S (formerly Amollan® S) is a surface-active wetting-back and degreasing agent for leather and fur skins. The last two products are manufactured by BASF.

Pretanning

Goat skin pickled pelt was pretanned by Relugan® GT 50. The process was carried out by using procedure reported by Suparno et al.[5]

Oil tanning

Oil tanning was conducted by using a modified method of Suparno et al.[5] The modifications were the additions of oil diffusion process conducted in the tannery drum for 8 hours and oxidation process in the drum for 6 hours. The oxidation process was carried out by using two types of oxidizing agents, i.e. sodium percarbonate and hydrogen peroxide with concentrations of each agent of 2%, 4%, and 6% based on the weight of rubber seed oil applied. Three goatskin pickled pelts were taken for each set of trials. The experiment was undertaken using randomized complete factorial design to estimate the significance in test result differences between trials.

Leather analyses

Tensile strength and elongation at break were measured by using SLP 6.[6] Other physical properties, namely tear strength and water absorption, were measured by using SLP 7 and SLP 19, respectively.[6] Chemical properties, i.e. pH, ash content, and oil content, were tested by using SLC 13, SLC 6, and SLC 4, respectively.[6] Organoleptic properties, i.e. softness, color, and odor, were analyzed by two experts.

Microscopic studies

Cross sections of samples of goat skin pickled pelt and its chamois leather were examined for the changes in fibre structure by JSM-500 scanning electron microscope. The SEM analysis was conducted at 200 × magnifications.

Results and Discussion

Tanning Process

Shrinkage temperature (T_s) of the pickled pelt was 42 °C, whereas the T_s of the pelt after pretanning using glutaraldehyde increased to 79°C. The increase in T_s of the pelt after pretanning shows that the fiber structure of the pelt changed; they became more resistant to heat.[7,8,9] This was due to glutaraldehyde used in the pretanning was capable of undergoing the crosslinks to amine group on the pelt, so that the skin structure that originally separated became merge together into a stronger structure. In this study, rubber seed oil, which was diffused into the pelts, was then oxidized. The oxidation was facilitated by the oxidizing agent in the tannery drum for 6 hours and continued by outside air on a toggle dryer for two days. In this study, oil diffusion process was conducted in the rotating drum for 8 hours. Therefore, the use of oxidizing agents could shorten the oxidation process, i.e. from 9-14 days to about three days (6 hours in the drum and two days on the toggle dryer). The pelt was initially yellowish-white became dark brown after the oxidation.

T_s of the leather after the oil tanning were in the range of 71 to 78°C or slightly decreased compared to the T_s of the skin after pretanning (Table I). This can be caused by the loss of some tanning effects of the aldehyde on the leather due to the washing process using a soaking agent. Besides that, the oil, which was diffused and filled the cavities in inter-fiber fabric of the skin causing the fiber structure apart[9] can also caused the leather's T_s decreases. Leather with fluffy fiber structure is relatively easier to shrink compared to leather with compact fiber structures. Chamois tanning is an example of the tanning agent having more affinity for itself than that of for the substrate.[9] In this study, the oxidation process was accelerated by various combinations of type and concentration of the oxidizing agents. The highest T_s (78°C) were given by 4% and 6% sodium percarbonate. The lowest T_s (71°C) was resulted by 4% hydrogen peroxide, as shown in Table I.

The type of oxidizing agents and interaction between the oxidizing agent types with their concentrations affected significantly the T_s of the leather. Treatment by hydrogen peroxide gave a lower shrinkage temperature. This could be due to oxidation reaction produced by hydrogen peroxide was higher than that by sodium percarbonate, so that the diffused and oxidized oils into the skin were higher. This resulted in keeping the fiber structure apart, which make it was easier to shrink.

Chemical properties of leather

Chemical properties of chamois leather are pH, ash content, and oil content. Results of chemical testing are shown in Table II.

pH

The pH's of leather samples used in this study were 6.4 to 6.6. The highest pH was resulted by the treatment using 4% sodium percarbonate, whereas the lowest one was given by the treatment using 6% hydrogen peroxide (Table II). In general, the pHs of leathers in this study met the quality requirement for the chamois leather according to Indonesia National Standard (SNI) 06-1752-1990, i.e. maximum of 8.[10]

Ash content

This test was used to determine the amount of minerals contained in leather. The leather's ash contents in this study were in the range of 1.0 to 1.5% (Table II). Therefore, the ash contents of the chamois leathers met the standard, i.e. maximum of 5%.[10] Minerals contained in leather, such as potassium, calcium, iron, and phosphors, affect ash content of

TABLE I
Shrinkage temperature of chamois leather

Oxidizing agents	Concentration (%)	Shrinkage temperature (°C)
Sodium percarbonate	2	75
Sodium percarbonate	4	78
Sodium percarbonate	6	78
Hydrogen peroxide	2	74
Hydrogen peroxide	4	71
Hydrogen peroxide	6	72

TABLE II
Chemical properties of chamois leathers

Oxidizing agents	Concentration (%)	pH	Ash content (%)	Oil content (%)
Sodium percarbonate	2	6.6	1.0	7.9
Sodium percarbonate	4	6.6	1.2	6.8
Sodium percarbonate	6	6.5	1.2	8.7
Hydrogen peroxide	2	6.5	1.5	6.8
Hydrogen peroxide	4	6.5	1.2	7.9
Hydrogen peroxide	6	6.4	1.3	7.2

the leather. In addition to those minerals, there are also small amount of SiO_2, Zn, Ni, As, and Fe in leather.[1]

Oil content

Oil content test was conducted to determine the quantity of oil in the leather, especially oil remaining due to oil tanning. Good quality chamois leather is indicated by low oil content, i.e. below 10%.[10] Leather with high oil content will cause a bad odor, sticky and uncomfortable when it is used. Based on this experiment, oil contents of the chamois leathers were in the range of 6.8 to 8.7%. The highest oil content was found in the treatment using 6% sodium percarbonate, whereas the lowest one was given by the treatment using 2% hydrogen peroxide (Table II). In general, the oil content of the leather fulfilled the standard, i.e. maximum of 10%. Oil content of the leather is strongly influenced by the final washing process of the leather using warm alkaline water. This process is useful to eliminate the excess of oil attached to the leather. The use of warm alkaline water is intended to saphonificate the oil, so that it could be washed together with running water.

Physical properties of leather

Thickness

The thickness of the chamois leather resulted in this trial were in the range of 0.51 to 0.68 mm. This demonstrates that the leather thickness met the standard, i.e. 0.3 to 1.2 mm.[10]

Leather thickness can be adjusted at manufacture process of the leather, i.e. through the shaving and buffing processes. Shaving process is to remove the grain and flesh as well as to adjust the leather thickness, whereas buffing process is to smooth the surface of leather, and at the same time, it can also be used to adjust the leather thickness.

Tensile strength

Tensile strengths of chamois leathers obtained from this experiment were 28.3 to 32.1 N/mm^2. The highest tensile strength was given by the treatment using 4% hydrogen peroxide, while the lowest one was obtained from the treatment using 4% sodium percarbonate (Figure 1). Therefore, they met the standard, i.e. minimum of 7.5 N/mm^2.[10]

Effects of sodium percarbonate and hydrogen peroxide were not significantly different on the tensile strength of the leather. These results indicate that the fixation of oxidized oil in the leather fibers by these two types of oxidizing agents were not significantly different. Tensile strength is strongly influenced by the direction of the fiber weaves. Greater tensile strength was provided by the fiber weave which are parallel to the direction of stretch and vice versa. The direction of collagen fiber weave was not only influenced by the thickness of the skin, but also was influenced by its location on the skin.[9]

Elongation at break

Elongation at break is one of the important factors in determining the quality of chamois leather. It indicates the elasticity of the leather. Leather which has high elongation at break allows the leather to not easily torn or broken during its use. In general, elongations at breaks of the leathers in this trial were in the range of 122.2 to 137.6%. The highest elongation at break was obtained from the treatment using 2% sodium percarbonate and the lowest one was given by the treatment using 6% sodium percarbonate (Figure 2). They met the requirement for the chamois leather, i.e. higher than 50%.[10]

Tear strength

Tear strengths of the leather in this trial were in the range of 74.4 to 93.4 N/ mm. The highest value was given by the treatment using 2% sodium percarbonate and the lowest one was obtained from the treatment with 6% sodium percarbonate (Figure 3). In general, the tear strength of the leather fulfilled the standard, i.e. above 15 N/mm.[10]

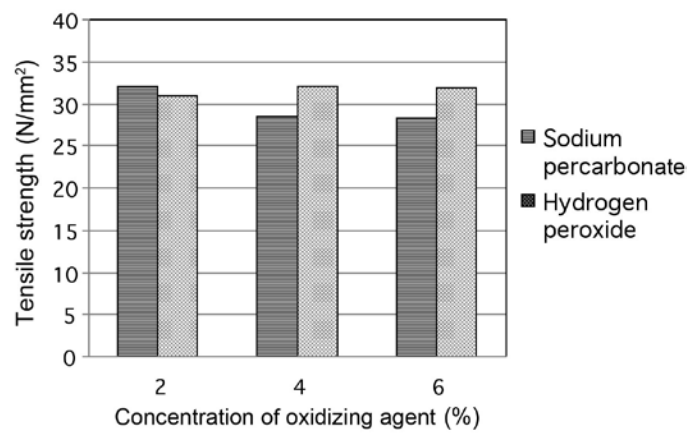


Figure 1. Effects of oxidizing agents' types and concentrations on the tensile strength of chamois leather

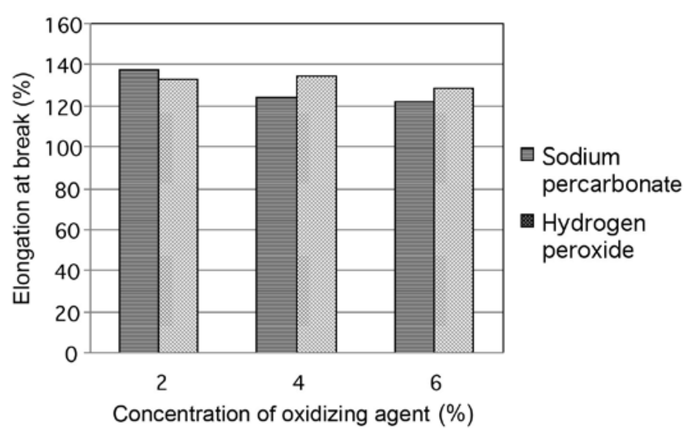


Figure 2. Effects of oxidizing agents' types and concentrations on the elongation at break of chamois leather

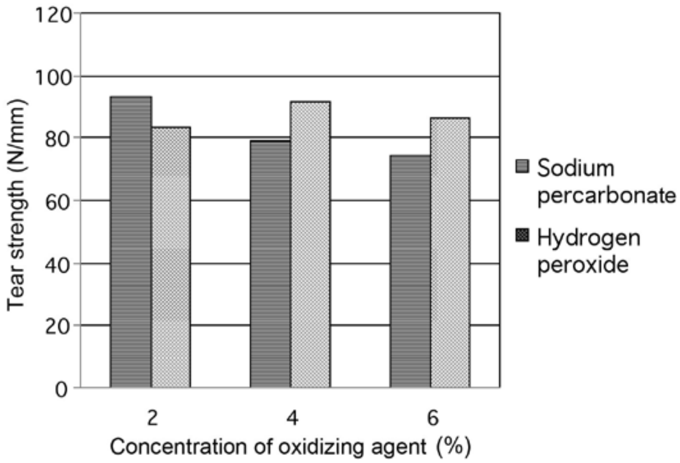


Figure 3. Effects of oxidizing agents' types and their concentrations on the tear strength of chamois leather

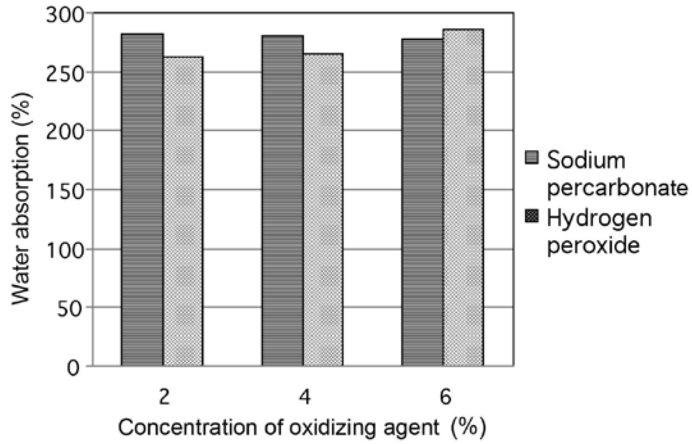


Figure 4. Effects of oxidizing agents' types and concentrations on the 24 hours-water absoption of chamois leather

Water absorption

Chamois tanning is a fixation of oil oxidation products to the protein fiber.[11] It gives the effect of keeping the fiber structure apart. Therefore, the collagen can hold excess water within the hydrophobic polymerized oil matrix.[9]

Water absorption is an important variable in determining the quality of chamois leather, as it relates to its use as absorbing, drying, cleaning or filtering agents. The higher the water absorption of the chamois leather, the better the quality of the leather. Measurement of water absorption was performed twice, i.e. for the duration of 2 hours and 24 hours. Water absorptions for 2 hours duration were in the range of 240.2 to 266.7%, whereas those for 24 hours measurements were in the range of 262.0 to 285.7% (Figure 4). In general, water absorptions of chamois leathers produced in this study met the standard, i.e. minimum of 100% (2 hours) and 200% (24 hours).[10] Water absorption for 24 hours was higher than that of for 2 hours, as the longer the absorption time, the more water absorbed by the leather; the absorption will end when the leather has been saturated by water.

Organoleptic properties

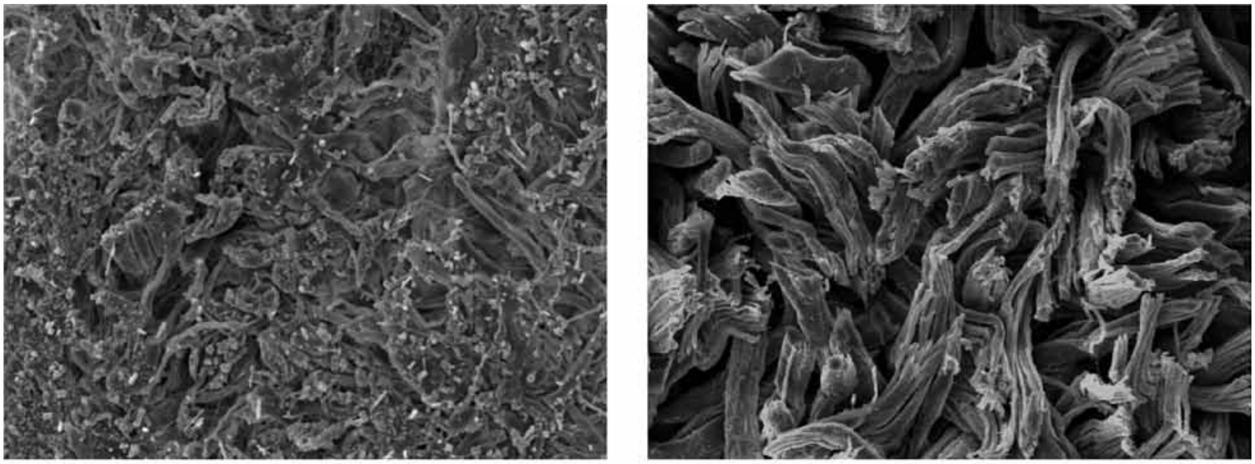
Organoleptic properties are the main parameters used to determine the quality of chamois leather, since these properties are directly related to the comfort and safety of the leather application. The organoleptic properties of the leather are softness, color, and odor. The results of the organoleptic properties measurements are shown in Table III.

Based on Table III, the highest value of softness was found in the treatment using 2% sodium percarbonate and the lowest one was given by the treatment using 2% hydrogen peroxide. Softness was not influenced by the type and concentration of oxidizing agent, but only influenced by the interaction between the oxidizing agent type and its concentration. The color requirement for chamois leather is light yellow to white.[10] The best color which means the lowest color intensity was given by the treatment using 6% hydrogen peroxide. The types and concentrations of oxidizing agents as well as their interactions affected the color of the leather. The treatment produced the highest odor was 6% hydrogen peroxide. The odor of the leather was generally caused by the excess of oil in the product. A good chamois tanning does not give odor to the leather.

TABLE III
Organoleptic properties of chamois leather*

Oxidizing agents	Concentration (%)	Softness	Color	Odor
Sodium percarbonate	2	7 – 8	7	7 – 8
Sodium percarbonate	4	6 – 7	5	7 – 8
Sodium percarbonate	6	5 – 6	6	7 – 8
Hydrogen peroxide	2	4 – 5	6 – 7	6
Hydrogen peroxide	4	5 – 6	7	7
Hydrogen peroxide	6	7	8	8

* In 10 point scale: 1 = poor, 10 = excellent.



a. SEM of goat skin pickled pelt

b. SEM of chamois leather with oxidation using 6% hydrogen peroxide

Figure 5. Scanning electron micrographs of goat skin pickle pelt and chamois leather with magnification of 200×

Based on the organoleptic properties, water absorption, and strengths of the leathers, the best treatment for the oxidation process in the chamois tanning was the treatment using 6% hydrogen peroxide. This treatment gave the highest average values of those properties compared to those of the other treatments.

Microscopic studies

The scanning electron micrographs of the goat skin pickled pelt and chamois leather samples are demonstrated in Figure 5. The micrographs indicate that the chamois leather produced by the oxidation process using 6% hydrogen peroxide (Fig. 5b) had more opened up fibrous structures compared to the getskinn pickled pelt (Fig. 5a). This was due to the ability of the oxidized rubber seed oil to lubricate or coat the collagen fibers.

The opened up collagen fiber structure is a result of the oil tanning, i.e. a matrix of polymerized hydrocarbon chains in the collagen matrix.[9] It retains the structure of collagen fiber structure apart, as a form of lubrication to prevent the fiber structure coming together and sticking. The system is able to hold excess water.

Conclusions

Sodium percarbonate and hydrogen peroxide can be used to accelerate the oxidation process in the chamois leather making, as demonstrated by the leather quality resulted in by both oxidizing agents fulfilled the standard. The oxidizing agent type used in this trial significantly affected the shrinkage temperature, ash content, color, odor of the chamois leather, while the oxidizing agent concentration significantly affected the color and odor of the leather. Oil oxidation process using 6% hydrogen peroxide was the best treatment in this trial to produce chamois leather. The treatment resulted in the leather that has the best organoleptic, water absorption, and strength properties. The use of hydrogen peroxide could shorten the oxidation process in the chamois tanning, i.e. from 9-14 days to about three days (6 hours in a tannery drum and two days on a toggle dryer). Leather tanning using that treatment produced chamois leather with the properties as follows: shrinkage temperature of 71.5^{o}C, tensile strength of 31.8 N/mm^2, elongation at break of 128.9%, tear strength of 86.4 N/mm, water absorption of 259.7% (2 hours) and 285.7% (24 hours), pH of 6.4, oil content of 7.2%, ash content of 1.3%; softness, color and odor were good to very good.

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Appendix

SNI 06-1752-1990 is a quality standard for chamois leather in Indonesia, published by *Badan Standardisasi Nasional* (National Standardization Agency of Indonesia). The standard states that chamois leather must meet quality requirements for chemical, physical, and organoleptic properties. Chemical requirements: pH: max 8; ash content: max 5%; oil content: max 10%. Physical requirements: thickness: 0.3-1.2 mm; elongation at break: min 50%; tensile strength: min 7.5 N/mm^2; tear strength: min 15 N/mm; water absorption: 2 hours: min 100%; 24 hours: min 200%. Organoleptic requirements: handle: soft; color: light yellow to white.