An Innovative New Application of Hydrogen Peroxide to Accelerate Chamois Leather Tanning. Part II: The Effect of Oxidation Times on the Quality of Chamois Leather

by

Ono Suparno,* E. Gumbira-Sa'id, Ika A. Kartika, Muslich and Shiva Amwaliya

Department of Agroindustrial Technology, Faculty of Agricultural Engineering and Technology, Bogor Agricultural University (IPB)

Darmaga Campus, PO Box 220, Bogor 16002, Indonesia

Abstract

The use of oxidizing agent, such as hydrogen peroxide, was reported to shorten the oxidation process time of chamois tanning. Appropriate conditions for this tanning are needed in order to improve its process efficiency, and to obtain a satisfactory leather quality. The objectives of our study were to investigate the effects of oxidation times in chamois tanning on the quality of the resulting leather, and to determine the best condition of the oxidation time. The experiments were conducted by tanning pickled goatskin for 4, 6, and 8 hours oxidation times inside a rotary drum, and 1, 2, and 3 days of oxidation times outside the drum. The physical, chemical, and organoleptic properties of the leathers were then tested. This study showed that they fulfilled the quality requirements for chamois leather. The best conditions for oxidation were oxidation times of eight hours inside, and one day outside a rotary drum. Therefore, the use of hydrogen peroxide oxidizing agent shortened the oxidation process outside the rotary drum in chamois leather production from nine to two days.

Resumen

El uso de un agente oxidante, tal como el peróxido de hidrógeno, fue informado como reductor del tiempo de proceso de oxidación en el curtido de gamuza. Las condiciones apropiadas para este curtido son necesarias con el fin de mejorar su eficiencia de proceso, y para obtener una calidad satisfactoria de cuero. Los objetivos de nuestro estudio fueron investigar los efectos de los tiempos de oxidación en el curtido de gamuza en la calidad del cuero resultante, y para determinar las mejores condiciones del tiempo de oxidación. Los experimentos se realizaron curtiendo pieles de cabra pickeladas con tiempos de oxidación de 4, 6, y 8 horas dentro de un fulón giratorio, y 1, 2, y 3 días de oxidación fuera del fulón. Las propiedades físicas, químicas y organolépticas de los cueros fueron ensayadas a continuación. Este estudio demostró que las pruebas cumplen con los requisitos de calidad para gamuza. Las mejores condiciones para la oxidación fueron tiempos de oxidación de ocho horas en el interior, y un día fuera de un fulón giratorio. Por lo tanto, el uso del agente oxidante peróxido de hidrógeno acorta el proceso de oxidación en el exterior del fulón rotativo en la producción de cuero de gamuza de nueve a dos días.

*Corresponding author e-mail: ono.suparno@ipb.ac.id

Manuscript received December 16, 2012, accepted for publication February 16 2013

INTRODUCTION

Demand for chamois leather in the global market continues to increase.[1] This implies that chamois leather is a popular article, because it has many uses and has aesthetic value. Use of chamois leather is widespread and diverse. This leather is used for cleaning and drying of optical instruments, windows, car body, manufacturing of gloves; garments; and orthopedic leather as well as in the filtration of high-grade gasoline. Chamois leather is produced by oil tanning. The oil tanning practiced nowadays has some weaknesses, such as requiring a relatively long oxidation time, i.e. nine days to two weeks.[2,3] Consequently, its overall production time is relatively long; thereby, reducing the efficiency of this tanning process and directly affecting the leather industry production capacity.

The use of hydrogen peroxide (H_2O_2) oxidizing agent, was shown in a previous study, to accelerate the oxidation time in the production of chamois leather.[4] However, the appropriate oxidation time for chamois leather specifically using rubber seed oil and hydrogen peroxide is not known. The suitable oxidation time in this tanning process is necessary to improve its efficiency, and the quality of the resultant leather, so as to increase the added value of the product. The objectives of this study were to investigate the effect of oxidation time in the chamois tanning on its leather quality, and to determine the best condition of oxidation time for this tanning which was accelerated by hydrogen peroxide.

EXPERIMENTAL

Materials and Equipment

Pickled goatskin, hydrogen peroxide, glutaraldehyde (Relugan® GT50), rubber seed oil, degreaser, formic acid, sodium carbonate, and salt (NaCl) were used in this study. The equipment used were rotary drum, stacking, buffing machine, shaving machine, sammying machine, toggle dryer, horses, and thickness gauge. Kubelka glass apparatus, tensile strength tester (UTM Instron), JSM-5000 scanning electron microscope were used for the physical and microscopic tests.

Pretanning

Relugan® GT50, an aldehyde tannage, was used for pretanning of pickled goat skin. A procedure reported by Suparno et al.[5] was employed for the tanning process.

Oil Tanning

A modification of procedure reported by Suparno et al.[5] was used for the oil tanning. The modifications undertaken in the trials were the additions of oil diffusion process conducted in the rotary drum for 8 hours and oxidation processes inside the rotary drum for 4, 6, and 8 hours. The inside rotary drum oxidation process was undertaken by using hydrogen peroxide as oxidation agent with concentrations of 6% based on the weight of rubber seed oil used for the trials. Besides that, the modification was the outside rotary drum oxidation processes by hanging the leathers on the toggle dryer for 1, 2, and 3 days. The tanning procedure is shown in Appendix I.

Microscopic Studies

Microscopic studies were undertaken to investigate the changes in fiber structure of the chamois leather. Cross sections of samples of goat skin pickled pelt and its chamois leather were scanned by using JSM-500 scanning electron microscope at 500× magnification.

Analyses of Leather

Physical, chemicals, and organoleptic properties of the chamois leathers were tested. Tensile strength and elongation at break were measured by using SLP 6.[6] Tear strength and water absorption of the leathers were tested by using SLP 7 and SLP 19, respectively.[6] The pH, ash content, and oil content of the leathers were measured by using SLC 13, SLC 6, and SLC 4, respectively.[6] Softness, color, and odor of the leathers were examined by two experts of chamois leather.

RESULTS AND DISCUSSION

Most of hydrogen peroxide uses are based on the utilization of its decomposition reaction, which results in oxygen. Besides it produces oxygen, the decomposition reaction of hydrogen peroxide generates water and heat. The exothermic decomposition reaction is as follows:[7]

$$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2 + 23.45 \text{ kcal/mol.}$$

In chamois tanning, oxygen produced by the decomposition of hydrogen peroxide is used for oil oxidation. Sharphouse[8] described that in the oxidation process, initially, it is formed peroxide and hydroperoxide, and their reaction with skin proteins will give characteristic of 'full oil' tanning. Furthermore, the unbound oil can be further oxidized into volatile aldehyde or non-volatile aldehyde, and then undergo chemical changes, such as polymerization, forming a more viscous product. These products can also bind to the skin fiber during its formation.

In this study, physical, chemical, and sensory properties of the chamois leathers were measured. The physical properties were tear strength, tensile strength, elongation at break, and water absorption capacity.

Microscopic Studies

Figure 1a shows that the structures of the fibers in the pickled goatskin were very tight and closed. Fiber structure affects the leather's ability to absorb water. Leather with tightly interwoven fibers tends to have low water absorption. In the skin after oil tanning (Figure 1b), it appeared that very loosely interwoven fibers. There were void spaces between the fibers. This is caused by the oxidized oil filling the cavity among the fibers, so fiber that is initially tight become apart (looser).

A more open the fiber structure associates with the ability to penetrate the oil and coat the fibers more effectively.[1] The oxidation process produced the oil polymer matrix. The polymerized products will then form a polymer matrix in the collagen matrix that will hold the structure of collagen fibers apart, so they can increase the water absorption capacity.

Tear Strength

Tear strength of the chamois leathers resulted in this study met the chamois leather requirements according to the Indonesian chamois leather standard, SNI 06-1752-1990,[10] where it must be at least 15 N/mm. The tear strengths were in the range of 58.4-70.8 N/mm (Figure 2).

Based on this study, the oxidation times inside the drum and interaction of both treatments did not affect significantly the leather tear strength. The highest average tear strength was obtained from the treatment of 8 hours oxidation time inside the drum (64.4 N/mm) and the lowest was given by the 6 hours treatment (61.3 N/mm). However, they were not significantly different. The results of variance analysis shows that the oxidation times outside the drum and interactions of both factors gave significantly different effect on the value of tear strength. The oxidation process outside the drum was assisted by oxygen from the air, so more oil can be oxidized. In addition, with oxidation outside the drum, leather was stretched

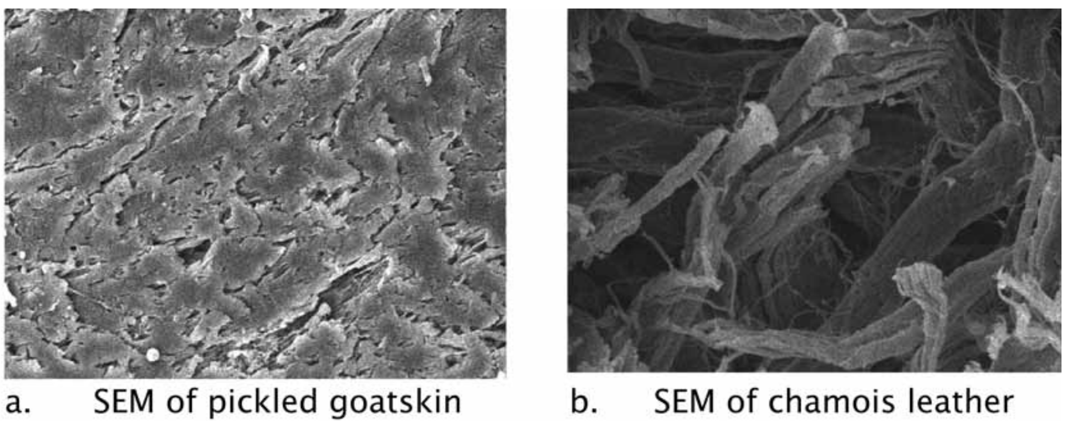

Figure 1. Scanning electron micrographs of pickled goatskin and chamois leather with magnification of 500×.

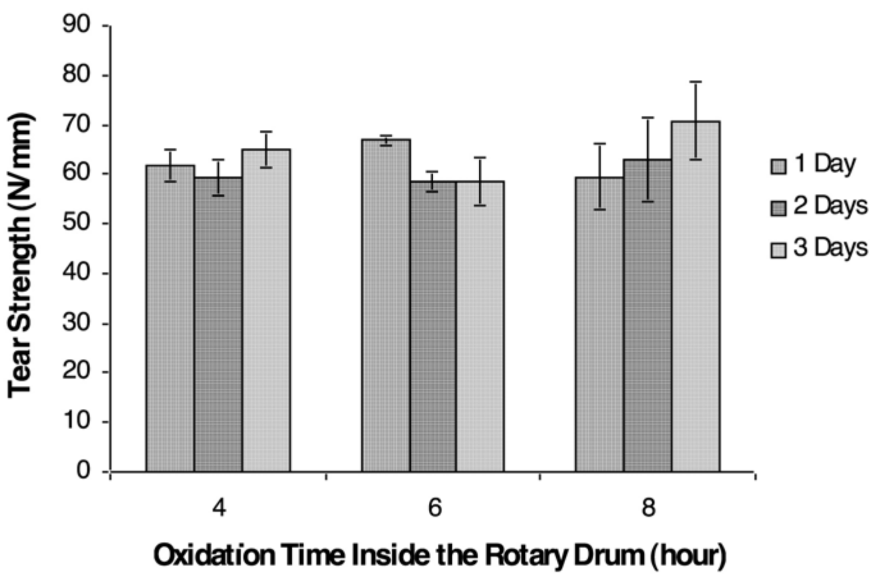

Figure 2. Tear strength of chamois leather at different oxidation times inside and outside the drum.

on a toggle dryer, so there was a dry air flowing on both sides of the leather that causes the leather to be stiffer, drier, and stronger; inline with the increases of oxidation time outside the drum.

Based on further analysis, one day oxidation time outside the drum gave insignificant different effect on the treatments of 2 days and 3 days. However, treatment of 2 days gave significantly different effect from treatment of 3 days. Treatment of 3 days outside the drum gave the highest average value, i.e. 64.8 N/mm.

Tensile Strength

Tensile strengths of chamois leathers resulted from this study were in the range of 25.0-32.7 N/mm^2 (Figure 3). The tensile strengths fulfilled the standard of SNI 06-1752-1990,[10] i.e. minimum of 7.5 N/mm^2.

Oxidation time outside the drum gave a significantly different effect on the tensile strength, while oxidation time inside the drum and the interaction between those two factors did not give significantly different effect. When the leather is oxidized outside the drum, the presence of oxygen in the air can help the oxidation process. The oxidation by oxygen from the air occurs spontaneously if material containing oil or fat is left in contact with air. In addition, with oxidation outside the drum, the leather was stretched on a toggle dryer, so there was a dry air flowing on both sides of the leather causing the leather became stiffer, drier, and stronger.

The oxidation time outside the drum for 3 days did not give significantly different effect on the treatment of 1 day and 2 days; meanwhile the 1 day treatment outside the drum gave a significantly different effect on 2 days treatment. Treatment of 2 days outside the drum gave the highest average value of the leather tensile strength, 30.2 N/mm^2.

Elongation at Break

Elongation at break of chamois leathers resulted from this study were between 138 and 176% (Figure 4). In general, elongation at break of the leathers met the standard requirement for chamois leather, SNI 06-1752-1990,[10] i.e. minimum of 50%.

Oxidation times inside and outside the drum, as well as the interaction between those two factors did not give significantly different effect on the average values of elongation at break. This means that the treatments used in this study gave similar effects on the elongation at break of the leathers.

Water Absorption

Water absorptions of the leather samples for 2 hour absorption were in the range of 291.4-357.6% (Figure 5). This result demonstrated that the water absorption of the chamois leathers in this study fulfilled the standard of SNI 06-1752-1990,[10] i.e. minimum of 100%.

Oxidation time inside the rotary drum affected significantly water absorption, while oxidation time outside the drum and the interaction between those two factors did not. The treatment with a combination of 4 hours inside the drum oxidation time and 2 days outside the drum oxidation time gave the highest water absorption (Figure 4).

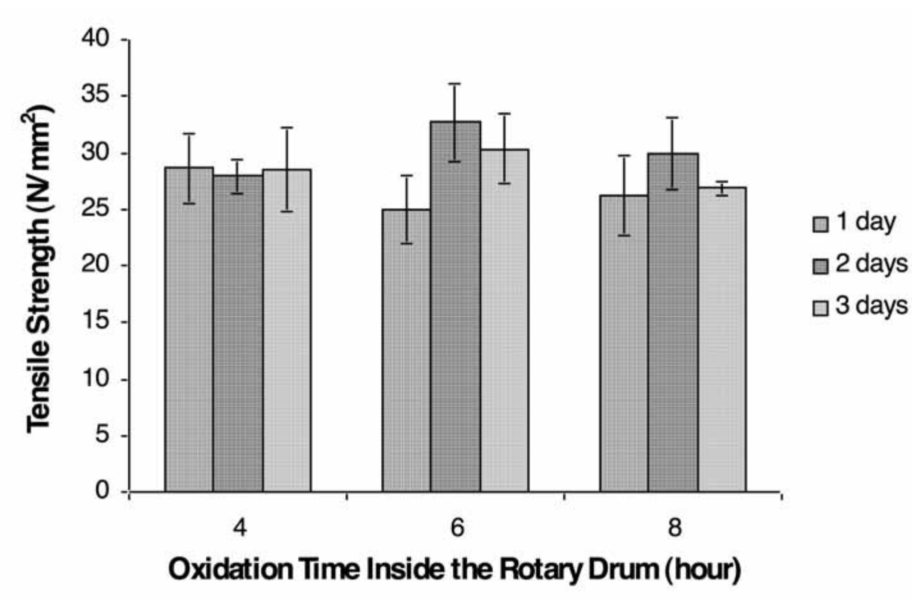

Figure 3. Tensile strength of chamois leather at different oxidation times inside and outside the drum.

The inside the rotary drum oxidation time of 4 hours gave a significantly different effect on the oxidation time of 6 hours and 8 hours, whereas the treatment of 6 hours and 8 hours did not give significantly effect. Oxidation time of 4 hours produced the highest average value of water absorption, 344%. It might be due to the longer oxidation time in the drum can lead to oxidative reaction on the leather surface occur more dominantly. Consequently, when the leather was oxidized in the open air outside the drum, oxygen from the air cannot oxidize the oil in the deeper layer of the leather, because it was blocked by the oxidation products.

Chemical Properties

The pH, ash content, and oil content of the chamois leathers were investigated. Table I demonstrates the chemical properties.

pH

This studies shows that pHs of chamois leathers were in the range of 6.8-7.2 (Table I.) The results of variance analysis showed that factor of outside rotary drum oxidation time gave a significantly different effect on the pH value, while the factor of inside rotary drum oxidation time and interaction

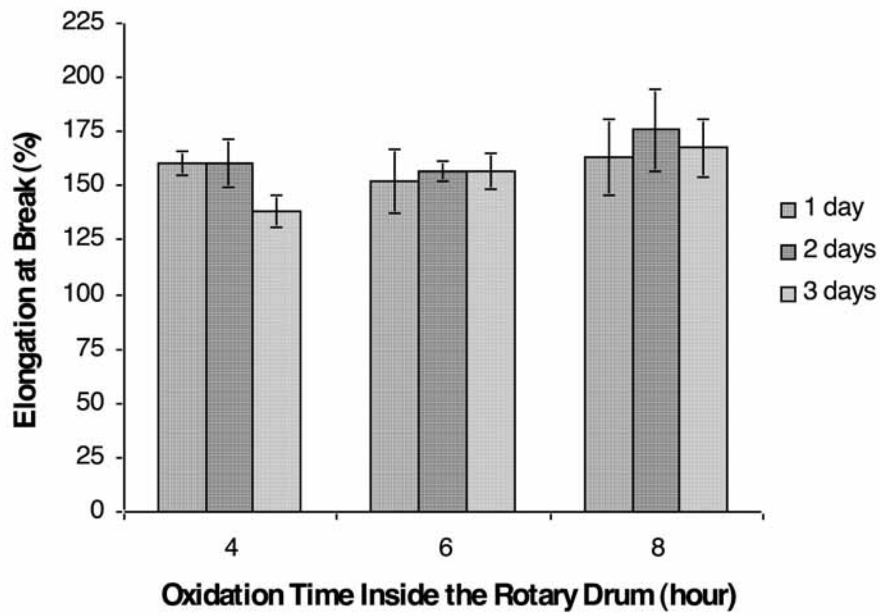

Figure 4. Elongation at break of chamois leather at different oxidation times inside and outside the drum.

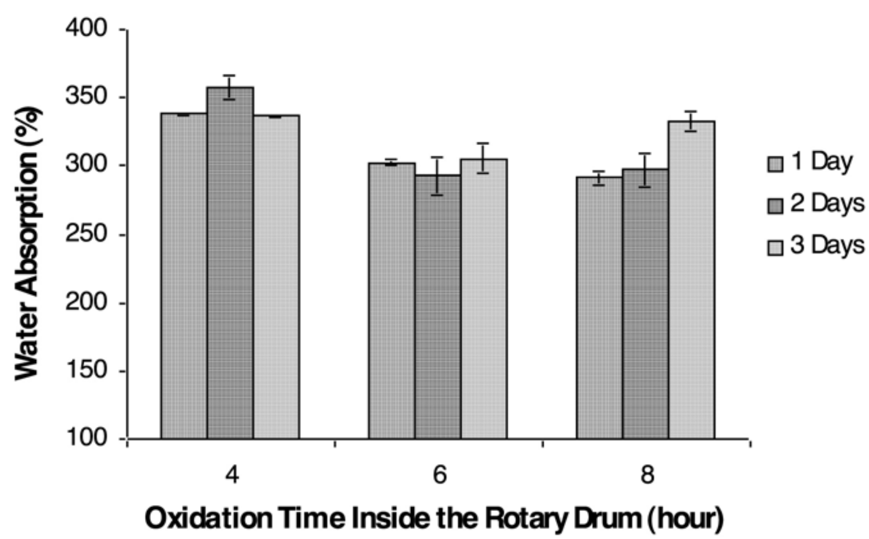

Figure 5. Water absorption of chamois leather at different oxidation times inside and outside the drum.

TABLE I
Chemical properties of chamois leather at different oxidation times inside and outside the drum.

Oxidation Time Inside the Rotary Drum (hour)	Oxidation Time Outside the Rotary Drum (day)	pH	Ash Content	Oil Content
4	1	7.0 ± 0.03	1.6 ± 0.55	2.1 ± 0.43
4	2	7.2 ± 0.05	1.7 ± 0.51	4.1 ± 1.12
4	3	7.2 ± 0.08	1.7 ± 0.41	3.9 ± 1.50
6	1	6.8 ± 0.05	1.7 ± 0.69	3.8 ± 1.28
6	2	7.1 ± 0.09	2.0 ± 0.38	4.3 ± 1.14
6	3	7.2 ± 0.08	2.0 ± 0.29	3.9 ± 1.42
8	1	6.9 ± 0.11	1.9 ± 0.30	2.7 ± 1.27
8	2	7.2 ± 0.17	2.6 ± 1.02	3.7 ± 1.48
8	3	7.2 ± 0.01	2.9 ± 0.71	3.4 ± 1.02

between these two factors did not give a significantly different effect. Generally, the pH value of the leather was affected by skin washing process after oxidation and the process of setting out to remove residual washing water containing large amounts of sodium carbonate. Overall, the pH values were compliant to the chamois leather standard of SNI 06-1752-1990,[10] with a maximum pH value of 8.

Oil Content

The oil content of chamois leather is oil residue after the washing process. The oil is not attached or bound to the collagen fibers.[3] The test is conducted to determine the quantity of oil that are not washed away and eventually left on the leather. High levels of oil on the leather result in excessive odor, and the leather being sticky and uncomfortable during use.

Based on this study, oil contents of chamois leather were in the range of 2.1-4.3% (Table I.) The oxidation time inside and outside the rotary drum as well as the interaction between these two factors did not give significantly different effect on oil content of the leathers. This was because the oil content was generally influenced by the washing process of the leather after oxidation and the process of setting out to remove residual washing water. Overall, the oil contents were compliant to the chamois leather standard of SNI 06-1752-1990,[10] i.e. maximum oil content of 10%.

An excess of oil in the process of oil tanning can be removed through the washing process using warm alkaline water. The use of warm alkaline water is intended to saponify the oil, so it can be washed together with water. In the washing process, discarding the remaining oil in the leather is assisted by a mechanical treatment or setting out. Therefore, the oil content remaining in the leather is very dependent upon the washing process and the setting out. In addition, the oil content in the leather is also affected by beam house process, for example liming, which aims to dissolve the epiderm and hydrolyze fats and substances that are not needed in the tanning process, so that during the process of liming, a part of the fats on the skin are removed.[3]

Ash Content

The ash content of a material indicates the number of inorganic minerals contained in the material. Testing of ash content of the chamois leather provided results that the ash contents of the leathers were in the range of 1.6-2.9% (Table I.) The factors of oxidation times inside and outside the rotary drum as well as the interaction between these two factors did not give significantly different effect on the ash content. This indicates that the oxidation time treatments did not have a significant effect on the ash content, because ash content of the leather is generally influenced by the minerals contained in the skin or hide. The minerals include potassium, calcium, iron, and phosphorous, which are generally found in the skin or hide as salts of chloride, sulfate, carbonate, and phosphate.

In addition, there are also SiO_2, Zn, Ni, As, Fe, and S in very small amounts.[3] In general, the ash contents were compliant with the chamois leather standard of SNI 06-1752-1990,[10] i.e. a maximum ash content of 5%.

Organoleptic Properties

Organoleptic properties of the leather, i.e. softness, color, and odor, are shown in Table II. The results show the effects of oxidation times inside and outside the rotary drum on the organoleptic properties.

Softness of chamois leather is very important to prevent the items cleaned or dried from scratching, as the chamois leather is usually used for cleaning or drying. Besides that, soft leather tends to increase its water absorption and flexibility, so it will provide comfort during use. Table II demonstrated that softness of the leathers obtained from this study were in the range of 4 to 9, meaning that the softness of the leathers were good to very good.

Color indicates the level of lightness and chromaticity of an object.[11] According to the SNI 06-1752-1990, preferred color of chamois leather is yellow to nearly white.[10] Organoleptic test on color provided the results that leather color values were in the range of 7 to 8 (Table II). The leathers were pale yellow. The yellow color was mainly due to the oxidation of linoleic glycerides forming a yellow unsaturated ketone compound. The yellow color can also be produced from protein and nitrogen bases extracted together with oxidized oil.

Odor contained in the chamois leather is generally caused by oil residue left on the leather due to an insufficient washing process. Undesirable odor will decrease the aesthetic and consumer appeal on the product. From the odor test, all combinations of treatments provided the same odor value, i.e. 7 to 8 (Table II). This suggests that the combinations of oxidation times tried in the tanning did not give significantly different effect on the odor of leather. Generally, odor of chamois leather is dependent upon sufficiency of washing process of the leather after oil oxidation. Insufficient washing process can leave an undesirable odor, since the odor is generated by the oil residue sticking to the leather, if it is not washed away completely.

CONCLUSION

Chamois tanning produced leather having a different fiber structure than that of pickled skin. Pickled goatskin had a closed fiber structure. By comparison, its chamois leather had more opened up fibers with a looser inter fiber structures. The oxidation time factors of inside versus outside the rotary drum in the chamois tanning process influenced the quality of its leather. Oxidation time inside the drum affected water

TABLE II
Organoleptic properties of chamois leather of at different oxidation times inside and outside the drum.*

Oxidation Time Inside the Rotary Drum (hour)	Oxidation Time Outside the Rotary Drum (day)	Softness	Color	Odor
4	1	4-5	8	7-8
4	2	6-7	7	7-8
4	3	6-7	7	7-8
6	1	7-9	7-8	7-8
6	2	6-8	7-8	7-8
6	3	6-8	7	7-8
8	1	7-9	8	7-8
8	2	8	7	7-8
8	3	8-9	7	7-8

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

absorption and softness of the leather; interaction between two factors affected the tear strength; and oxidation time outside the drum did not give any significantly effects to the leather quality.

From this study, the selected treatment to produce the optimal chamois leather was the combination of oxidation times inside the drum of 8 hours and outside the drum of 1 day. This treatment produced chamois leather with a high water absorption capacity. Besides that, the organoleptic properties of the leather produced from that treatment were very good.

ACKNOWLEDGEMENT

The authors thank to the Directorate General of Higher Education of the Indonesian Ministry of Education and Culture for its financial support and Bogor Agricultural University (IPB) for its facilities for conducting this study.

REFERENCES

1. Krishnan, S.H., Sundar, V.J., Rangasamy, T., Muralidharan, C., Sadulla, S.; Studies on Chamois Leather Tanning Using Plant Oil, *J. Soc. Leather Technol. Chem.* **89**, 260-262, 2005.
2. Hongru, W., Yuanyue, M., Yue, N.; An Oil Tanning Process Accelerated by Oxidation with Sodium Percarbonate, *J. Soc. Leather Technol. Chem.* **92**, 205-209, 2008.
3. Suparno, O.; Optimization of Chamois Leather Tanning Using Rubber Seed Oil, *JALCA* **105**, 189-194, 2010.
4. Suparno, O., Gumbira-Sa'id, E., Kartika, I.A., Muslich, Mubarak, S.; An Innovative New Application of Oxidizing Agents to Accelerate Chamois Leather Tanning. Part I: The Effects of Oxidizing Agents on Chamois Leather Quality, *JALCA* **106**, 360-366, 2011.
5. Suparno, O., Kartika, I.A., Muslich; Chamois Leather Tanning Using Rubber Seed Oil, *J. Soc. Leather Technol. Chem.* **93**, 158-161, 2009.
6. SLTC; Official Methods of Analysis, Society of Leather Technologists and Chemists, Northampton, 1996.
7. Skuler; 2007. Introduction to Hydrogen Peroxide. http://www.forumsains.com/ artikel/mengenal-hidrogen-peroksida-h2o2/. [7 February 2011].
8. Sharphouse, J.H.; Theory and Practice of Modern Chamois Leather Production, *J. Soc. Leather Technol. Chem.* **69**, 29-43, 1985.
9. Covington, A.D.; Tanning Chemistry, the Science of Leather. The Royal Society of Chemistry, Cambridge, 2009.
10. BSN; Indonesia National Standard for Chamois Leather-SNI 06-1752-1990, Badan Standarisasi Nasional, Jakarta, 1990.
11. Suparno, O., Covington, A.D., Evans, C.S.; Application of Diphenols for Dyeing. *J. Soc. Leather Technol. Chem.*, **91**, 139-141, 2007.

APPENDIX I
Procedure of tanning using rubber seed oil (modification from Suparno et al.[5])

Process	Chemical	Amount	Duration	Remark
pH adjustment	Water	200%		Drum at 8 rpm Measure pH at 3 and °Be at 8
	NaCl	10%	10 mins.	
	Formic acid			
Pretanning	Relugan® GT50	1.5%	4 x 15 mins., then 1 h	Dilute with water 3 times Drum at 12 rpm
Fixation	Sodium formic	1%	4 x 10 mins.	Dilute 20 times
	Sodium carbonate	1%		Measure pH at 8
	Drain			
Aging			Overnight	Cover with plastic
Shaving				Shave both sides
Washing	Water	1000%	3 x 15 mins.	
	Drain			
Oil tanning	Water	200%	10 mins.	Drum at 8 rpm
	Sodium carbonate	0.5%		
	Rubber seed oil	30%		Leave overnight Drum for 8 h
	Oxidation inside the rotary drum		4, 6, and 8 hours	Rotate in the drum
	Oxidation outside the rotary drum		1, 2, and 3 days	Hang on the toggle dryer at room temperature
Washing	Sodium carbonate	3%		Stake Repeat 3 times
	Degreaser	0.2%		
	Water	300%		
	Drain			
Toggling and drying			1 day	
Buffing				Buff both sides
Dedusting				