The Impact of Potassium Persulfate on Linseed Oil Tanning

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Abstract

The tanned collagen is the stabilized form of skin. Tanning collagen with oil is a particular class of tanning known as chamois tanning. Chemically the oil tanning involves autoxidation of unsaturation present in the oil. This study focuses on potassium persulfate as a catalyst to accelerate the oxidation rate of unsaturated bonds in the linseed oil with an increase in water absorption capacity (586%) of oil-tanned leather. Results indicate eccentrically reduction in the duration of the chamois process from 15 to 2 days. Shrinkage temperature, tensile strength and other organoleptic properties of experimental leathers are better than the control leathers.

Introduction

Tanning stabilizes collagen fibers through crosslinking with tanning agents. Various tanning agents are used for tanning purposes, such as oil, chromium and its complexes, vegetable barks and powders, and metal, along with their compounds. Each tanning method has its significance and limitations.[1]

Oil tanning is a particular class of tanning where highly unsaturated oils are utilized to stabilize skin fibers. Chamois leathers used to make various soft leather products such as filters, cleaners, gloves, and garments due to their high-water absorption properties.[2,3,4]

Chemically oil tanning is an oxidation reaction where fatty acids undergo a chain reaction involving initiation, propagation, and termination steps.[5] Various oils are used for the oil tanning, such as fish oil,[6] linseed oil,[7] rubber seed oil,[8] animal tallow,[9] fleshing oil,[10] egg oil,[11] jatropha [12] epoxidized oil,[13,14] castor oil [9], and sunflower oil.[9] However, highly unsaturated oils such as fish oil and linseed oil are preferred because of their high affinity towards oxidation.

Linseed oil is known for its high unsaturation and odor-free characteristics, making it suitable for the chamois process.[7] The most common pathways associated with the oxidation of linseed oil are autoxidation and photo-oxidation of fatty acids.[5] The mentioned oxidation pathways require 10 to 15 days to complete the process.

Various oxidizing agents have been used to accelerate the tanning process, such as hydrogen peroxide,[15,16,17] sodium percarbonate,[18] ozone,[19,20] benzoyl peroxide,[7] and benzenecarboperoxoic acid.[21] Each oxidizing agents has their specific operating mechanisms, restrictions, and importance depending upon the reaction conditions and parameters.

The present study predominantly focuses on the effect of different percentages of potassium persulfate on the duration and properties of chamois leather.

Materials and Methods

Materials

Linseed oil was procured from a local supplier, Chennai. Potassium persulfate was procured from Sigma-Aldrich, Chennai. All the other chemicals were analytical grade. For pre-tanning, 20 defect-free wet salted sheepskins were taken.

Method of oil tanning

For the experimental process, linseed oil (25%), soda ash (0.5%), and potassium persulfate (0.25, 0.5, 0.75, and 1% separately) were pre-mixed in a beaker with the help of a stirrer for complete mixing of the chemicals. Further, the mixture was applied to the leather in a rotating drum to distribute the oil throughout the surface. The process was carried out for 2 h continuously. The skins were hung up for oxidation in open drying stands. The completion of oil tanning was visually judged by the color of the skins turning to golden yellow. Then, the leathers were washed with water (100%), soda ash (1%), and wetting agent (1%) for the complete removal of unfixed oil. Final leathers were dried and subjected to staking, buffing, and milling. Control chamois leather was made as explained above without potassium persulfate. Detail description of leather processing is seen in Table I.

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Table I
Oil Tanning Process

Process	Chemical	Percentage (%)	Time	Remarks
Soaking	Water	300	One day	
	Preservatives	0.25		
	Wetting agents	0.50		
Unhairing and Liming	Water	20	Two days	
	Lime	10		
	Sodium sulfide (60%)	3		
Reliming	Water	300		
	Lime	10		
Fleshing				
Deliming	Water	100		
	Ammonium chloride	2	40 min	Check de-liming using phenolphthalein
	Alkaline bate	0.5	30 min	Drain
Washing	Water	200	10 min	Wash and drain
Partial pickling	Water	80		
	Salt	8	30 min	
	Formic Acid	0.5	30 min	In 1:10 dilution with water
	Sulfuric Acid	0.2		In three feeds with 1:10 dilution with water, adjust pH to 4
Depickling	Sodium bicarbonate	1		
Glutaraldehyde tanning	Glutaraldehyde	1	90 min	Drain, pile for overnight
	Soda ash dissolved	2		
Next day				
	Linseed oil	25		
	potassium persulfate (experiment)	0.25, 0.5, 0.75 and 1		
	Sodium carbonate	0.5		Mix using stirrer, make paste. add to drum along with skin

Scanning electron microscope analysis
SEM analysis was carried out to understand better the morphology of leather fibers. The Phenom Pro desktop scanning electron microscope (SEM) was used to analyze the fiber structure of the leather.

Water absorption
The most important property of chamois leather is its water absorption capacity. The higher the water absorption of the chamois leather, the better its quality. The standard procedure determined the water absorption of experimental leather.[22]

Shrinkage temperature measurement
Shrinkage temperature measurement provides information about the leather resistance towards heat. The leathers were subjected to shrinkage temperature as per standard test procedures.[23]

Strength and organoleptic properties of the chamois leather
The experimental leathers were examined for physical characteristics such as tensile strength organoleptic properties.[24]

Results and Discussion

The potassium persulfate acts as a catalyst for oil oxidation, which shortens the reaction duration from 15 days to 2 days. The experimental leathers have been characterized for various physical, chemical, and organoleptic properties, and the results are discussed in the following sections.

Plausible chemistry
The autoxidation of monounsaturated fatty acid (oleic acid) is achieved at high temperatures, while polyunsaturated fatty acids

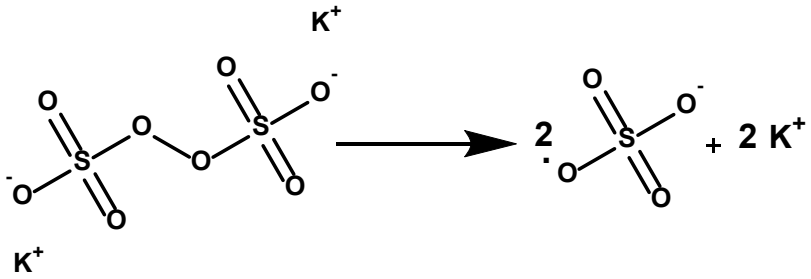


Figure 1. Generation of sulfate-free radical

undergo rapid oxidation even at room temperature.[25] Linseed oil contains polyunsaturated fatty acids, consisting of more active methylene groups, which start the chain reaction through free radical generation.[26,27] As shown in figure 1, potassium persulfate readily dissociates into the sulfate-free radicals, which act as free radical initiators for the oil tanning process. These free radicals stimulate the active methylene groups present in the oil moiety.[28]

These polyunsaturated fatty acid (PUFA) radicals quickly get attached with oxygen to form resonating stabilized peroxyl radicals. The peroxyl radical adds hydrogen atom from another polyunsaturated fatty acid chain of linseed oil to create the primary oxidation product, a lipid hydroperoxide (LOOH), leaving behind another reactive PUFA radical that can again start the process, and the propagation will continue.[29] LOOH on further decomposition generate alkoxyl radical and several secondary oxidized products such as saturated aldehydes, unsaturated aldehydes, short-chain ketones, alcohols, acids, esters, ethers, and hydrocarbons.[30] The aldehydes, a highly diffusible compound, interact with skin amino acids and form stabilized cross-linked protein.[31]

Water absorption

Water absorption is an essential property of chamois leather. The results for water absorption of experimental and control leathers are provided in Table II. The table indicates that leather tanned with 0.25% offer of potassium persulfate show better water absorption value (586%) than control (441%)[7] and other experimental leathers. Moreover, from the table, it could be seen that an offer of 0.50, 0.75, and 1% of potassium persulfate has shown the decreasing values of water absorption, respectively. The conclusion may be drawn from the observation that the offer of 0.25% of potassium persulfate is sufficient for complete oxidation of linseed oil. Much addition of potassium persulfate may not affect the results of water absorption.

Insight on role of potassium persulfate

The 0.25% of potassium persulfate with linseed oil shows a water absorption value (586%) which is better than the 0.25% of benzoyl peroxide with linseed oil (463%)[7]. The standard oxidizing potential value of potassium persulfate is 2.01V[32] which is higher than that of benzoyl peroxide (+1.5 V) therefore, the oxidizing power of potassium persulfate is found to be higher than that of benzoyl peroxide.

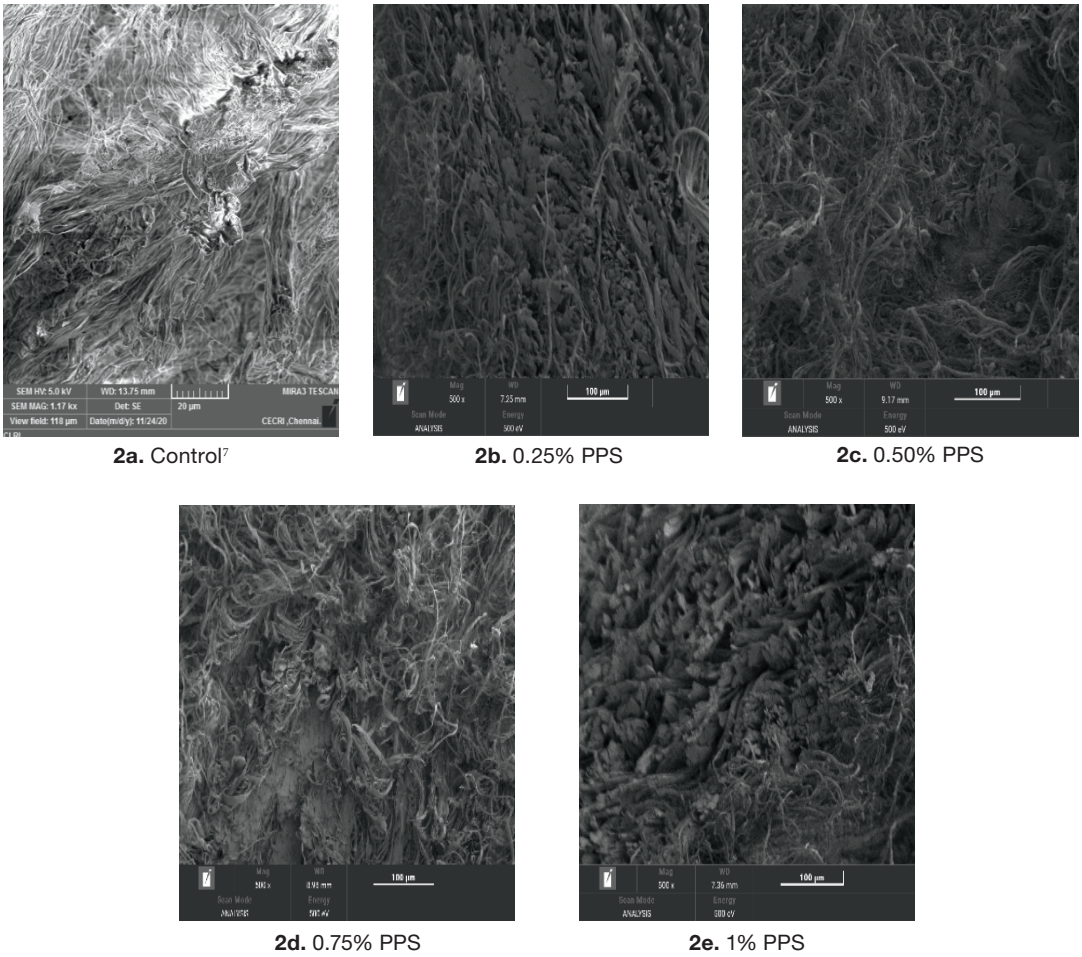
The free radical initiation chain reaction depends upon the ease of generation of free radicals and their half-life.[33] The half-life of potassium persulfate relies on the pH of the solution and operating temperature. At pH 1, the half-life is found to be 20 hours at temperature 50°C, whereas at pH 10, it showed 210 hours.[34] In the case of benzoyl peroxide, it is one hour at 92°C and one minute at 131°C.[35] Therefore, the less percentage (0.25%) of potassium persulfate can bring the desired properties of chamois leather within two days than that of benzoyl peroxide

Scanning electron microscopy analysis of chamois leathers

Scanning electron microscopy images of control and experimental leathers are shown in Figures 2 (a-e). The fiber compactness in

Table II

S No		Water Absorption (%)
1	Control[7]	441±20
2	Potassium persulfate (1.00%)	500±20
3	Potassium persulfate (0.75%)	550±20
4	Potassium persulfate (0.50%)	570±20
5	Potassium persulfate (0.25%)	586±20



2a. Control[7] **2b.** 0.25% PPS **2c.** 0.50% PPS

2d. 0.75% PPS **2e.** 1% PPS

Figure 2. a-e. SEM analysis of experimental chamois leathers against control[7]

control[7] and experimental leathers are very much aligned. Therefore, it may be inferred that the addition of potassium persulfate will not affect the morphology of leather fibers.

Physical testing data of chamois leathers

Experimental leathers were tested for strength and organoleptic properties. Table III indicates that the tensile strength of the chamois leather is almost 60 to 70% more than that of control where skin is treated only with linseed oil.

Shrinkage temperature measurement

Shrinkage temperature measurement of chamois leather gives information about the resistance of the leather due to hydrothermal shrinkage. Table IV indicated the increase in the shrinkage temperature of experimental chamois leathers obtained from 0.50% to 1%. Moreover, experimental leathers with 0.25 and 0.50% show the same shrinkage temperature value (78 °C), more significant than the control values (74°C).

Table III

Physical testing data of chamois leathers

S. No.		Tensile strength (N/mm²)
1	Control	14±2
2	Potassium persulfate (1.00%)	21±2
3	Potassium persulfate (0.75%)	22±2
4	Potassium persulfate (0.50%)	21±2
5	Potassium persulfate (0.25%)	24±2

Table IV

Shrinkage Temperature measurement of chamois leather

S. No.		Shrinkage Temperature (°C)
1	Control	74±1
2	Potassium persulfate (1.00%)	76±2
3	Potassium persulfate (0.75%)	78±2
4	Potassium persulfate (0.50%)	78±1
5	Potassium persulfate (0.25%)	78±1

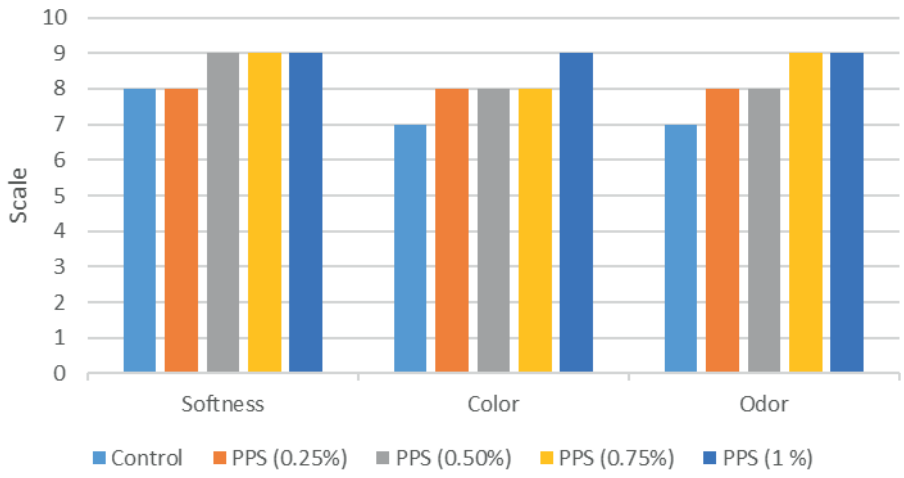


Figure 3. Organoleptic properties of chamois leathers

Organoleptic Properties

Chamois leather organoleptic properties were evaluated for softness, color, and odor. From Figure 3, observation can be drawn that the softness of chamois leathers improved with the increase in the percentage of oxidizing agents. Similarly, the color of the experimental chamois leathers with 1% of potassium per persulfate showed lighter yellow compared to the golden yellow of the control leathers. Although chamois leathers are made, using linseed oil as the leading tanning agent, the odor is one of the essential qualities to assess.

Conclusions

The present study focuses on the accelerated linseed oil tanning process with an optimized offer of 0.25% of potassium per persulfate as an accelerant. The study also emphasis on completion of oil tanning process within two days. The oil-tanned leather shows better water absorption and physical strength than control leathers. The conclusion may be drawn from the study that the use of 0.25% potassium per persulfate in chamois making, reduces the duration of oil tanning to within two days with better water absorption properties.

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