

RAPID OXIDATIVE DEHAIRING WITH MAGNESIUM PEROXIDE AND POTASSIUM PEROXYMONOSULFATE^{§†}

by

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ABSTRACT

Sodium sulfide is traditionally used to remove hair from animal hides during tanning operations. However, alternatives to sodium sulfide are desired because sodium sulfide is an environmental pollutant that is quickly converted to highly toxic hydrogen sulfide gas if accidentally exposed to acid. In past research, we demonstrated that either alkaline calcium peroxide or alkaline hydrogen peroxide may be used as an effective substitute for concentrated sodium sulfide for rapid dehairing. More recently, we demonstrated the effectiveness of alkaline hydrogen peroxide with potassium cyanate. Here we similarly present alternative oxidative dehairing reagents/conditions, using magnesium peroxide and potassium peroxymonosulfate, which may also find application in either the packing plant or beamhouse. As observed with previously reported rapid dehairing, dehairing often is not thorough, leaving very short stubble. However, residual hair was readily removed with a sodium sulfide sharpening/hairburn, indicating that hair stubble was not immunized by the oxidative treatment. Dehairing reaction conditions that rapidly removed 80% or greater of hair from cattle hide pieces were observed for magnesium peroxide (5%, 15% NaOH, 200% float, 45°C, 8 min, hairburn process) and potassium peroxymonosulfate (5%, 15% NaOH, 200% float, 45°C, 7 min, hairburn process). Leather produced from matched side pieces that were subjected to these oxidative dehairing treatments was determined to take up less chromium yet was tougher than leather produced using conventional hairburn with sodium sulfide. Other physical testing results are also reported.

ABSTRACTO

Sulfuro de sodio se emplea tradicionalmente para remover el pelo de las pieles de animales durante las

operaciones de curtición. Sin embargo, alternativas al sulfuro de sodio son deseables ya que el sulfuro de sodio es un contaminante del entorno ya que se convierte rápidamente en un gas altamente tóxico, ácido sulfhídrico, si accidentalmente se expone a ácido. En investigaciones anteriores, hemos demostrado que el peróxido de calcio alcalino tal como peróxido de hidrógeno alcalino puede utilizarse en un efectivo reemplazo de sulfuro de sodio concentrado en un pelambre rápido. Más recientemente hemos demostrado la efectividad de peróxido de hidrógeno alcalino en combinación con cianato de potasio. Aquí similarmente presentamos un pelambre alternativo oxidativo con reactivos y condiciones, utilizando peróxido de magnesio y peróxidomonosulfato de potasio, el cual podría encontrar aplicación ya sea en el matadero o en la ribera. Tal como observado en informes previos de pelambre rápido, la caída del pelo no es absoluta, dejando pelillos cortos. Sin embargo, estos pelillos residuales fácilmente son removibles con sulfuro de sodio utilizado ya sea como acelerante de un pelambre o como destructor total del pelo, indicando que los pelillos residuales no han sido inmunizados por el tratamiento oxidativo. Las condiciones de la reacción del pelambre fueron tales que rápidamente se observó la remoción el 80% o más del pelo de pedazos de piel bovina expuestos a peróxido de magnesio (5%, 15% NaOH, 200% de baño, 45°C, 8 minutos de proceso destructivo del pelo) y peróxidomonosulfato de potasio (5%, 15% NaOH, 200% de baño, 45°C, 7 minutos de proceso destructivo de pelo). Cuero producido de muestras cortadas de lados aparejados, demostraron menor absorción de cromo, pero resultaron más tenaces que cueros producidos por un pelambre destructivo del pelo convencional con sulfuro de sodio. Otros resultados de pruebas físicas efectuadas también se reportan.

INTRODUCTION

Conventionally, a mixture of sodium sulfide, lime and soda ash has been employed by tanneries for the reductive degradation and removal of hair (keratin) from animal pelts, skins and hides in a 4- to 6-hour process. This process has been modified for spray application of concentrated sulfide salts to achieve rapid (less than 10 minutes) hair removal,^{1,5} with the intended use on animal carcasses in a packing plant. Rapid dehairing has been demonstrated to prevent cross-contamination by dirt or fecal-borne bacteria on the hide to the meat during flaying and could become a part of a pathogen reduction program.⁶⁻⁸ The major drawback to the use of sulfide salts is the adverse environmental impact it may have on resultant waste streams since sulfide salts contribute to chemical and biological oxygen demand.^{9,10} An added concern is the potential for the generation of hydrogen sulfide, a severe health threat to tannery (or packing plant) workers,¹¹ through accidental reaction with acids.

Previously we have reported on the use of calcium peroxide (CaO₂) and alkaline hydrogen peroxide as potential replacements for sodium sulfide in rapid dehairing processes.^{12,13} The chemicals oxidatively cleave the disulfide linkages, in keratin, yielding the sodium salt of the corresponding sulfonic acid. Generally speaking, as observed with sulfide-based rapid dehairing, the oxidative chemicals do not completely remove the hair from the hide. Usually short stubble remains that is either removed in a subsequent dehairing step or with a sharpening agent in the relime. Sharpening with sulfide or a subsequent dehairing not only removes the residual stubble, but may also hydrolyze the basement membrane that cements the hair bulb in the hair pore.¹⁴ The removal of the basement membrane results in the opening up of the hide.¹⁵ It follows that the opening up of the hide may be accomplished using oxidative dehairing if the proper choice of base concentration and oxidative chemicals, along with the proper choice of temperature and reaction time, are made. Unfortunately, the rapid oxidative reaction conditions are stringent and if not carefully monitored, damage to the grain of the hide can occur.

In addition to alkaline hydrogen peroxide^{13, 16-18} or CaO₂,¹² we observed that other oxidative chemicals have the potential of replacing sulfide salts as dehairing agents. Results of cursory investigations with alkaline preparations of these other oxidatives (including magnesium peroxide, sodium perborate, sodium percarbonate, and potassium peroxymonosulfate) were surveyed by us in prior reports,^{15,20} and we later reported on an effective rapid dehairing process using alkaline hydrogen peroxide/potassium cyanate.¹³ Further studies by us subsequently demonstrated the effectiveness of peroxide/cyanate,²¹ perborate,²¹ and percarbonate²² for slower dehairing in the beamhouse. In addition to magnesium peroxide (MgO₂) and CaO₂,¹² other inorganic peroxides including lithium peroxide and sodium peroxide (Na₂O₂) were not studied as they both react violently with moisture even though they are stable in solution at high pHs. A paste of Na₂O₂, water, isopropyl alcohol, and kaolin has been used to dehair hides.²⁷ The dehairing process was not rapid and formulation as a paste makes it unsuitable for a spray application.

In the present report, we discuss the screening of three oxidative chemicals for use as rapid dehairing agents based on the following criteria: a) the dehairing reaction time had to be rapid (≤ 8 min) so it could be considered suitable for in-line, continuous processing in a slaughterhouse, and b) the residual hair stubble had to be short enough so that manure balls could no longer potentially cling to the hide. Removal of manure balls allows fleshing (without the need for soaking) and splitting-in-the-raw of green hide. Stubble is not an issue so long as immunization of the hair does not occur during dehairing; as demonstrated in past research, stubble that remains after oxidative dehairing has been easily removed by a subsequent dehairing process using sulfide (although not yet tested in these systems, it would be preferable to employ an oxidative agent). Reaction conditions for oxidative dehairing are corrosive and may result in grain damage if not carefully applied and monitored. However, if rapid dehairing is only applied as a food safety measure, then damage to grain may not be a consideration. This is typical with the dehairing of swine carcasses. To this end, we report laboratory-scale results of three oxidative chemicals-sodium hypochlorite, MgO₂, and potassium peroxymonosulfate.

TABLE I
Dehairing with Magnesium Peroxide^a

% Magnesium Peroxide	% NaOH	pH ^b	% Removal of Hair ^c
0	15	14.6 ^d	85
5	10	13.3	70
5	15	13.3	80
5	20	13.2	75
10	10	13.2	40
10	20	13.2	70
15	10	13.2	30
15	20	13.2	75
15	25	13.1	85
15	30	13.0	95

^a Reaction conditions; 45°C, 200% float, 8 min.

^b Initial pH of dehairing solution prior to addition of hide piece.

^c Visual estimate of amount of hair removed by the process. This was a hairburn process with residual hair typically remaining as short stubble.

^d Theoretical

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[†] Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

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EXPERIMENTAL

Materials

Sodium hypochlorite (5.25%; The Clorox Co., Oakland, CA) was obtained from a local supermarket. Magnesium peroxide (technical grade; empirical formula $MgO_2 \cdot xMgO$), potassium peroxymonosulfate (Oxone®; empirical formula $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), and all other chemicals used in this project were obtained either from Sigma-Aldrich (Milwaukee, WI) and were of reagent grade unless indicated otherwise. Steer hides were obtained from a local abattoir. The hides were soaked and fleshed before use.

Procedures

The rapid dehairing screening reactions were performed on hide pieces that were either approximately 6 cm in diameter ("cookies") or approximately 10.2" x 15.2" matched side pieces taken from shoulder to butt along the backbone. Cookies were used for sodium hypochlorite studies whereas matched side pieces were used for all other experiments reported herein. Potassium peroxymonosulfate readily dissolved into solution during preparation in water whereas MgO_2 was prepared as a mixture in a similar manner to that of CaO_2 mixtures as used in a previous study.¹² In short, sodium hydroxide solution was prepared and allowed to cool to a little above room temperature prior to addition of MgO_2 solids. Like CaO_2 , MgO_2 contains a high percentage of oxide impurity that is sparingly soluble in base. Prior to dehairing, dehairing solutions or mixtures were adjusted to the desired reaction temperature using water baths.

All experiments were laboratory-scale carried out using either cookies placed into approximately 1 L canning jars (further placed and rotated in a heated, home-built apparatus that simulated the tumbling that occurs in a drum) for hypochlorite reactions only or matched side pieces placed into 4-in-1 drums (Dose Maschinenbau GmbH, Lichtenau, Germany) for MgO_2 and potassium peroxymonosulfate reactions. For all tests, hide pieces (in duplicate unless indicated otherwise) were

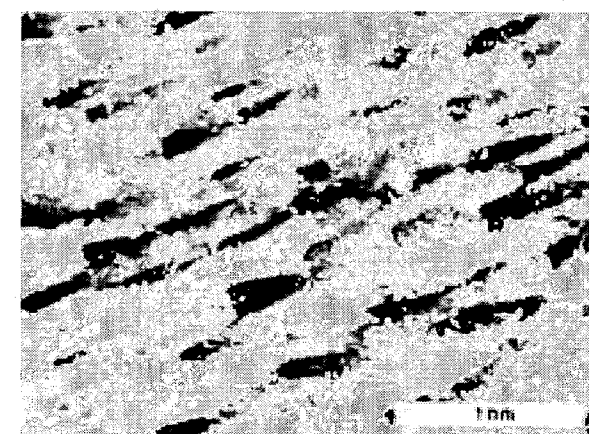
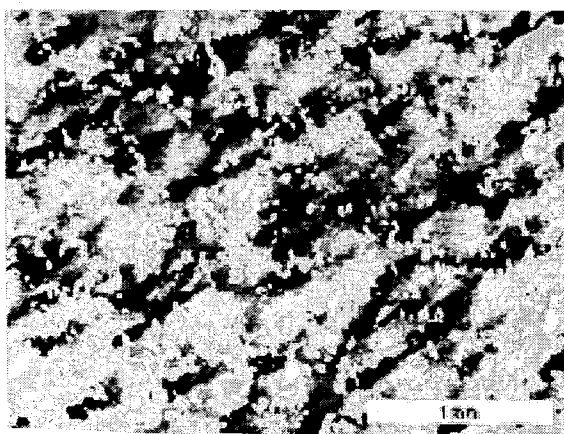


Fig. 1 Qualitative assessment of oxidative dehairing. Photomicrographs of green hide pieces dehaired with (A) 5% magnesium peroxide and 20% NaOH for 8 min and (D) 5% potassium peroxymonosulfate and 15% NaOH for 7 min.

submerged in a 200% float of oxidative chemical dehairing solutions (or mixtures) unless indicated otherwise. Details of the reaction mixtures, dehairing times, and reaction conditions are found in the accompanying text and tables.

Control hide pieces were dehaired 4 h using 2% sodium sulfide, 2% lime and 1% soda ash (Na_2CO_3) in a 100% float.²³ All hide pieces were converted to crust leather using the procedure described by Cabeza et al.²⁴ with the exceptions noted by Gehring et al.²⁵ The stubble remaining on hide pieces that had undergone a rapid oxidative dehairing step was removed with subsequent sharpening using 2% sodium sulfide, 2% lime and 1% soda ash in a 100% float (1 h, room temperature) immediately prior to reliming.

MEASUREMENTS

Following dehairing reactions, any hair removed was reported herein as the difference between the bulk hair associated with a hide piece before and after treatment. Hair removed, leaving stubble of varying length, was visually assessed as a qualitative measure of this bulk hair loss from hide pieces and the error of this determination was estimated to be between 5-10%.

Qualitative assessment of grain appearance was aided by the use of a Nikon SMZ-2T stereo dissecting microscope (Nikon, Inc., Japan) equipped with a Pixera PVC 100C charge-coupled device (Pixera Corp, Los Gatos, CA). The contrast of the images was adjusted (to accentuate the grain of the leather) and the images were resized using Adobe Photoshop 6.0 (San Jose, CA). The magnification of all images was 17x.

Physical measurements of stress, strain and toughness of crust leather were performed using an upgraded Instron Tensile Tester (Model #1122) running TestWorks version 3.07 software (MTS Systems, Eden Prairie, MN). Prior to testing,

TABLE II
Dehairing with Potassium Peroxymonosulfate^a

% Potassium Peroxymonosulfate	% NaOH	pH ^b	% Removal of Hair ^c
0	15	14.6 ^d	75
5	10	13.4	30
5	15	13.4	80
5	20	13.5	70
10	10	13.4	70
10	15	13.4	70
10	20	13.4	85

^aReaction conditions; 45°C, 200% float, 7 min.

^bInitial pH of dehairing solution prior to addition of hide piece.

^cVisual estimate of amount of hair removed by the process. This was a hairburn process with residual hair typically remaining as short stubble.

^dTheoretical

the crust leather samples had been pre-conditioned for 48 h at 24°C and 50% relative humidity. The physical properties were measured with a gauge length (clamp distance) of 67 mm and a strain rate (cross head) speed of 254 mm/min. All physical tests were performed in quadruplicate.

Chromium content was determined, using a Perkin Elmer Atomic Absorption Spectrometer, Model 3000 (Norwalk, CT), on wet blue leather samples that were air-dried overnight at 50°C and cooled in a desiccator. As previously described, the samples were hydrolyzed, the hydrolysate was filtered into volumetric flasks and diluted so that the final chromium concentration would be between 1 and 10 ppm, and the percent chromium was determined.²⁶ The results were reported as % Cr_2O_3 . Each determination was performed in quadruplicate.

RESULTS AND DISCUSSION

Cursory investigations into oxidative dehairing achieved relative success with the application of common household bleach (5.25% sodium hypochlorite) to small hide pieces. Reactions at room temperature with hide pieces in 100% float of undiluted bleach achieved 60, 70, and 80% dehairing in 5, 15, and 30 min of respective reaction with agitation. Though promising, further studies with household bleach were halted since the oxidizing agent, hypochlorite, is also a chlorinating agent that has the potential to form undesirable chlorinated organic products, including volatiles like methylene chloride and chloroform, upon reaction with soil and other organic matter potentially associated with hides.

Unlike hypochlorite, magnesium peroxide (MgO_2) generates hydrogen peroxide when dissolved in water and therefore serves strictly as an oxidizing agent. Under alkaline conditions, the hydrogen peroxide oxidizes sulfide linkages in keratin to the sodium salt of the corresponding sulfonic acids. Alkaline MgO_2 rapidly dehaired hide pieces under a variety of conditions (Table I). Since a higher concentration of base appeared to promote better dehairing consistency, the

dehairing mixture of 5% MgO_2 and 20% NaOH (at 45°C and 200% float) was used for physical testing studies herein. After a dehairing treatment, any hair that did remain was typically short stubble (Figure 1A). Higher concentrations of both base and MgO_2 also remove hair, but there was not a significant difference in the amount of hair removed except when 15% MgO_2 and 30% NaOH were used as the dehairing mixture. One drawback to using such high concentrations of base is the potential for grain damage.¹³

Oxone® (potassium peroxymonosulfate) has been used as a bleaching agent in laundry detergent formulations.²⁸ The standard electrode potential (E°) of potassium peroxymonosulfate is -1.44 V. This potential is high enough to reduce the disulfide linkage in glutathione [glutamic acid-cysteine-glycine (Glu-Cys-Gly)] ($E^\circ = -0.26$ V).²⁹ Potassium peroxymonosulfate is not stable at the alkaline pH range required for dehairing and it decomposes exothermically (251 kJ/kg, 108 BTU/lb),³⁰ making temperature control a challenge. In preliminary experiments with potassium peroxymonosulfate, the difficulties in controlling the temperature led to grain damage. Despite the temperature control problems, conditions (5% potassium peroxymonosulfate, 15% NaOH, 45°C) were found that resulted in a good dehairing of the hide pieces, in 7 min, with no observable grain damage and only a short stubble remaining (Figure 1B). Other tested combinations of base and potassium peroxymonosulfate did not significantly change the amount of hair removed during the dehairing reaction (Table II).

After rapid dehairing, the resulting stubble often had to be removed by a subsequent dehairing step prior to reliming. There was concern that either the residual stubble would be immunized against a second dehairing or that damage to the grain would occur during the second dehairing. Wet blue and crust leather samples were prepared, in triplicate, from matched side pieces (along with matched pieces for sulfide hairburn control) that were oxidatively dehaired with potassium peroxymonosulfate or MgO_2 . All residual hair stubble was

TABLE III
Shrink Test Results and % Chromium of Wet Blue

Dehairing Protocol	Shrink Temperature ^c	% Chromium ^d
Magnesium Peroxide ^a	106.5 ± 0.71	3.25 ± 0.4
Sulfide Control	104.3 ± 0.35	3.88 ± 0.09
Potassium Peroxymonosulfate ^b	97.5 ± 2.1	2.79 ± 0.05
Sulfide Control	103.8 ± 0.35	3.69 ± 0.08

^a Reaction conditions; 45°C, 200% float, 8 min; 10% potassium peroxy-monosulfate and 20% NaOH.

^b Reaction conditions; 45°C, 200% float, 7 min; 15% MgO₂ and 30%NaOH.

^c Average of a single measurement for each of three pieces

^d Average of three determinations. Reported as %Cr₂O₃

TABLE IV
Physical Tests Results for Finished Leather Sample Thickness

Sample	Thickness(mm)	Tensile Strength (MPa) ^c	% Elongation	Toughness Index
Magnesium Peroxide ^a	2.36 ± 0.087	9.46 ± 1.2	38.6 ± 0.35	0.51 ± 0.04
Sulfide Control	2.45 ± 0.14	16.2 ± 2.9	21.4 ± 1.4	0.20 ± 0.02
Potassium Peroxymonosulfate ^b	2.53 ± 0.13	10.5 ± 2.8	38.9 ± 8.1	0.66 ± 0.33
Sulfide Control	2.04 ± 0.10	15.8 ± 3.9	24.9 ± 7.8	0.21 ± 0.09

^a Reaction conditions; 45°C, 200% float, 8 min; 10% potassium peroxy-monosulfate and 20% NaOH.

^b Reaction conditions; 45°C, 200% float, 7 min; 15% MgO₂ and 30%NaOH.

^c 1 MPa = 145 PSI

readily removed with a sulfide hair burn immediately following oxidative dehairing. No residual grain damage was observed as a consequence to this sharpening step.

Though the %Cr in the wet blues prepared from hide pieces that were oxidatively dehaired was lower than the %Cr in wet blue prepared from pieces dehaired with sulfide, the shrink temperature for MgO₂-dehaired samples was higher than the corresponding sulfide controls, whereas the opposite was observed for potassium peroxy-monosulfate samples (Table III). Regarding the latter, a similar trend between shrink temperatures and %Cr was observed in a previous study for wet blue made from hide pieces that had undergone rapid oxidative dehairing with alkaline hydrogen peroxide containing lime.¹³

Table IV displays additional physical test results for the oxidatively dehaired test pieces relative to sulfide-dehaired control samples. These results include tensile strength, % elongation, and toughness index. The toughness index is the ratio of the tensile strength to the Young's modulus and a dimensionless parameter that is independent of thickness, width, or shape of the samples.²¹ Leather made from hide pieces that were oxidatively dehaired with potassium peroxy-monosulfate had similar, within observed error, tensile strength and % elongation relative to the leather made from the corresponding pieces that were dehaired with sulfide. However, samples dehaired with alkaline MgO₂ exhibited lower tensile strength, and higher % elongation relative to the sulfide control samples.

Both potassium peroxy-monosulfate- and MgO₂-dehaired samples exhibited a higher toughness index when compared with sulfide-dehaired controls.

The physical test results for MgO₂- and potassium peroxy-monosulfate-dehaired leather did not exhibit similar trends to those previously reported for rapid dehairing methods that employed alkaline hydrogen peroxide.¹³ However, with the exception of the shrinkage temperature trend for pieces dehaired with MgO₂, the test results contradicted those reported for the usage of alkaline hydrogen peroxide in a relatively longer beamhouse process.¹⁷

Though it was not elucidated what role the rapid dehairing chemical alternatives to hydrogen peroxide had on the uptake of Cr by the hide pieces, there was the trend of lowered uptake of Cr in oxidatively dehaired pieces as was previously observed with alkaline hydrogen peroxide (not containing potassium cyanate).¹³ By itself, NaOH has demonstrated ability to rapidly remove hair, but must be used cautiously since grain damage occurs if the base is exposed to hide too long and especially at elevated reaction temperatures. Interestingly, it was observed that the oxidative chemicals appeared to "buffer" this potentially detrimental effect of NaOH (data not shown). The oxidative chemicals, MgO₂ and potassium peroxy-monosulfate, studied were observed to yield truly rapid dehairing processes that may be suitable for application in a packing plant.

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