Mapping Alkyl Phenol Ethoxylates in Leathers Treated with Surfactants and Fatliquors: Role of Enzymes in the Removal of APEO†

by

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Abstract

Alkyl phenol ethoxylates (APEO) in general, nonyl phenol ethoxylates (NPEO) and octyl phenol ethoxylates (OPEO) in particular, are nonionic surfactants, which are widely used as components of a range of leather chemicals. APEO have a low biodegradable rate, reported as 0-9% per year, and are known to generate most persistent and toxic metabolites. In this study, APEO containing wetting agents and fatliquors have been chosen and treated with leather separately at various concentrations. The amount of APEO present in the treated leather was mapped based on their concentration of application. The results show that the APEO content in the leather increases with the increase in the concentration of fatliquor or wetting agent containing APEO. An attempt has also been made to adopt some special treatment methods in post tanning process such as treating with formic acid at elevated temperature and use of specific enzymes to reduce APEO content in the final leather. Formic acid treatment led to poor APEO reduction as well as unsatisfactory leather quality. Out of the different oxidizing enzymes employed, horseradish peroxidase treatment on APEO containing leathers resulted in 60% APEO removal. It has also been observed that the physical and bulk properties of the leathers treated with enzymes are satisfactory compared to the control leathers. This study shows, for the first time, a way for an efficient eco-friendly treatment method for removing APEO from leathers.

Resumen

Etoxilados alquilfenolicos (APEO) en general, así como etoxilados nonilfenólicos (NPEO) y etoxilados octílfenólicos (OPEO) en particular, son tensoactivos no iónicos los cuales son extensivamente utilizados como componentes de un rango de agentes químicos para el cuero. APEO tiene una reducida tasa de biodegradabilidad, reportada como entre 0-9% anual, y es reconocido generador de metabolitos tóxicos y persistentes. En este estudio, agentes químicos conteniendo APEO que conforman humectantes y engrasantes, se seleccionaron y se usaron para tratar cuero por separado a varias ofertas. La cantidad de APEO presente en el cuero así tratado se localizó dimensionalmente de acuerdo a la concentración de su oferta. Los resultados demuestran que el contenido de APEO en el cuero se incrementa según el aumento de la concentración de APEO en el engrase o humectante que lo contiene. También se trató de utilizar tratamientos especiales en el recurtido tales como el de tratar con ácido fórmico a elevadas temperaturas y el uso de enzimas específicas para reducir el contenido de APEO en el cuero final. Tratamiento con ácido fórmico no condujo a una reducción del APEO en el cuero final, pero sí a deficiencias en calidad. Entre las enzimas oxidantes ensayadas se encontró que tratamiento por peroxidasa de rábano picante, logró remover el 60% del APEO en el cuero resultante. También se determinó que las propiedades físicas y generales de los cueros tratados enzimáticamente se compararon favorablemente con los cueros usados como controles. Este estudio demuestra, por primera vez, un camino hacia un eficiente eco-amigable método de tratamiento para remover APEO de los cueros.

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Introduction

Alkyl phenol ethoxylates (APEO) are non-ionic surfactants, consisting of a branched-chain alkyl phenol, which has been reacted with ethylene oxide, producing an ethoxylates chain.[1] APEO have been important surfactants for more than 50 years. The most common APEO in commercial use today is the group of nonylphenol ethoxylates (NPEO), comprising about 80% of the market, while octylphenol ethoxylates (OPEO) comprise most of the remaining 20% of the market.[1-3] Alkyl phenol ethoxylates are components of a wide range of leather chemicals such as wetting agent, fat liquors, degreasing agent, binders, dispersion aids, thickeners, antifoam agents, pigment pastes and wax.

Alkylphenols are environmentally hazardous due to their toxicity;[1] some alkylphenols are known as endocrine-disrupting chemicals that mimic estrogenic compounds causing adverse effects such as developmental and reproductive toxicity in animals.[1-5] The endocrine system is comprised of glands and hormones in the body. Different endocrine glands release small, specific amounts of hormones into the bloodstream. These hormones mediate many bodily functions, including reproduction, growth, development, maturation, immune system functioning and metabolism. Endocrine disrupting chemicals (EDCs) interrupt normal bodily functioning by blocking, interfering with, or mimicking natural hormones in the body.[6,7] The Directive 2003/53/EC entered into force in 2003 and implementation in all EU member states, including Germany, was by January 2005. It states that "APEO may not be placed on the market or used as a substance or constituent of preparations in concentrations equal to or higher than 0.1% by mass", in other words, the permissible level is 1000 mg/kg. In most applications, APEO can be replaced by linear alcohol ethoxylate surfactants, which are readily biodegradable. However, direct replacement can be difficult in some situations, because of their higher prices and lack of branching.

This study aims at analyzing and mapping the sources of alkyl phenol ethoxylates in leather by treating with a wetting agent and a fatliquor containing APEO and their removal efficiency from leather. Enzymes are playing a vital role in breaking the phenol and related aromatic components into simpler units in commercial effluent treatment plants.[8-10] Consequently, it is possible to use the oxidative enzymes to degrade the APEOs since their structure is analogous to phenol derivatives. Hence, another objective of our study is to find out the removal efficiency of the treatment processes using specific enzymes and using formic acid. Different enzymes, namely catalase, tyrosinase, horsehradish peroxidase (HRP), and commercial effluent treatment enzyme have been used in this study to treat the leather containing APEO. The efficiency of the treatments is analyzed and the results are discussed.

Materials and Methods

Materials

Ten wetblue goat leathers were chosen as raw material for this study. APEO containing wetting agent (X) and fatliquor (Y) was purchased from leather chemical houses and the APEO content was analyzed.[2] All the chemicals used for processing were of commercial grade. A commercial enzyme, Hypergo R, (active at pH 5.0-5.5 and catalase activity 4,625 U/ml) used for different applications was procured from Southern Petrochemical Industries Corporation (SPIC) Ltd., India. The laboratory grade tyrosinase and horse radish peroxidase were purchased from Sigma-Aldrich. The enzyme SCD, which was used for commercial effluent treatment, was purchased from M/s Eco Systems and Technologies, India.

Process Details

Trial with APEO containing wetting agent

Two wetblue goat leathers were used for each of the following trials. Leathers were wetback with the chosen wetting agent (X) with different concentrations such as 0.5 and 1.0% along with 200% water (percentages based on shaved weight). The samples were neutralized to pH 6.0-6.2 using 150% water, 2.0% Neutrigan, 1.0% sodium bicarbonate and 1.0% sodium formate. The samples were fatliquored with 150 % water and 16% APEO-free fatliquor and fixed with 1.0% formic acid.

Trial with APEO containing fatliquor

Two wetblue goat leathers were used for each of the following trials. Leathers were wetback with 200% water and 1.0% APEO-free wetting agent. The samples were neutralized to pH 6.0-6.2 using 150% water, 2.0% Neutrigan, 1.0% sodium bicarbonate and 1.0% sodium formate. The samples were fatliquored with the APEO containing fatliquor (Y) with different concentrations such as 8.0 and 16.0% along with 150% water and fixed with 1.0% formic acid.

Trial with APEO containing wetting agent and fatliquor

Two wetblue goat leathers were used. A combination of 1.0% APEO containing wetting agent (X) and 16.0% APEO containing fatliquor (Y) was used in this trial. All other chemicals and process conditions are similar to the above processes. A control trial was carried out with APEO-free wetting agent and APEO-free fatliquor as above.

All the leathers were piled overnight and then hooked for drying. The dried leathers were conditioned, staked, trimmed and milled for 2 hrs. All the leather samples were analyzed for APEO content using standard procedures.[2]

Process for APEO Removal from Leathers

For the removal of APEO from leathers, only leathers processed with a combination APEO containing fatliquor and wetting agent were chosen since they will contain higher

amount of APEO. Two rectangular size (10x6 cm) leather samples were used for each of the following trials. A trial was carried out with 3.0% formic acid and 300% water at 70ºC followed by two hot and cold washes, each 300% water. Both effluent treatment enzyme SCD and Hypergo R were employed at 5.0% along with 300 % water individually. In the case of tyrosinase, concentration was varied as 393, 786, 1179, and 4719 units along with 300% water. Finally, horshradish peroxidase was varied as 10, 30, 50, and 200 units along with 300% water. All the above treatment processes were carried out for 30 minutes duration.

Analysis of APEO Content in Leather

The leather sample was extracted using solvents as per standard procedure.[2] The extract was analyzed with combined high performance liquid chromatography and mass spectrometry with positive mode electro spray ionization (HPLC/MS) following standard procedure.[2]

Physical Testing and Hand Evaluation of Leathers

Samples for various physical tests from experimental and control crust leathers were obtained following IUP method.[11] Specimens were conditioned at 20±2 °C and 65±2% R.H. over a period of 48 h. Physical properties such as tensile strength, %elongation at break, and stitch tear strength, were examined following standard procedures.[12,13] Experimental and control crust leathers were assessed for softness, fullness, grain smoothness and general appearance by hand and visual examination. The leathers were rated on a scale of 0–10 points for each functional property by four experienced tanners, where higher points indicate better property.

Results and Discussion

APEO Mapping in Leather

The selected wetting agent and fatliquor were screened for APEO content present in them. It was found that the wetting agent X contains 24900 ppm APEO while the fatliquor Y contains 15100 ppm APEO. The wetblue goat leathers processed with 0.5 and 1.0 % wetting agent X exhibit APEO content of 663 and 1320 ppm, respectively as shown in Fig. 1. On the other hand, the wetblue goat leathers processed with 8 and 16% fatliquor Y show APEO content of 2680 and 4000 ppm, respectively, as shown in Fig. 2. Observing the above results, the APEO content in the leather increases with increasing concentration of fatliquor Y or wetting agent X. Although the APEO content of fatliquor Y is less than that of wetting agent X, the leathers treated with fatliquor Y exhibit higher amount of APEO compared to wetting agent (X) treated leathers. This is because the offer of fatliquor (Y) is much higher than the offer of wetting agent (X).

The wetblue goat leathers processed with a combination of 16% fatliquor Y and 1% wetting agent X display a APEO content of 4260 ppm. Hence, leathers with the maximum APEO content (combination of 16% fatliquor Y and 1% wetting agent X) were chosen for treatment processes intended for APEO removal.

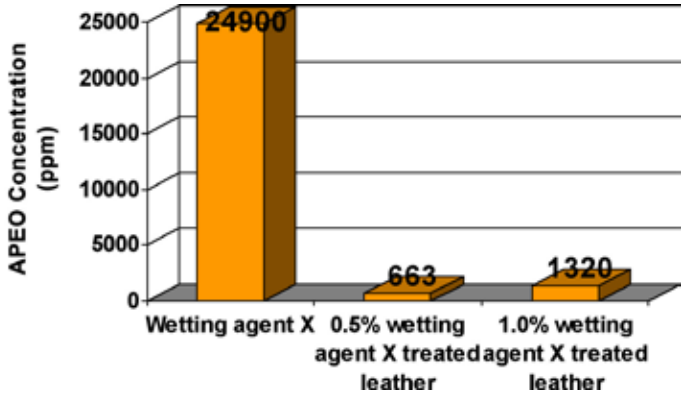

Figure 1. APEO Mapping for Wetting Agent and Treated Leathers

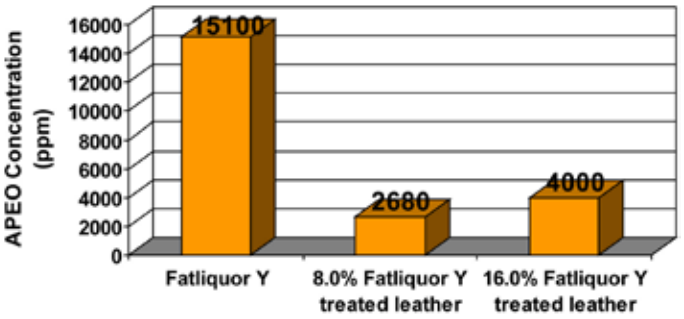

Figure 2. APEO Mapping for Fatliquor and Treated Leathers

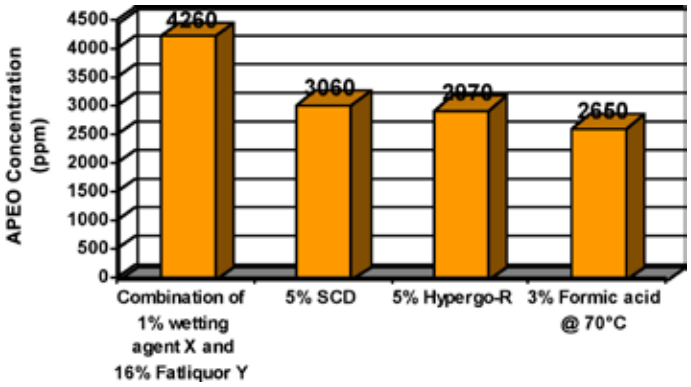

Figure 3. APEO Removal Efficiency for Commercial Enzymes and Formic Acid

APEO Removal from Leathers Treated with APEO Containing Wetting Agent and Fatliquor

The commercial enzymes such as Enzyme SCD and Hypergo–R resulted in 28 and 30% reduction in APEO content of the leather, respectively, when offered at 5%. On the other hand, 3.0% formic acid treatment at 70°C resulted in 38% reduction in APEO content of the leathers, as shown in Fig. 3.

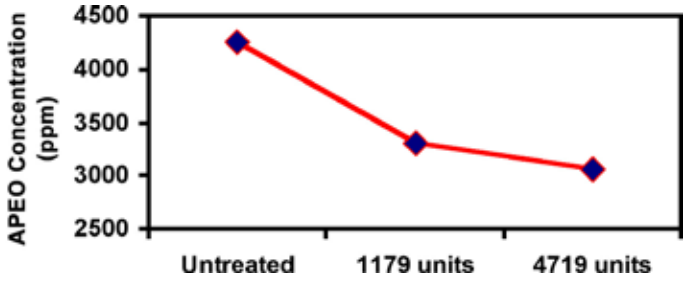

Figure 4. APEO Removal Efficiency for Tyrosinase

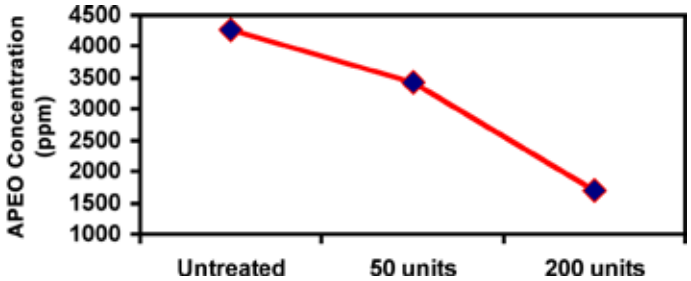

Figure 5. APEO Removal Efficiency for HRP

The APEO containing goat leathers were treated with tyrosinase and HRP in different concentrations and only select leathers were analyzed for APEO content. As can be seen from Fig. 4, treatment with a concentration of 1179 units tyrosinase reduces the APEO content in the leather by 22% while 4719 units treatment reduces only up to 28%.

Hence, it is evident that tyrosinase did not reduce the APEO content significantly in spite of a higher concentration of the enzyme. On the other hand, goat leathers treated with HRP enzyme show appreciable reduction in APEO content as a function of concentration, as shown in Fig. 5. Application of HRP concentration of 50 units reduces the APEO content in the leather by 20% while 200 units offer results in 60% reduction. This reduction is significant since these results are obtained for leathers containing higher concentration of APEO (4260 ppm), which was treated with a combination of wetting agent and fatliquor at high concentrations. Further, in this study, HRP enzyme was used without the presence of hydrogen peroxide. In general, the use of hydrogen peroxide at very low dosage along with HRP is expected to increase the activity of the enzyme and also degrade the phenolic compounds more efficiently.[14] Such an attempt will remove the APEO from leather more effectively; however, care should be taken not to alter the properties of leather and also the leather chemicals by the use of formaldehyde.

Physical and Bulk Properties of Leathers After Treatment with APEO Removal Agents

As can be seen from Table I, physical properties of the enzyme or acid treated leathers such as tensile strength, elongation and stitch tear strength did not alter significantly. The bulk

TABLE I
Physical Properties of the Enzyme and Acid Treated Leathers

Treatment Process	Tensile strength (N/mm^2)	% Elongation at break	Stitch tear strength (N)
Control	35.5± 4.7	87±4	80.5±2.1
HRP	33.4±2.9	89±4	76.5±2.2
Tyrosinase	32.2±2.6	86±6	77.8±1.5
Hypergo-R	34.8±1.6	84±8	73.5±1.0
SCD	32.7±4.0	85±3	74.8±3.5
Formic acid	33.6±1.6	82±4	75.2±3.0

TABLE II
Bulk Properties of the Enzyme and Acid Treated Leathers

Treatment Process	Softness	Fullness	Grain smoothness	Appearance
Control	8	7	9	8
HRP	8	7	8	7
Tyrosinase	8	7	8	8
Hypergo-R	8	7	9	8
SCD	8	7	9	8
Formic acid	6	5	5	4

properties of the enzyme treated leathers did not change drastically, while that of formic acid treated leathers show appreciable changes; especially due to higher concentration of the acid and higher temperature of the process, as seen from Table II. Specifically, grain smoothness and softness of the final leathers were reduced significantly. Hence, it can be inferred that the enzyme treatments, especially HRP, not only reduces the APEO content in leathers significantly but also did not alter the properties of leathers drastically and hence may be suitable for commercial level applications.

Conclusions

Wetblue goat leathers were treated with selected wetting agent and fatliquor containing APEO at various concentrations. The amount of alkyl phenol ethoxylates present in the leather was estimated and mapped to the concentration of wetting agent or fatliquor. The results show that the APEO content in the leather increases with the increase in the concentration of fatliquor or wetting agent. APEO removal from the leathers containing maximum APEO content (combination of 16% fatliquor Y and 1% wetting agent X) was attempted using specific enzymes as well as formic acid at 70°C. Formic acid treatment for removing APEO content in the leathers leads to poor APEO reduction as well as unsatisfactory leather quality. Out of the different enzymes employed such as enzyme SCD, Hypergo-R, tyrosinase and HRP, treatment of APEO containing leathers with HRP results in 60% APEO removal. It should be noted that these results are obtained for leathers containing higher concentration of APEO (4260 ppm), which was treated with a combination of wetting agent and fat liquor at high concentrations. It has also been observed that the physical and bulk properties of the leathers treated with enzymes are satisfactory and comparable to the control sample. However, a semi-technical level trial would be required in order to ascertain the observed results and before recommending for commercial level applications. Nevertheless, it is recommended to use chemicals without APEO for leather processing in a phased manner, for example, linear alkyl ethoxylate or sodium lauryl sulfate containing chemicals.

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