EFFECTS OF STRETCHING AND DRYING RATE ON THE MECHANICAL PROPERTIES OF CHROME-FREE LEATHER

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ABSTRACT

Stretching chrome-free leather tanned with glutaraldehyde during vacuum drying may possibly be the best drying method for this particular type of leather, because it results in an improved area yield and better mechanical properties due to a lower drying temperature. We explored this composite drying method and investigated how drying variables affect the drying rate and mechanical properties of chrome-free leather that was tanned with glutaraldehyde. Using a statistical experimental design, a second order polynomial equation was derived to quantitatively describe the relationship between the drying rate and three major independent variables: drying temperature, stretch %, and drying time. Drying rate models derived from this investigation provide a clear understanding of the drying process for chrome-free leather. The drying constant indicates that chrome free leather dries faster than chrome-tanned leather. These models will help the leather industry estimate the proper drying parameters. Our studies showed that stretch % during vacuum drying is the most significant variable affecting the stiffness and area retention of leather. This research indicated that stretching should not be overdone and the preferable length increase should not be greater than 10%; otherwise poor leather properties may result, such as an elongation less than 40% and toughness index less than 1.

ABSTRACTO

El estiramiento de cuero libre de cromo curtido con glutaraldehído durante el secado al vacío podría ser el método más adecuado para el secado de este tipo de cuero, porque resulta en mayor rendimiento de área así como en mejores propiedades físicas debido a menor temperatura del secado. Exploramos este método de secado compuesto e investigamos como las variables de secado afectan la velocidad del secado y las propiedades mecánicas de cuero, exento de cromo, curtido al glutaraldehído. Utilizando un diseño estadístico experimental, una ecuación polinómica de segundo grado se derivó para cuantitativamente describir la relación entre la velocidad del secado y tres variables principales independientes: temperatura de secado, porcentaje de estiramiento, y tiempo de secado. Modelos derivados de esta investigación basados en la velocidad de secado proveen una clara comprensión del proceso de secado para cuero exento de cromo. La constante del secado indica que cuero exento de cromo seca más rápido que cuero al cromo. Estos modelos ayudarán a la industria curtidora a estimar los parámetros de secado apropiados. Nuestros estudios indican que el porcentaje de estiramiento durante el secado al vacío es la más significante variable afectando la rigidez y la retención del área del cuero. Esta investigación indica que el estiramiento no debe exagerarse y que el incremento en longitud no debe sobrepasar el 10%; de otra manera podría resultar en deficientes propiedades físicas, tales como elongación menor al 40% y un índice de tenacidad inferior a 1.

INTRODUCTION

In recent years, environmental concerns over the use and disposal of chrome-tanned leather have propelled the use of chrome-free leather, particularly in the European automotive leather markets. One of the most common chrome-free leather is tanned with glutaraldehyde. This organic tannage was developed and established by Filachione et al. in the Eastern Regional Research Center (ERRC) in the early 1960's.[1-5] It has become the most popular alternative tanning agent to chrome salts, because it is less expensive, is readily available and is highly soluble in aqueous solution. Other alternatives to chrome-free leather were reported by Prentiss et al. on the development of a methylacrylate-based chrome-free tannage and pretanning processes that utilize soluble silicates commissioned by the European union.[6,7] However, the quality of chrome-free leather, particularly glutaraldehyde-tanned leather, in some respects is inferior to that of chrome-tanned leather, for example in lower resiliency and hydrothermal stability.[8-10] The drying process is one of the key steps governing leather quality. Although the relationship of drying conditions to the mechanical properties of chrome-tanned leather was determined in our previous investigation by mathematical modeling,[11] an analogous model on the drying of chrome-free leather is lacking, and poor mechanical properties often result. The basis for these poor properties needs to be determined and ways to improve the mechanical properties need to be developed.

Drying is one of the key mechanical operations in the leather making process. Leather acquires its final texture, consistency and flexibility in the drying operations. Vacuum drying leather in recent years has become very popular commercially because of its fast drying speed and reduced space requirement.[12] We recently conducted a comparison study on the physical properties of leather prepared with various drying methods selected from the most commonly used methods in today's tanneries. Results showed that the physical properties of leather, such as area retention and softness, were affected significantly by the drying method.[13] Data revealed that leather with inferior fracture energy often resulted in poor grain break. In addition, observations showed that drying methods using toggling produced higher area yield; however, it resulted in stiffer leather. Our research showed that residual water content plays an important role in controlling the softness of leather. Vacuum drying without toggling yields better toughness and softness. A dimensionless quantity "toughness index" showed a strong correlation with the resultant area retention, which agrees with our previous findings for chrome-tanned leather. This current study aims to establish a predictive drying model for chrome-free leather (drying variables vs. drying rate and physical properties of leather, from experimental physical and chemical testing data). Vacuum drying combined with leather is being stretched, thus mimicking toggle-drying, has been performed for glutaraldehyde-tanned leather. Based on the new model, we plan to identify the optimal drying conditions for chrome-free leather, using the response surface methodology.

EXPERIMENTAL

Materials

Bovine hide was tanned with glutaraldehyde using the retanning, dyeing and fatliquoring process previously reported for the preparation of the chrome-free samples.[13] The leather was then drained, washed at 50°C, drained again, and then placed in plastic bags. Wet rectangular shaped leather samples (1- x 10-cm) were cut near the standard test area as described in ASTM D2813-03 with the long dimension parallel to the backbone. The samples initial moisture content before drying was around 63% (based on wet weight).

Apparatus

We performed our experiments using an enclosed bench top vacuum oven. The vacuum was maintained at 23 Torr or 3.1 kPa absolute pressure for the drying experiments. Samples were stretched, according to the experimental design described later, onto a preheated thin stainless steel plate to simulate the vacuum-drying table and were then clamped at both ends to simulate toggle-drying. The plate with the stretched leather and clamps were then placed in the bench vacuum oven for the designated time and at the desired temperature determined by the experimental design.

Measurements

Water content was determined gravimetrically, as determined by the following Equation 1:

$$\text{Water content (\%)} = 100 \times (M - M_o)/M \qquad (1)$$

where M is the sample weight (including water), Mo is the dry weight of sample, after vacuum drying at 60°C to constant. Before physical property testing, the samples were stored in a conditioned room at 23°C and 50% RH according to ASTM D1610-01. The final length of the samples (Lf) after equilibration in a conditioning room was measured to calculate the percent of length increase comparing to the original length, i.e. before the drying/stretching experiments (L_o); the equation for calculating length increase % after equilibration can be written as follows:

$$\text{Length increase \%} = 100\% \times (L_f - L_o)/L_o \qquad (2)$$

Mechanical property measurements included tensile strength, elongation, and initial strain energy. An upgraded Instron mechanical property tester, model 1122, and Testworks 3.1 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Tensile strength is the maximum stress in tension that the leather may sustain without breaking. Elongation is defined as the maximum strain. The initial strain energy of leather, defined as the energy needed to stretch the leather to 10% strain,[14] is the area under the stress-strain curve from 0 to 10% strain. It is a physical quantity representing the stiffness of a material. These properties were measured with a sample length of 5 cm between the two grips. The strain rate (crosshead speed) was set at 50 mm/min.

Environmental Scanning Electron Microscopy

To examine the fibrous structure of the leather samples from various drying conditions, we used the field-emission environmental scanning electron microscope (ESEM) to examine the cross section of the leather samples. ESEM is advantageous over conventional scanning electron microscopy because a relatively high vacuum in the specimen chamber is not needed to prevent atmospheric interference with primary or secondary electrons, an ESEM may be operated with a poor vacuum (up to 10 Torr of vapor pressure, or one seventy-sixth of an atmosphere) in the specimen chamber. Our ESEM was operated at low vacuum (0.3 Torr) with the voltage set at 15 kV, spot size 5.0 and working distance of approximately 10mm. The samples were uncoated, thus preserving the original characteristics of the leather samples.

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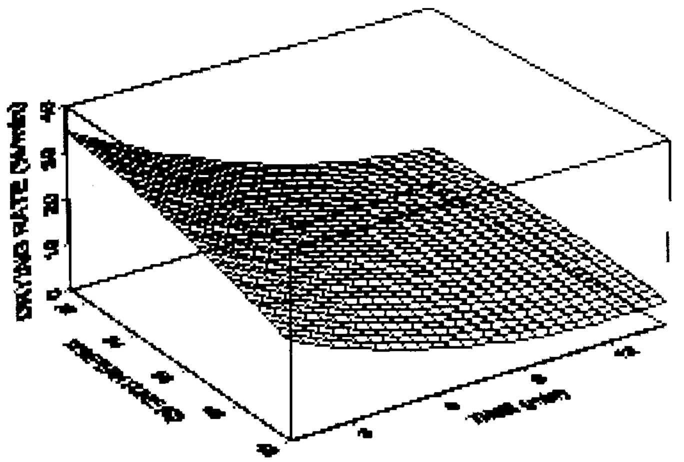

Figure 1. Drying rate as a function of drying time and temperature.

Experimental Design

A central composite design provided by SAS statistical software (version 8e) was applied to arrange experimental conditions, thereby establishing regression models. This experimental design was developed by Box and Hunter[15] and is the most widely used design for fitting a second-order model. The three factors selected were drying temperature (x'_1), drying time (x'_2), an stretch % (x'_3). To simplify the calculations, the independent variables was transformed to coded variables: x_1, x_2, and x_3 by means of the following formulae: $x_1 = (x_1'-60)/10$, $x_2 = (x_2'-10)/5$, and $x_3 = (x_3'-10)/10$. A regression model was derived having the form of a polynomial equation in which the variables are presented as their linear and quadratic terms as well as their bifactorial cross products as shown later in Equation (4). It is desirable to visualize the relation between the response and the factor levels geometrically. Response surfaces (a surface plot of the resultant property as a function of multiple independent variables) were constructed based on the regression equation as shown in Equation 1, using graphics and data analysis software Axum version 6 developed by MathSoft, Inc, Cambridge, MA.

RESULTS AND DISCUSSION

Drying Rate

To understand a process, the rate evaluation as a function of the variable is essential. It provides insight into the mechanism underlying a process. Unfortunately this subject has not been addressed very often for the leather drying process, particularly for vacuum drying. The drying rate was calculated by dividing the difference between the initial water content and residual water content by the drying time interval. Equation (3) can be written as follows:

$$\varpi = (W_o - W_t)/t \qquad (3)$$

where, ϖ is the drying rate, Wt is the water content at time t (residual water content), Wo is the initial water content. The data was processed by the SAS statistical program. We observed that the stretch % is not a significant factor in the drying rate therefore X_3 was removed from the second order regression model as expressed in Equation 4:

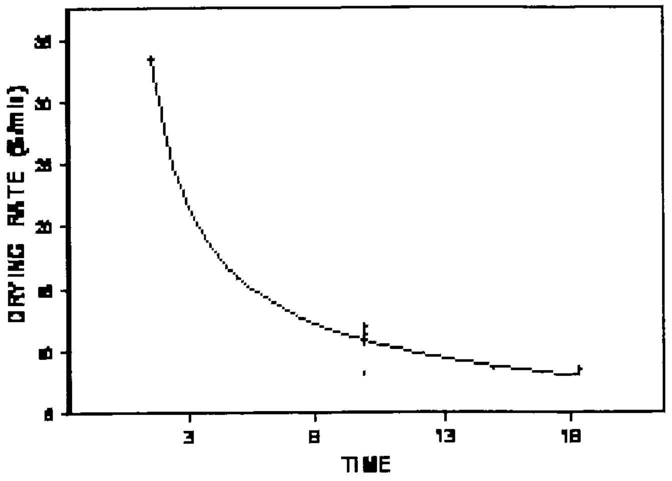

Figure 2. Time dependence of drying rate.

$$\varpi = 11.03 + 1.52\,X_1 - 5.22\,X_2 - 1.20\,X_1\,X_2 - 0.59\,X_1^2 + 3.15\,X_2^2 \quad (4)$$

The multiple correlation determination (R^2) for this quadratic model is 0.90. Figure 1 is a 3-D plot of the response surface of drying rate as a function of drying time and temperature according to Equation 4 for a leather sample with a stretch of 10%. As shown clearly here, vacuum drying does not go through a constant rate period, in contrast to air drying. In fact, Figure 2 shows that the rate of vacuum drying starts to slow down at the very beginning. Vacuum drying is a speedy drying process; it bypasses the constant rate period, and goes directly to the so-called "falling rate period."

In regular air drying, water is evaporated from its surface and is constantly replaced by the migrated water from inside driven by capillary force. As reported by van Vlimmeren and many others in the first phase of drying, evaporation occurs from a thin film of water forming on the surface of leather at a constant rate, which is controlled by the rate of heat transfer to the surface.[16, 17] In contrast, in the vacuum drying process the water not only evaporates from the surface, but also from the inside of leather, once its temperature reaches the boiling point of water at the reduced pressure. On the other hand, similar to the other drying processes and including the vacuum drying process, the drying rate increases with increasing temperature (Figure 1). This is simply because a higher temperature speeds up the evaporation of water.

Modeling Drying Rate

The statistical model presented in Equation 4 gives a quantitative description of how drying rate changes with three major drying variables. It also reveals the fundamental differences between vacuum drying and regular air drying processes. However, this polynomial equation is rather complicated, and it does not cover a wider range of drying conditions, for example changes in vacuum pressure. Therefore, an effort was made to build up a simpler model and to cover wider drying conditions. From previous studies, we learned that the drying rate increases with initial water content and decreases with time. We also believe that the drying rate may decrease with leather thickness because the heat transfer is slower for thicker leather. Moreover, it is also known that the vacuum pressure is an important factor for the drying rate. We may assume that at the same drying temperature, its ratio to the boiling point under a particular vacuum pressure may be proportional to the drying rate. With all these facts derived from experiments and reasonable assumptions, a rate equation (5) may be expressed as follows:

$$\varpi = K \text{ x } W_o \text{ x } (T/T_b) \text{ x } (1/d)^2 \text{ x } (1/t)^2 \text{ x } (1-f)^{1/2} \qquad (5)$$

Where K is a drying constant and needs to be determined, T the is drying temperature, T_b is the corresponding boiling point of water at a particular vacuum pressure, d is the thickness of leather being dried, and t is the drying time. It should be noted that the water content (%) applied to this model is based on the dry weight of leather. The data fit Equation 5 rather well, as demonstrated in Figure 3, with a correlation coefficient (r) of 0.98. The curve fitting thus gives the value K as 0.184, which is a little greater than we previously reported for chrome-tanned leather. The rate equation derived here is simple and easy to be understood. It can be used to predict the drying rate and subsequently the residual water content left in the leather after the drying cycle is completed.

Correlation between Tensile Strength and Drying Rate

Figure 4 shows a 3-D regression plot of the resultant tensile strength as a function of drying rate and apparent density simultaneously. The apparent density is defined as the weight per unit volume of leather (ASTM D 2346-00). It demonstrates that the tensile strength of leather steadily decreases as the drying rate increases. The rate of a process has been known as a key parameter to govern the resultant mechanical properties in other industries such as fiber, plastic, and metal. For example, the rate of solidification, the rate of annealing, the rate of coagulation, and the rate of crystallization have been reported to be dominant factors affecting the mechanical properties.[18, 19] Further more, Figure 4 shows that the greater the apparent density, the better the tensile strength. We believe that apparent density is an indication of the degree of packing in the dried leather; presumably more packing gives more resistance to tensile stress and results in better tensile strength. This finding agrees with Wang and Attenburrow's report for goatskin leathers, stated that the strength of leather was strongly associated with its apparent density, which in turn could be related to the compactness of its fiber bundle weave in the skin.[20]

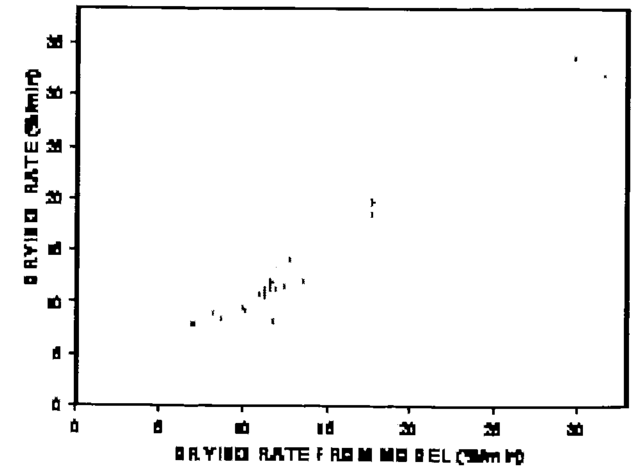

Figure 3. Drying rate model.

Length Increase

During water removal as in a drying process, the space originally occupied by water in leather is slowly squeezed and decreased, driven by internal pressure release; therefore leather shrinks. Shrinkage produces less area yield. This is the most common problem involved in the leather drying process. Although vacuum drying offers many advantages as mentioned before, many leather manufacturers are still hesitant to use this drying method. Toggle drying therefore is still widely used in tanneries. The current drying method used in this study actually combines toggling and vacuum drying, in which the leather is stretched in a wet stage and then placed in a vacuum oven. Hopefully, by using this composite method, one may obtain the advantages of both methods. Figure 5 illustrates the effects of stretch % on the dimensional increase in terms of % length increase (refer to Equation 2) compared to the original length of the leather drying samples. It is interesting to note that the % length increase does not equal the % stretch applied to the leather during vacuum drying. This discrepancy is due to the contraction of leather during equilibration in the conditioning room. The extent of contraction is dependent on many factors, particularly drying rate.

Figure 6 shows a 3-D plot of % length increase as a function of stretch % and drying rate. It clearly demonstrates that the higher the drying rate the smaller the % length increase. This can be attributed to a higher drying rate's generation of a greater residual stress memorized in the leather. During conditioning, the leather relaxed, contracted and recovered a certain length gained from the stretching process.

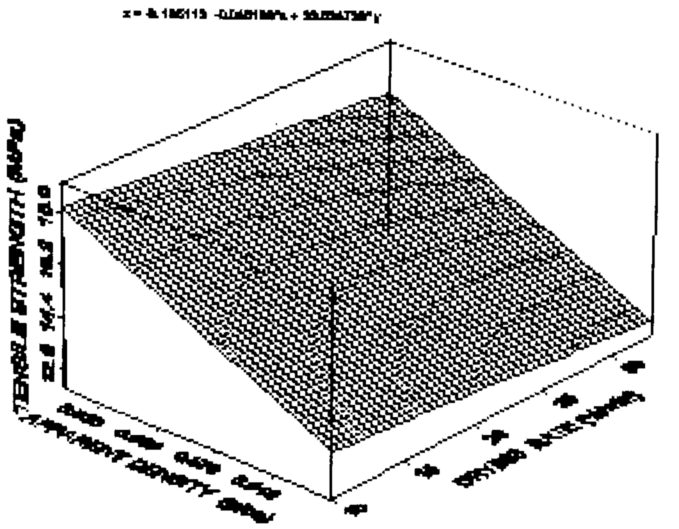

Figure 4. Tensile strength as a function of apparent density and drying rate.

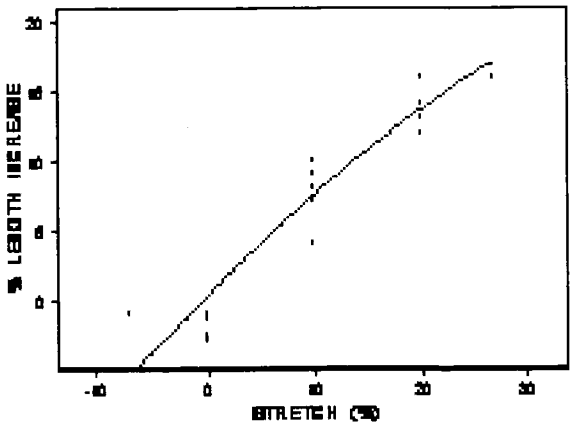

Figure 5. The relationship between % length increase and stretch %.

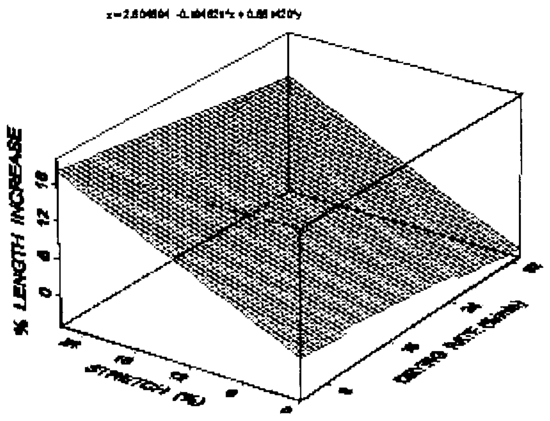

Figure 6. % length increase as a function of stretch and drying rate.

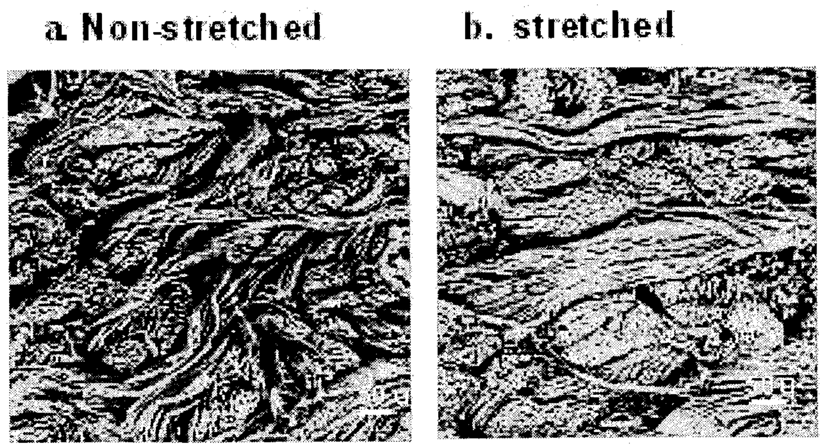

Figure 7. Micrographs of cross-sections of leather (a) non-stretched (b) stretched.

Fiber Orientation and Stiffness

Stretch-induced morphological changes can be illustrated by micrographs shown in Figure 7. The stretched leather (Figure 7b) shows a more highly oriented fiber structure than that of the un-stretched leather sample (Figure 7a). Because of this highly oriented fiber structure, all of the fibers are aligned mostly in one direction and stiffer leather is the result.

Adequate softness or pliability is a very important quality requirement for certain leather products, particularly for garments, upholstery and footwear. It provides comfort and a good "handle" to the user. The quantitative assessment of softness or its reverse term "stiffness" can be based on measurements of the resistance to a small deformation by tensile stress. The resistance may be quantitatively represented by the initial strain energy.[17] Figure 8 shows a close relationship between initial strain energy and % length increase. This indicates that drying conditions with increased stretch % will produce stiffer leather.

Elongation

Elongation indicates the maximum extent to which the material can be stretched without fracture when a tensile stress is applied to it. It is one of the key physical properties closely associated with leather quality. It is commonly expressed as the percent increase in original length when the stress applied equals the tensile strength of the material. Figure 9 presents a plot of the resultant elongation for the various stretch %. This figure clearly illustrates the trend that the elongation of leather decreases greatly when the stretch % increases. Apparently the stretch action makes the resultant dried leather less extensible. As shown in Figure 9, the elongation drops below 40%, when % length increase reaches 10%. Since an elongation less than 40% is not acceptable for most leather products, stretching the leather to 10% in length appears to be the upper limit.

Toughness Index

Figure 10 presents a plot of the resultant toughness index for various % length increases. Toughness index is a dimensionless parameter.[21] It is interesting to note that most fibrous materials have a toughness index lower than one; i.e. the value of young's modulus is often greater than tensile strength. Only a very few tough fibrous materials such as leather have toughness indices greater than 1. The data shown on this plot clearly illustrate the trend that the toughness index of leather decreases drastically with the % length increase. Apparently the stretch action makes the resultant dried leather stiffer, rigid, and less extensible, thereby reducing the toughness index of leather.

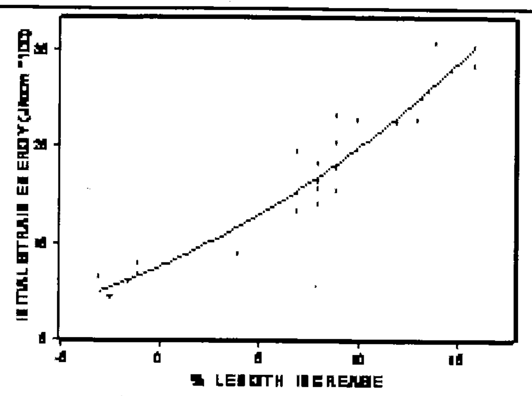

Figure 8. Initial strain energy as a function of % length increase.

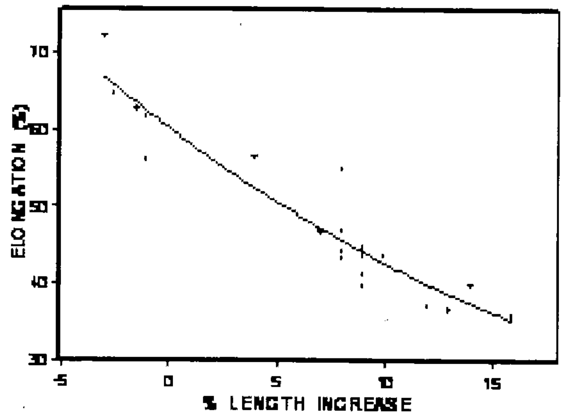

Figure 9. Elongation as a function of % length increase.

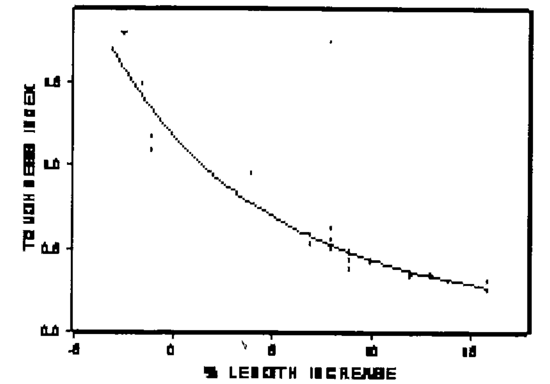

Figure 10. Toughness index as a function of % length increase.

CONCLUSIONS

The objective for this research is to obtain an improved drying method, merging toggling and vacuum drying together. Vacuum drying offers fast speed and low temperature drying that particularly is advantageous to chrome-free leather, since it often has a lower denaturation temperature. Adding a toggle action, such as stretching during vacuum drying, can increase area yield. However this research indicated the stretching should not be overdone and should not be greater than 10% in length; otherwise the leather will not pass certain mechanical property specifications with an elongation less than 40% and a toughness index less than 1. This research also formulated a mathematical model to estimate the drying rate for chrome-free leather. The drying constant indicates that chrome-free leather dries faster than chrome-tanned leather. The model presented for the drying rate may benefit the leather industry in estimating the right drying parameters to dry leather.

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