

THERMAL STABILITY OF HIDE AND LEATHER AT DIFFERENT MOISTURE CONTENTS

by

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Abstract

Differential scanning calorimetry was used to determine the phase transition of hide and chrome-tanned leather at different moisture contents. In both products phase transition occurs over a wide temperature range and is irreversible. The melting temperature of hide increases progressively from about 66°C at 200% moisture content to 221°C at approximately 0% moisture content, while the melting temperature of chrome leather remains almost constant at about 105°C down to about 30% moisture content and then increases sharply to 204°C at about 0% moisture content. It is significant, however, that at all moisture contents below 30%, the melting temperature of hide is higher than that of chrome leather and (according to published research data) higher than that of vegetable-tanned and formaldehyde-tanned leathers. The feasibility of adapting present commercial shoe-manufacturing technology to the utilization of non-chrome leathers is discussed in light of the research findings obtained.

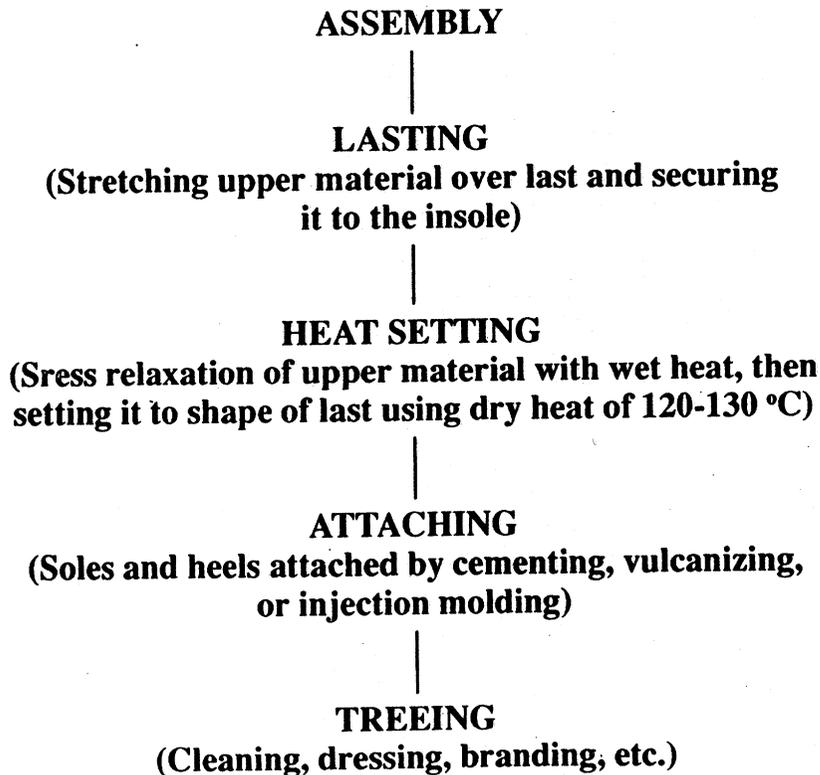
Introduction

A great amount of effort is presently being expended worldwide in an attempt to replace chrome with an ecologically more acceptable inorganic or organic tanning agent. While retannage of vegetable-tanned leather with a masked basic aluminum sulfate yields a shrinkage temperature of 100°C⁽¹⁾, it is doubtful that sufficient quantities of vegetable tannins are commercially available to replace all of the chrome which is presently being used. It is taken for granted that the lower-cost, high-speed, conveyorized manufacturing methods presently used in the shoe industry, such as the ones used to produce the direct-molded-sole and the injection-molded-sole shoes, require leathers with a shrink temperature equal to that of chrome leather. In fact, it has been reported that vegetable-tanned leather absolutely cannot withstand the high machine temperatures required during vulcanizing of soles with shoe uppers⁽²⁾. According to the literature, even chrome leathers have to have a low enough moisture content to render them sufficiently heat stable. Indeed, a cursory examination of the commercial processing requirements readily appears to substantiate the irreplaceability of chrome leather in commercial processing requirements readily appears to substantiate the irreplaceability of chrome leather in commercial shoe manufacture. Figure 1 gives a sequence of the principal operations used in the manufacture of shoes. These operations involve assembly, lasting, heat setting, (sole and heel) attachment, and treeing. While these five operations are common to all commercial manufacturing

methods, each of these operations involves preparatory steps which differ widely and depend on such factors as the style of shoe produced and the amount of man-made materials utilized. For example, before the shoe upper and component parts of the shoes are brought together in the first operation, the assembly, the shoe uppers have to be cut and stitched together. A last is a block or form shaped like a person's foot. Lasting is the term applied to the second operation in which the upper material is stretched over the last and secured to the bottom of the insole either with tacks or adhesive. Lasting leaves the shoe upper leather unevenly stressed in different parts. The third operation, heat setting, is needed to relax these stresses and to cause the material to lie down tight and smooth, and to acquire permanently the shape of the last. This is a very important operation from the standpoint of thermal stability of leather: It may subject the leather to damaging heat treatment because it involves the use of wet heat for stress relaxation and dry heat of up to 120-130°C to set the shoe to the required shape. As will be shown later, the sole and heel attachment, the fourth operation, may be equally damaging to the leather used because it may involve even higher temperatures (up to 170°C) depending on whether cementing, vulcanizing, or injection molding is used. In contrast, treeing, as the final step is called, involves cleaning, dressing, branding, and similar finishing operations which do not require leather to have unusually high thermal stability.

FIG. 1. —

MAIN PROCESSING STEPS OF SHOE MANUFACTURE



During moisture removal, physical changes occur in hides and leather which may greatly influence their technological properties. Yannas⁽³⁾ and Luescher *et al.*⁽⁴⁾ found that the melting temperature of tissues rich in collagen increases with decrease in moisture content, and Witnauer⁽⁵⁾ observed similar results in vegetable- and formaldehyde-tanned leather. Consequently, a study aimed at elucidating the mechanisms involved during heat-denaturation of collagen tissues was undertaken at the Eastern Regional Research Center (ERRC) using differential scanning calorimetry (DSC)⁽¹⁴⁾ and nuclear magnetic resonance (NMR) with the ultimate goal of obtaining a better understanding of the reason why different tanning agents yield leathers with different shrink temperatures. While this study is still ongoing, much useful information has been obtained already to explain some important functional properties observed in leather during processing. This paper discusses the effect of moisture content on melting temperature of cattlehide and chrome leather and examines the feasibility of making non-chrome leathers compatible with the requirements of modern, commercial shoe-manufacturing processes through prudent control of moisture content. It explores the possibility of giving the leather-products manufacturers a wider choice in the selection of leathers based primarily on consumer satisfaction (such as comfort, performance in wear, price, and appearance) rather than on shrink temperature.

Experimental

The thermal denaturation (melting) of hide and chrome-tanned leather was measured with a Perkin-Elmer Model DSC-2 calorimeter inside hermetically sealed aluminum sample pans with an empty aluminum pan as the reference sample. The DSC was calibrated for temperature and heat flow with indium (melting point, mp = 430°K, latent heat of melting, $\Delta H_m = 6.8$ cal/g) and benzoic acid (mp = 395°K, $\Delta H_m = 33.9$ cal/g). The sample weight was approximately 30 mg. The drybox of the DSC was dried with desiccant and dry nitrogen. The chrome-tanned leather was obtained using the ERRC process described by Taylor *et al.*⁽⁶⁾. The hide sample had been limed and neutralized in a commercial tannery before being ground by the process described by Komanowsky *et al.*⁽⁷⁾. Preliminary experiments had shown that the experimental results varied over a wide range because the samples utilized were too small to be representative; consequently, the leather used was also pre-ground in a large Wiley mill. Samples of both materials were lyophilized for 3 days under vacuum of about 0.01 torr and then equilibrated over saturated salt solutions for at least 2 weeks at room temperature in desiccators. The salts used were LiCl, CH₃COOK, CaCl₂, K₂CO₃, NaNO₂, NH₄Cl, and K₂CrO₄, giving the following water activities, respectively: .126, .20, .323, .45, .66, .79 and .88. To obtain hide samples with higher moisture contents, predetermined amounts of water were added to samples of the lyophilized material which were then equilibrated for a week at refrigeration temperature. All moisture measurements were made by heating representative samples at 70°C overnight under a vacuum of about 0.01 torr. To measure the melting temperature and the heat absorbed or enthalpy of melting, samples of varying moisture contents weighing about 30 mg were sealed in DSC pans inside a low-humidity room and scanned in the DSC at 5°C/min. The areas of the transition peaks were measured by a planimeter. The heats of absorption due to thermal denaturation, ΔH , were calculated from these areas. The melting temperature, T_m , was assumed to correspond to the temperature of the peak rate of heat flow because its determination is more precise than, for example, the determination of the temperature of the onset of melting.

Results and Discussion

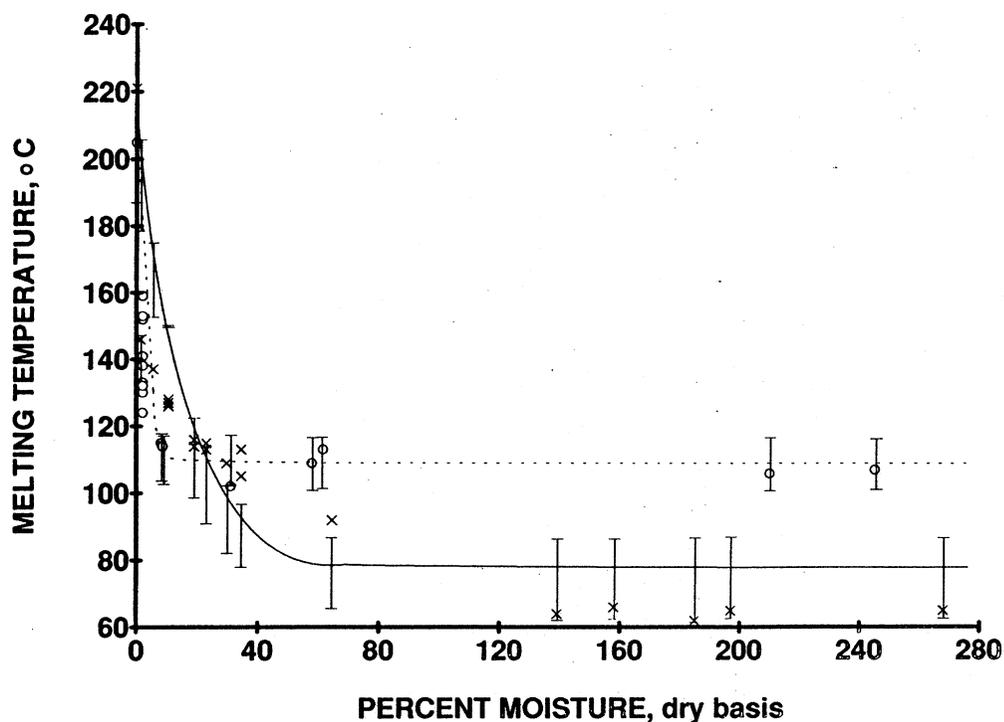
Figure 2A shows the dependence of the melting temperature, T_m , on the water content of limed cattlehide and chrome leather. Following the example of Kopp *et al.*⁽⁸⁾, the following function was fitted by the method of least squares to the experimental data

$$T_m = A \cdot e^{(B \cdot X)} + C$$

where X = moisture content on dry basis.

FIG. 2A. —

Increase of denaturation or melting temperature, T_m , of hide and chrome leather with decrease in percent moisture content (X):

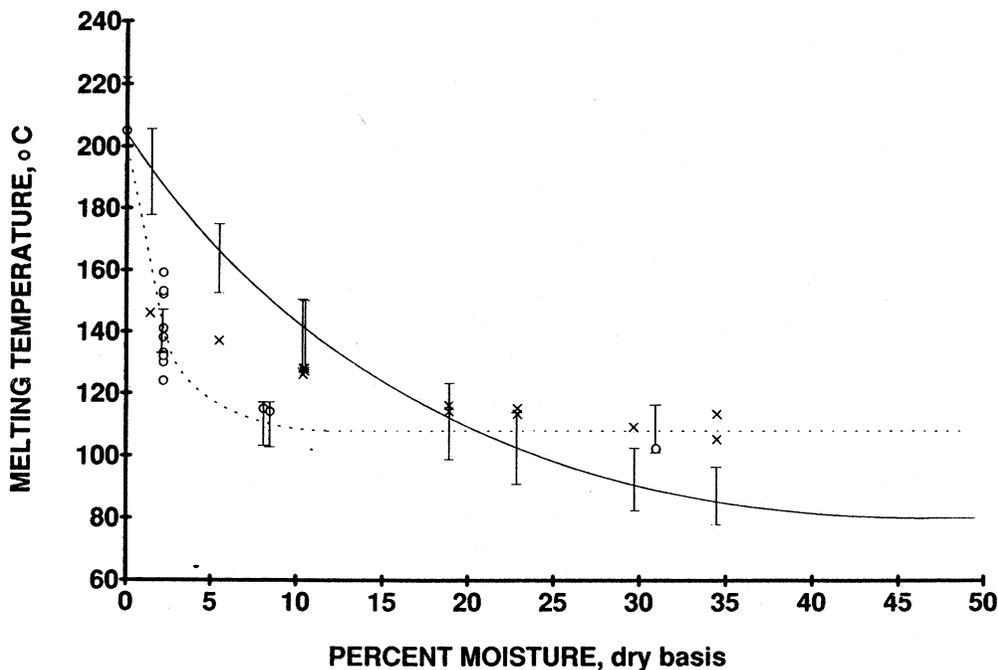


- x Hide (data points)
- |— Line fitted to hide data: $T_m = 128.9 \cdot e^{-0.06729 \cdot X} + 74.87$
with confidence boundaries at 95% confidence level
- o Leather (data points)
- ..|.. Line fitted to leather data: $T_m = 95.79 \cdot e^{-.5051 \cdot X} + 108.8$
with confidence boundaries at 95% confidence level

Figure 2A gives the experimental data, the fitted curves, and the corresponding confidence limits calculated at a .95 confidence level for both hide and leather. For clarity, an enlarged view for the lower moisture range of Fig. 2A is presented in Fig. 2B. From the latter figure it is readily seen that the confidence regions for both curves overlap in the moisture range between 15% and 30%, indicating that in that range the melting temperatures are practically the same for both materials. In the presence of more than about

10% moisture (on dry basis), T_m for hide was found to decrease slowly with increase in moisture content while T_m for leather remained almost constant and, as is well known in the tanning industry, above 100°C. For both materials, T_m increased sharply with decrease in moisture below 10% as expected from published results obtained on collagen^(3,8). Surprisingly, T_m for hide was found to be higher at very low moisture contents than T_m for leather, indicating that at that moisture content, below about 15%, untanned hide is thermally more stable than the crosslinked leather. This does not mean, however, that - from the standpoint of heat stability during shoe manufacture - untanned hide is superior to leather because after the lasting operation (and occasionally before lasting) the moisture content of leather, which is initially usually about 20%, has to be increased to about 35% which causes T_m of hide to drop whereas T_m of chrome leather remains high.

FIG. 2B. — Increase of denaturation or melting temperature, T_m , of hide and chrome leather with decrease in moisture content (X). Expanded view of Fig. 2A at low moisture content.



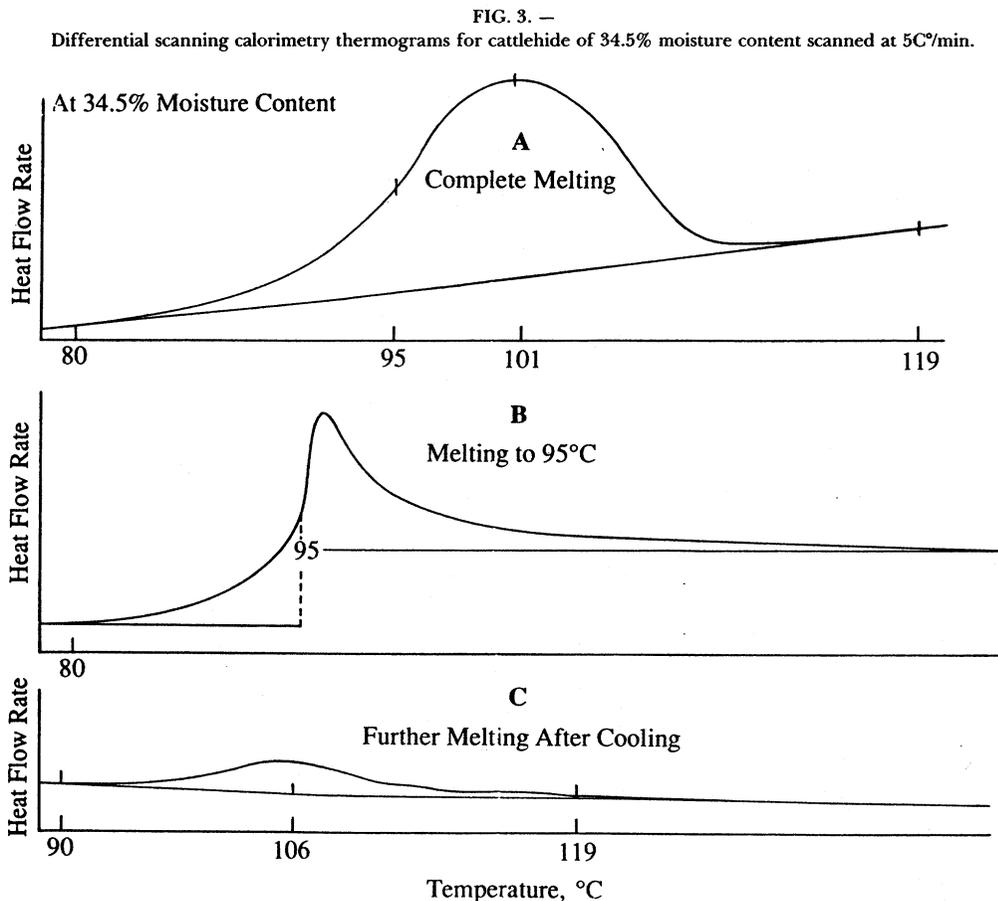
Stretching of dry leather during lasting does not result in sufficiently fast and permanent elongation and stress relaxation of the leather. Wet heat softens the shoe-upper leather and permits the stressed portions of it to elongate both quickly and permanently, most likely by the movement of fibrils and fibers relative to each other. Thus the increase in moisture permits the leather to adapt itself more closely to the shape of the last. This operating step is carried out below the melting temperature of leather.

The subsequent drying induces shrinkage or contraction of leather and forces it to assume more closely the shape of the last in the stressed areas, the unstressed areas, and even in the areas where wrinkles were formed during lasting. As described in detail by Komanowsky⁽⁹⁾, the degree of shrinkage during this drying step is a consequence of the action of capillary forces and can be regulated very accurately by careful control of drying

conditions such as relative humidity, air temperature, air velocity, and time. As long as the leather temperature is kept below the incipient denaturation temperature of the leather, no damage occurs to the leather during this stage of drying. To release the stresses induced during lasting more completely and more permanently and to remove some of the remaining wrinkles, the leather is exposed to intensive drying at elevated temperatures at the end of this drying step in the temperature range at which onset of melting occurs. This stabilization procedure, which is typically conducted at 95-120°C dryer temperature and raises the shoe surface temperature up to 70-90°C⁽¹⁰⁾, is called heat setting and results usually in a severe dehydration, often down to as low as 5% moisture content. Hide and leather were found in this study to denature and shrink over a wide temperature range depending on the scanning rate. At the scanning rate used (5C°/min), the incipient denaturation temperature (the temperature at which denaturation was first observed) for well-tanned chrome leather containing 10% or more moisture was approximately 10C° lower than that at the peak rate of heat flow reported in Figures 2A and 2B, i.e. at about 90-95°C. For poorly tanned chrome leather the incipient denaturation temperature would be lower, in the 70-90°C range, which is equal (as mentioned above) to the temperature range observed during commercial heat setting. As will be shown below, some denaturation at the final stage of drying is an integral part of the heat-setting phenomenon. Referring again to Fig. 2B, it is apparent that leather with moisture content reduced to such low values can be subjected at a later stage of shoemaking, during sole attachment, to very high temperatures without fear of denaturation. Thus heat setting accomplishes actually two goals: (a) It forces the shoe upper to conform more smoothly to the shape of the last and (b) it prepares it for the next operation, the sole attachment, by increasing its thermal stability through drying.

Figure 3A gives a thermogram (or temperature record) obtained for limed hide with a water content of 34.1% when it was heated at a rate of 5C° per min. At the peak rate of heat flow, corresponding to a temperature of 101°C, most of the sample can be considered to be denatured. Figure 3B shows the results obtained in an experiment which was carried out on another, identical sample by interrupting the melting process at 95°C (i.e., at approximately the middle of the temperature range for melting or one fourth of the melting peak) and keeping the temperature at that value for 30 min. This partially melted sample was cooled down to 5°C and then reheated at the same heating rate of 5C°/min to obtain another thermogram shown in Fig. 3C. The area of the endothermic peak obtained during reheating (Fig. 3C) is seen to be much smaller than that of the peak shown in Fig. 3A, while the temperature of the peak has been raised by 5C° from 101° to 106°C. The sum of the areas of the endothermic peaks obtained on the second sample (Fig. 3B and 3C) was found to be equal to the area of the peak obtained on the first sample (Fig. 3A) indicating that the corresponding amounts of heat absorbed during both denaturation procedures were also equal. From these results and from similar results obtained on leather it was concluded that (a) the denaturation process, which is known to involve breaking of hydrogen bonds and a concomitant thermal unfolding of the helical intramolecular structure, occurs in tissues rich in collagen over a wide range of temperatures and (b) the denaturation process is not readily reversible. If it were reversible, the energy absorbed during denaturation of the first sample would equal the energy absorbed during reheating of the second sample and the areas of the peaks in Fig. 3A and 3C would be equal. Considering that the degree of denaturation increases with increase of contraction of leather and that completely shrunk leather occupies only 1/3 of its original length, it becomes apparent why heat setting is a very effective method for conforming the shoe

upper to the last. It is interesting that this method might be expected to be especially effective in removing wrinkles because unstressed leather comprising these wrinkles shrinks at lower temperatures⁽¹¹⁾. Note that heat setting depends on three factors: moisture content, temperature, and time. Whereas heat setting does involve some heat denaturation, excessive denaturation of the leather should be avoided to prevent unwarranted damage to the leather. To optimize the result, all three variables have to be controlled carefully.



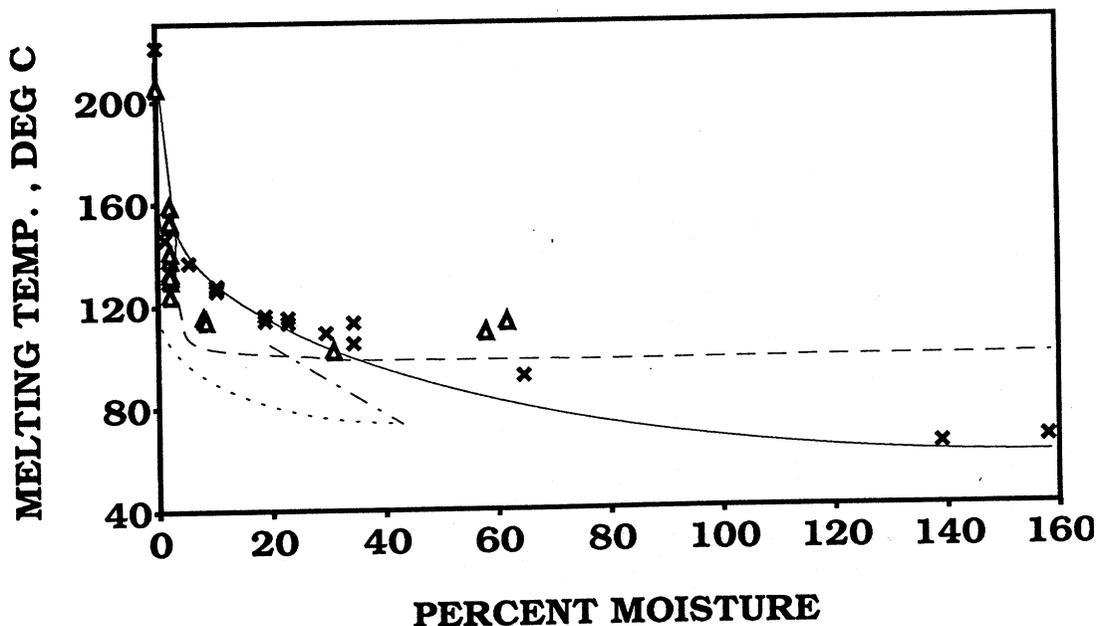
Curve A: Complete melting curve. Curve B: Thermogram obtained (on a sample which was identical to the sample used to obtain curve A) when scanning was interrupted at 95°C and the sample was kept at that temperature for 1/2 hour. Curve C: Complete melting curve for sample used to obtain curve B after the sample was cooled down from 95 to 5°C. Note that in Fig. 3B, the x-axis represents time, not temperature, at temperatures higher than 95°C. To determine time in minutes, multiply the temperature reading by 5 (the scanning rate in C°/min).

As described above, heat setting is carried out after the shoe upper, the insole, and the reinforcing parts of the shoe have been attached to the last and then subjected to hot moist air to relax the stresses induced during lasting. According to modern time-saving technology, the stress-relaxation step is quickly followed by the use of hot dry air at temperatures up to 120 or even 130°C to remove moisture quickly and to set the shoe to the desired shape. Control of the degree of heat setting is relatively simple with chrome leather because its denaturation temperature is constant down to 10% moisture. This is

not the case with non-chrome leathers whose denaturation temperatures increase with decrease in moisture content.

Figure 4 compares the experimental melting temperatures for hide and chrome leather with melting temperatures for formaldehyde-tanned and vegetable-tanned leathers at low moisture contents. The latter data were obtained by Witnauer⁽⁵⁾ using dilatometric techniques. The dotted line gives T_m for formaldehyde-tanned hide and the dashed line for vegetable-tanned leather. Interestingly, in all cases the melting temperature of leather is equal to about 120°C at 10% moisture content with the exception of vegetable-tanned leather which has a T_m equal to about 100°C at that moisture content. From these results it would seem that at low enough moisture contents (about 10%) all types of leather, with the possible exception of vegetable-tanned leather, should be able to resist melting and withstand normal heat-setting conditions. The only prerequisite is that the moisture content be reduced low enough before the higher heat is applied. In other words, the present practice of heat setting should be revised to include a drying step using milder drying conditions before heat setting is attempted. Thus in the proposed method the two types of leather shrinkage would be achieved in two stages under accurately controlled conditions: First the rewetted leather would be made to shrink through the action of capillary forces during moisture removal to the desired accurately measured moisture content, then additional shrinkage would be accomplished by application of dry heat at a predetermined temperature which would depend on the type of leather used. As a matter of fact, using this accurately monitored approach, there is no reason why heat setting of non-chrome leathers, even of vegetable-tanned leather, could not be carried out successfully at a lower temperature such as 85°C if the leather is predried properly.

FIG. 4. — Increase in denaturation temperature with decrease in moisture content of hide and different types of leather:



While there are several methods of sole attachment, only one of them, the direct vulcanization of rubber on to the shoe bottom, may exceed temperatures of 120 to 130°C. Sole attachment by vulcanization, however, is carried out after the leather has been dried to low moisture contents, often as low as 5%, whereas vulcanization may be effected at temperatures anywhere between 95°C and 150°C, lasting from seconds to hours depending on the accelerating agents employed⁽¹²⁾. Consequently, a careful choice of operating conditions with regard to leather moisture and type of accelerating agent used would allow adaptation even of this most stringent processing step to almost any type of leather. Of course, lowering of the temperature would slow down the vulcanization process somewhat if the same accelerating agent were to be used.

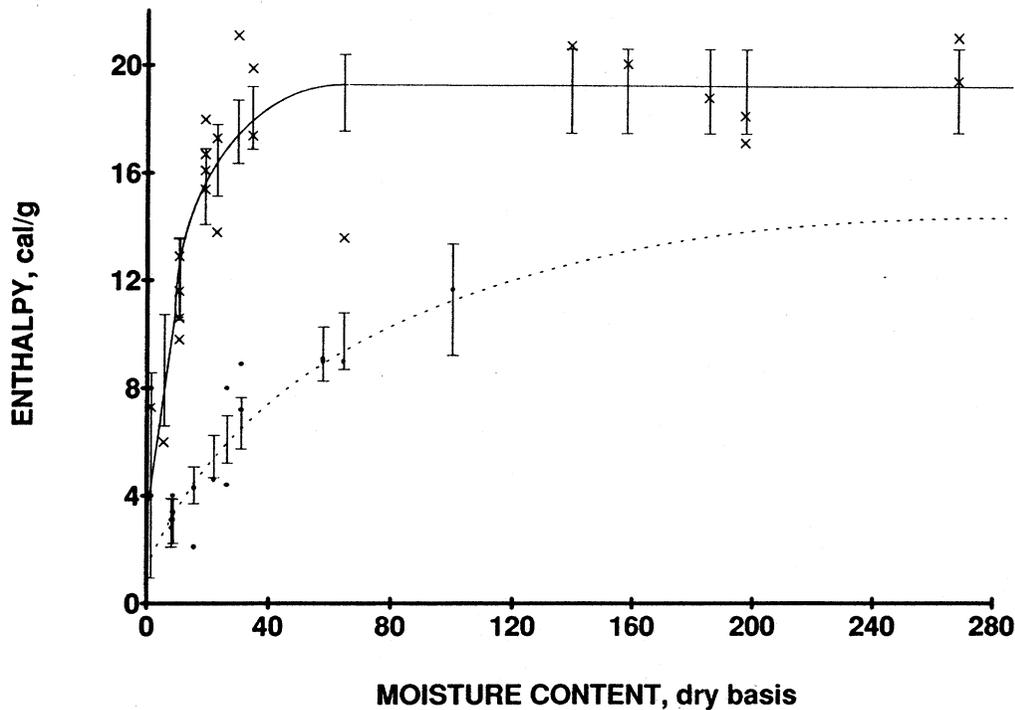
The thermoplastic polymer Polyvinylchloride (PVC) has a glass-transition temperature, T_g , equal to 87°C. As long as this temperature is exceeded, the plastic flows easily and injection molding to leather uppers of soles and heels is feasible. Considering, however, that the PVC is not directly molded to the leather but to a layer of polyurethane adhesive covering the whole shoe bottom, and that the injection time averages 10-20 seconds⁽¹³⁾, it is obvious that the leather does not have to be heated above 87°C in commercial manufacturing practice.

In the 1960's, thermosetting polymers such as polyurethane, PU, gained prominence due to their superior adhesive and wear properties. While PU has its drawbacks (it is expensive, it cannot be reprocessed, and it sticks too much to machine and molds), it does not require high temperature and pressure. As a matter of fact, the molds are only slightly warmed to 50-60°C.

More recently, the triblock copolymer polystyrene-block-polybutadiene-block-polystyrene, SBS, has found application in rubber soles of running shoes and sneakers because heat generated by sliding friction turns SBS into an adhesive which reduces slipping. Note that even this elastomer does not require application of higher heat than heat setting does.

As mentioned in the introduction to this paper, this research is part of an ongoing study conducted to obtain a better understanding of different tannages, especially the reason for the superior thermal stability of chrome leather. While this study is still rather far from being completed, many interesting results have been obtained to date. One such result is given in Fig. 5 which shows a plot of the heat of denaturation, ΔH , of hide and chrome leather as a function of moisture content. From this plot it is seen that ΔH for limed hide increases steeply from 0 to about 30% moisture content and then remains practically constant with further increase in moisture. With chrome leather, the steep increase in ΔH persists to about 70% moisture content. As can be seen, however, the ΔH is much lower for leather than for hide at all moisture contents, even at moisture contents as low as 3-5%. At this low moisture content all of the water is considered to be structural water involved in forming bridges between the three chains of the triple helix comprising the collagen molecule. This result suggests that chrome acts not only to form crosslinks between amino-acid side-chains but that it is, in addition, unique in being able to affect the strength of the intrahelical water bonds and possibly form some bonds between hydroxyl groups of hydroxyproline and chrome complexes and thereby contribute to the enthalpy and entropy of collagen melting. Preliminary studies using nuclear magnetic resonance support such an explanation.

FIG. 5. —
Change in enthalpy of melting, ΔH , of hide and chrome leather as a function of moisture content (X):



- x Hide (data points)
- |— Line fitted to hide data: $\Delta H = 15.96 \cdot (1 - e^{-0.7829 \cdot X}) + 3.159$
with confidence boundaries at 95% confidence level
- o Leather (data points)
- .-|.- Line fitted to leather data: $\Delta H = 11.58 \cdot (1 - e^{-0.02071 \cdot X}) + 1.215$
with confidence boundaries at 95% confidence level

Conclusion

While the mechanism which imparts superior thermal stability to chrome-tanned leather still eludes full clarification, a better understanding of the thermal properties of other tannages can be utilized successfully to minimize the obstacles encountered during conveyorized shoe manufacture due to the lower shrinkage temperatures of these tannages. Based on the experimental results obtained in this research study and based on the descriptions of current shoe-manufacturing technology found in the literature, it appears that only minor changes in processing techniques may be needed to adapt present commercial processes to the utilization of non-chrome leather in the manufacture of shoes and other leather products.

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Discussion

DR. ESA MANTYSAALO (Tampere University of Technology, Finland): It is not completely clear to me what kind of reference calorimeter you have used.

MR. KOMANOWSKY: Are you asking how I standardized the calorimeter? We standardized it with benzoic acid and indium using a Perkin-Elmer Model DSC-2 differential scanning calorimeter.

MR. STEVEN WREN (Struktol Company): When you talked about using chrome leather, was this just plain wet blue?

MR. KOMANOWSKY: Yes.

MR. WREN: Did you approach moisture equilibrium by sorption or desorption?

MR. KOMANOWSKY: We did it both ways. I lyophilized a sample, and then equilibrated it in dessicators in different relative humidities; I then determined the moisture content. Other samples of wet blue were exposed under similar conditions, to equilibration, and then the moisture contents were determined in this other direction. Samples produced in both ways yielded data which fell on the same line.

MR. WREN: The problem is, of course, that shoe factories use commercially-made fashionable leathers containing more than one tanning agent. Chrome may be the basic tanning agent, but there may also be aldehydes or vegetable extracts. Did you do any work on combinations of these using commercially available leathers, to test heat stability in shoe making?

MR. KOMANOWSKY: No, I have not gone that far. Of course, if it is chrome tanned, it would have a shrinkage temperature in excess of one hundred degrees centigrade; the addition of other tanning materials would not change it that much.

MR. WREN: There was some work done in South Africa on the combination of vegetable extracts and alum. There is a subsequent reaction which raises the shrinkage temperature to over a hundred degrees, and that might be a more practical application.

MR. KOMANOWSKY: As I mentioned in the introduction, there is a question as to whether there are enough tannins in the world to satisfy all the demands.

DR. ECKHART HEIDEMANN (Technische Hochschule, Darmstadt): You have told us that you can do heat setting also at eighty-five degrees centigrade with vegetable-tanned leather, but I would like to ask you what was the extent of the setting effect, if you compare chrome leather at one hundred and thirty degrees centigrade against vegetable-tanned leather at eighty-five degrees centigrade? With setting, you apply a certain tension, and after unloading, the leather does not spring so far back. In every case there is some return toward the original dimension. The question is, how far does it spring back after unloading?

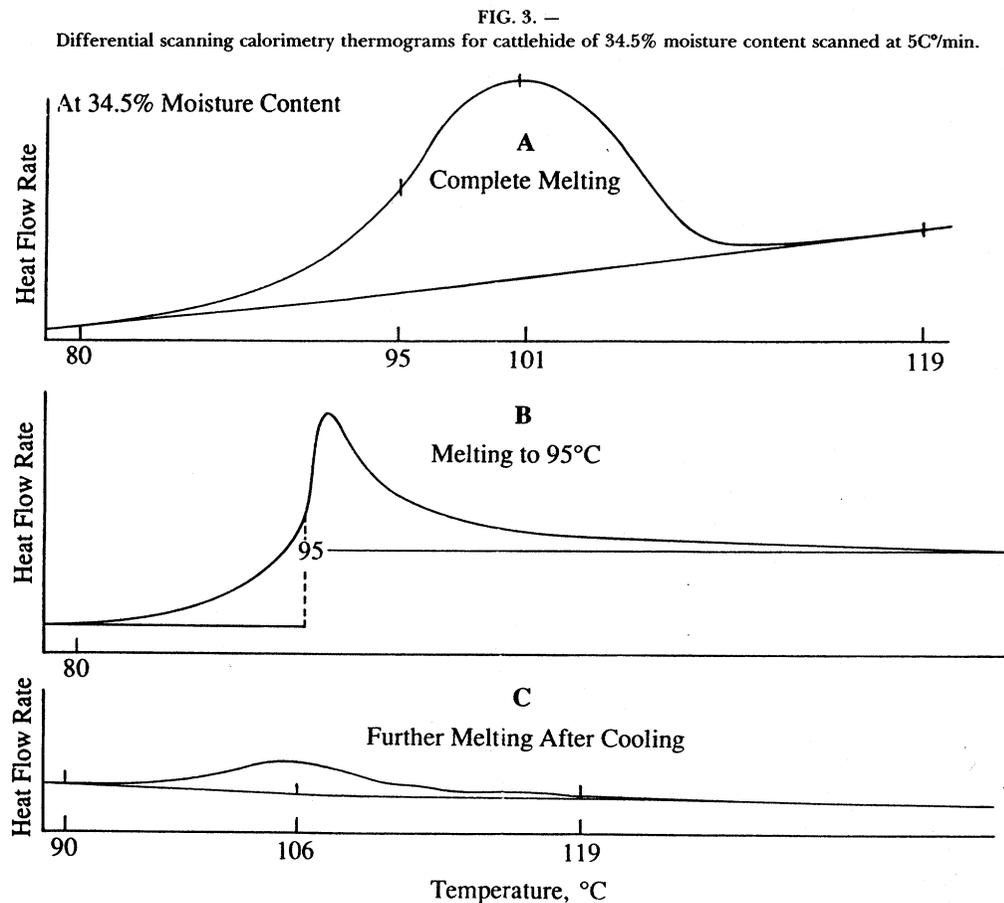
MR. KOMANOWSKY: We have not done additional experiments to show definitely that it is feasible. We have found that proton-NMR results carried out at our laboratory are in complete agreement with our Differential-Scanning Calorimetry data, but actual mechanical tests will have to be conducted to verify this.

DR. HEIDEMANN: It is very important to make this comparison.

MR. CHRIS EHRET (Garden State Tanning): If the same mechanisms are playing their part here, why do shoemakers go for chrome-tanned leather?

MR. KOMANOWSKY: I think that shoe manufacturers like chrome-tanned leather not only because of the high shrinkage temperature, but because you get the same melting temperature over a large moisture range. Thus, they can use high heat at any moisture content, which is why they prefer a high shrinkage temperature, and obtain reasonably consistent results. They can dry quickly by using a high temperature, and as it dries the leather contracts far enough to mold itself to most lasts, removing the remaining wrinkles. With other tannages the leather behaves more like untanned hide where the melting temperature progressively increases, leading to difficulties with control of the heat-setting operation.

upper to the last. It is interesting that this method might be expected to be especially effective in removing wrinkles because unstressed leather comprising these wrinkles shrinks at lower temperatures⁽¹¹⁾. Note that heat setting depends on three factors: moisture content, temperature, and time. Whereas heat setting does involve some heat denaturation, excessive denaturation of the leather should be avoided to prevent unwarranted damage to the leather. To optimize the result, all three variables have to be controlled carefully.



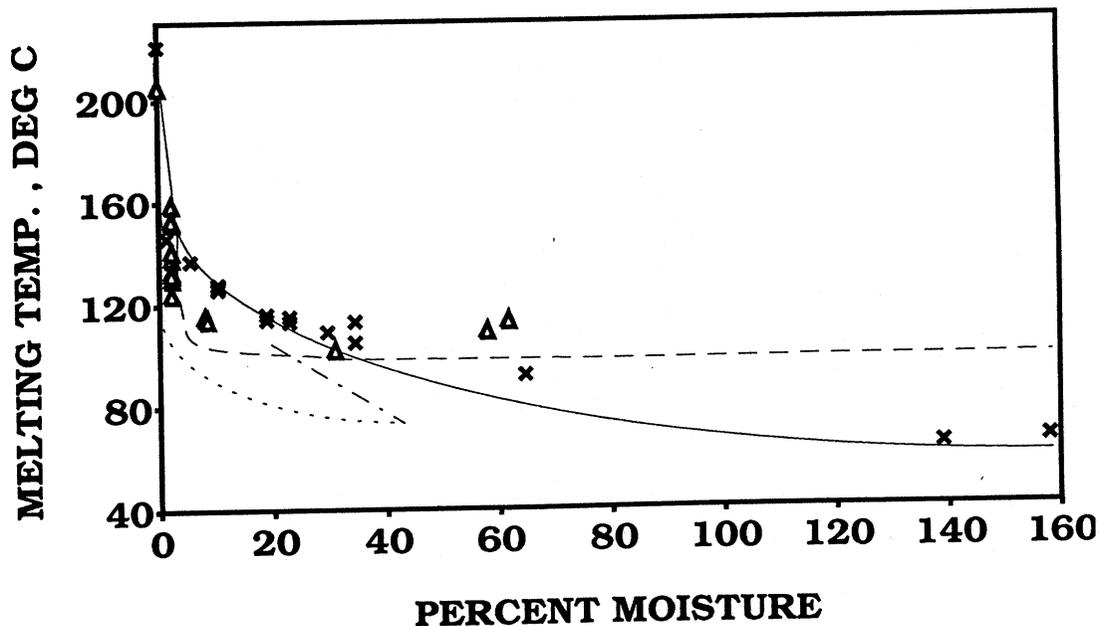
Curve A: Complete melting curve. Curve B: Thermogram obtained (on a sample which was identical to the sample used to obtain curve A) when scanning was interrupted at 95°C and the sample was kept at that temperature for 1/2 hour. Curve C: Complete melting curve for sample used to obtain curve B after the sample was cooled down from 95 to 5°C. Note that in Fig. 3B, the x-axis represents time, not temperature, at temperatures higher than 95°C. To determine time in minutes, multiply the temperature reading by 5 (the scanning rate in C°/min).

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Figure 4 compares the experimental melting temperatures for hide and chrome leather with melting temperatures for formaldehyde-tanned and vegetable-tanned leathers at low moisture contents. The latter data were obtained by Witnauer⁽⁵⁾ using dilatometric techniques. The dotted line gives T_m for formaldehyde-tanned hide and the dashed line for vegetable-tanned leather. Interestingly, in all cases the melting temperature of leather is equal to about 120°C at 10% moisture content with the exception of vegetable-tanned leather which has a T_m equal to about 100°C at that moisture content. From these results it would seem that at low enough moisture contents (about 10%) all types of leather, with the possible exception of vegetable-tanned leather, should be able to resist melting and withstand normal heat-setting conditions. The only prerequisite is that the moisture content be reduced low enough before the higher heat is applied. In other words, the present practice of heat setting should be revised to include a drying step using milder drying conditions before heat setting is attempted. Thus in the proposed method the two types of leather shrinkage would be achieved in two stages under accurately controlled conditions: First the rewetted leather would be made to shrink through the action of capillary forces during moisture removal to the desired accurately measured moisture content, then additional shrinkage would be accomplished by application of dry heat at a predetermined temperature which would depend on the type of leather used. As a matter of fact, using this accurately monitored approach, there is no reason why heat setting of non-chrome leathers, even of vegetable-tanned leather, could not be carried out successfully at a lower temperature such as 85°C if the leather is predried properly.

FIG. 4. — Increase in denaturation temperature with decrease in moisture content of hide and different types of leather:



---Δ--- chrome leather, -X- limed hide, -·-·- formaldehyde-tanned leather. vegetable tanned leather.

While there are several methods of sole attachment, only one of them, the direct vulcanization of rubber on to the shoe bottom, may exceed temperatures of 120 to 130°C. Sole attachment by vulcanization, however, is carried out after the leather has been dried to low moisture contents, often as low as 5%, whereas vulcanization may be effected at temperatures anywhere between 95°C and 150°C, lasting from seconds to hours depending on the accelerating agents employed⁽¹²⁾. Consequently, a careful choice of operating conditions with regard to leather moisture and type of accelerating agent used would allow adaptation even of this most stringent processing step to almost any type of leather. Of course, lowering of the temperature would slow down the vulcanization process somewhat if the same accelerating agent were to be used.

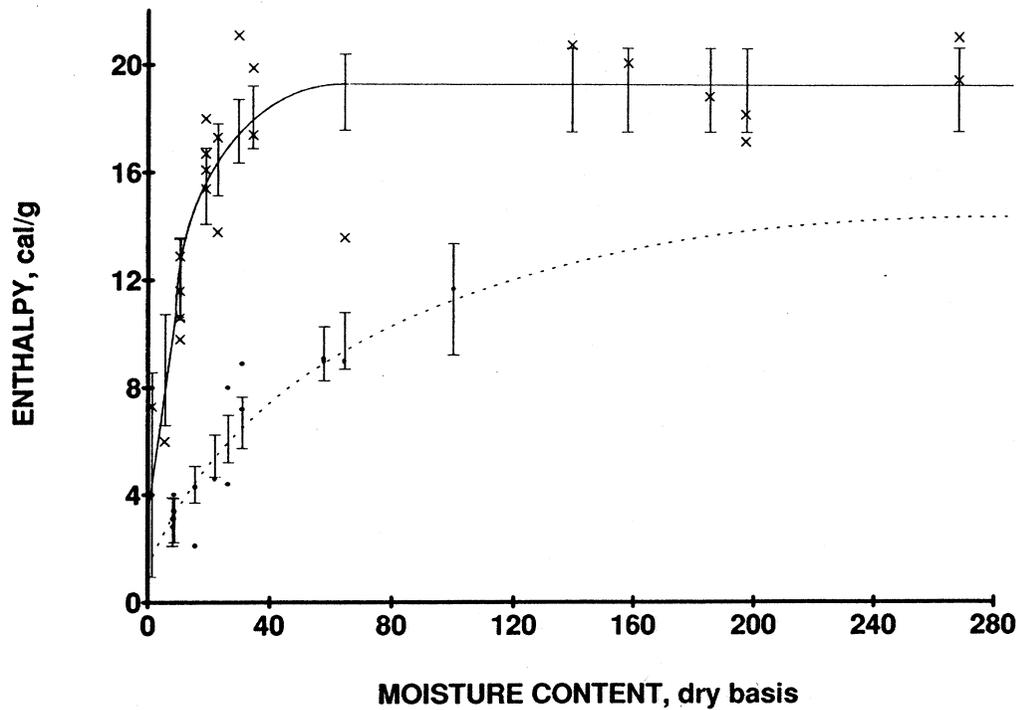
The thermoplastic polymer Polyvinylchloride (PVC) has a glass-transition temperature, T_g , equal to 87°C. As long as this temperature is exceeded, the plastic flows easily and injection molding to leather uppers of soles and heels is feasible. Considering, however, that the PVC is not directly molded to the leather but to a layer of polyurethane adhesive covering the whole shoe bottom, and that the injection time averages 10-20 seconds⁽¹³⁾, it is obvious that the leather does not have to be heated above 87°C in commercial manufacturing practice.

In the 1960's, thermosetting polymers such as polyurethane, PU, gained prominence due to their superior adhesive and wear properties. While PU has its drawbacks (it is expensive, it cannot be reprocessed, and it sticks too much to machine and molds), it does not require high temperature and pressure. As a matter of fact, the molds are only slightly warmed to 50-60°C.

More recently, the triblock copolymer polystyrene-block-polybutadiene-block-polystyrene, SBS, has found application in rubber soles of running shoes and sneakers because heat generated by sliding friction turns SBS into an adhesive which reduces slipping. Note that even this elastomer does not require application of higher heat than heat setting does.

As mentioned in the introduction to this paper, this research is part of an ongoing study conducted to obtain a better understanding of different tannages, especially the reason for the superior thermal stability of chrome leather. While this study is still rather far from being completed, many interesting results have been obtained to date. One such result is given in Fig. 5 which shows a plot of the heat of denaturation, ΔH , of hide and chrome leather as a function of moisture content. From this plot it is seen that ΔH for limed hide increases steeply from 0 to about 30% moisture content and then remains practically constant with further increase in moisture. With chrome leather, the steep increase in ΔH persists to about 70% moisture content. As can be seen, however, the ΔH is much lower for leather than for hide at all moisture contents, even at moisture contents as low as 3-5%. At this low moisture content all of the water is considered to be structural water involved in forming bridges between the three chains of the triple helix comprising the collagen molecule. This result suggests that chrome acts not only to form crosslinks between amino-acid side-chains but that it is, in addition, unique in being able to affect the strength of the intrahelical water bonds and possibly form some bonds between hydroxyl groups of hydroxyproline and chrome complexes and thereby contribute to the enthalpy and entropy of collagen melting. Preliminary studies using nuclear magnetic resonance support such an explanation.

FIG. 5. —
Change in enthalpy of melting, ΔH , of hide and chrome leather as a function of moisture content (X):



- x Hide (data points)
- |— Line fitted to hide data: $\Delta H = 15.96 \cdot (1 - e^{-0.7829 \cdot X}) + 3.159$
with confidence boundaries at 95% confidence level
- o Leather (data points)
- - -| - - - Line fitted to leather data: $\Delta H = 11.58 \cdot (1 - e^{-0.02071 \cdot X}) + 1.215$
with confidence boundaries at 95% confidence level

Conclusion

While the mechanism which imparts superior thermal stability to chrome-tanned leather still eludes full clarification, a better understanding of the thermal properties of other tannages can be utilized successfully to minimize the obstacles encountered during conveyorized shoe manufacture due to the lower shrinkage temperatures of these tannages. Based on the experimental results obtained in this research study and based on the descriptions of current shoe-manufacturing technology found in the literature, it appears that only minor changes in processing techniques may be needed to adapt present commercial processes to the utilization of non-chrome leather in the manufacture of shoes and other leather products.

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Discussion

DR. ESA MANTYSALO (Tampere University of Technology, Finland): It is not completely clear to me what kind of reference calorimeter you have used.

MR. KOMANOWSKY: Are you asking how I standardized the calorimeter? We standardized it with benzoic acid and indium using a Perkin-Elmer Model DSC-2 differential scanning calorimeter.

MR. STEVEN WREN (Struktol Company): When you talked about using chrome leather, was this just plain wet blue?

MR. KOMANOWSKY: Yes.

MR. WREN: Did you approach moisture equilibrium by sorption or desorption?

MR. KOMANOWSKY: We did it both ways. I lyophilized a sample, and then equilibrated it in dessicators in different relative humidities; I then determined the moisture content. Other samples of wet blue were exposed under similar conditions, to equilibration, and then the moisture contents were determined in this other direction. Samples produced in both ways yielded data which fell on the same line.

MR. WREN: The problem is, of course, that shoe factories use commercially-made fashionable leathers containing more than one tanning agent. Chrome may be the basic tanning agent, but there may also be aldehydes or vegetable extracts. Did you do any work on combinations of these using commercially available leathers, to test heat stability in shoe making?

MR. KOMANOWSKY: No, I have not gone that far. Of course, if it is chrome tanned, it would have a shrinkage temperature in excess of one hundred degrees centigrade; the addition of other tanning materials would not change it that much.

MR. WREN: There was some work done in South Africa on the combination of vegetable extracts and alum. There is a subsequent reaction which raises the shrinkage temperature to over a hundred degrees, and that might be a more practical application.

MR. KOMANOWSKY: As I mentioned in the introduction, there is a question as to whether there are enough tannins in the world to satisfy all the demands.

DR. ECKHART HEIDEMANN (Technische Hochschule, Darmstadt): You have told us that you can do heat setting also at eighty-five degrees centigrade with vegetable-tanned leather, but I would like to ask you what was the extent of the setting effect, if you compare chrome leather at one hundred and thirty degrees centigrade against vegetable-tanned leather at eighty-five degrees centigrade? With setting, you apply a certain tension, and after unloading, the leather does not spring so far back. In every case there is some return toward the original dimension. The question is, how far does it spring back after unloading?

MR. KOMANOWSKY: We have not done additional experiments to show definitely that it is feasible. We have found that proton-NMR results carried out at our laboratory are in complete agreement with our Differential-Scanning Calorimetry data, but actual mechanical tests will have to be conducted to verify this.

DR. HEIDEMANN: It is very important to make this comparison.

MR. CHRIS EHRET (Garden State Tanning): If the same mechanisms are playing their part here, why do shoemakers go for chrome-tanned leather?

MR. KOMANOWSKY: I think that shoe manufacturers like chrome-tanned leather not only because of the high shrinkage temperature, but because you get the same melting temperature over a large moisture range. Thus, they can use high heat at any moisture content, which is why they prefer a high shrinkage temperature, and obtain reasonably consistent results. They can dry quickly by using a high temperature, and as it dries the leather contracts far enough to mold itself to most lasts, removing the remaining wrinkles. With other tannages the leather behaves more like untanned hide where the melting temperature progressively increases, leading to difficulties with control of the heat-setting operation.