

# ABSOLUTE MEASUREMENT OF SHRINKAGE TEMPERATURE OF LEATHER BY DIFFERENTIAL THERMAL ANALYSIS\*

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## ABSTRACT

Differential thermal analysis (DTA) was employed for studying the thermal behavior of leather in the presence of excess water. All leather-water systems studied showed a pronounced minimum, an endotherm, on their DTA thermograms. Visual observations on the specimen during heating in the DTA apparatus revealed shrinkage taking place in the temperature range of the minimum. This was confirmed by conventional shrinkage temperature measurements. Thus, DTA measurements provide a fundamental and absolute method for determining the hydrothermal stability of leather materials.

## INTRODUCTION

Previously it was reported (1) that the extensive macroscopic shrinkage of leather in water was an outward manifestation of the helical-to-coil transition (melting) of collagen. Such a change is accompanied by the absorption of heat; that is, it is an endothermic process. Therefore, any method that is capable of detecting an absorption of heat should be suitable for shrink temperature measurements on leather-water systems. One technique that can be employed for studying the thermal behavior of materials as they undergo physical and chemical changes during heating is differential thermal analysis, commonly abbreviated DTA. The technique is a very old one having been used by Le Chatelier (2) in 1887; however, it has been only within the last few years that commercial instrumentation has become available for carrying out such investigations.

The method involves the continuous comparison of the temperatures in two materials, a sample and a reference, as both are heated at a uniform rate. The reference is so selected that it does not undergo a physical or chemical change

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in the temperature range investigated. The temperature differential between the sample and reference materials as they are being heated or cooled at constant rate is measured by means of thermocouples wired in opposition as shown in Fig. 1. If the size and heat capacity of the sample and reference are approximately the same there will be no temperature differential unless a physical or chemical change occurs in the sample. A typical physical change, melting, is shown in the thermogram (Fig. 2) for benzoic acid, a pure crystalline compound.

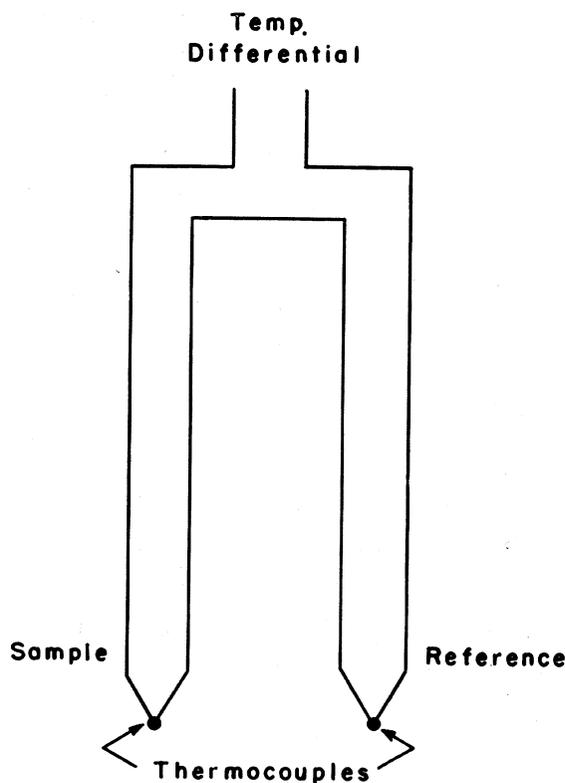


FIGURE 1.—Thermocouple arrangement.

A thermogram is a plot showing the differential temperature between a sample, benzoic acid, and an inert reference, glass beads, as a function of sample temperature as both are heated at the same rate. The thermogram of benzoic acid shows a large deviation for the base line in the temperature range  $118^{\circ}$ – $122^{\circ}\text{C}$  indicating a large absorption of heat by the sample in this region. The temperature at which the deviation is greatest, called the peak temperature, corresponds to the true melting point of benzoic acid as determined by the capillary tube method. The direction of the deviation from the base line indicates whether the

heat effect is exothermic or endothermic. In DTA the resulting curve is called a peak regardless of sign. The shape of the peak on a thermogram depends upon the type of transformation taking place and the molecular structure of the sample. Changes such as the melting of a pure crystalline compound give rise to a very sharp peak while partially ordered or semicrystalline materials give rise to broader peaks.

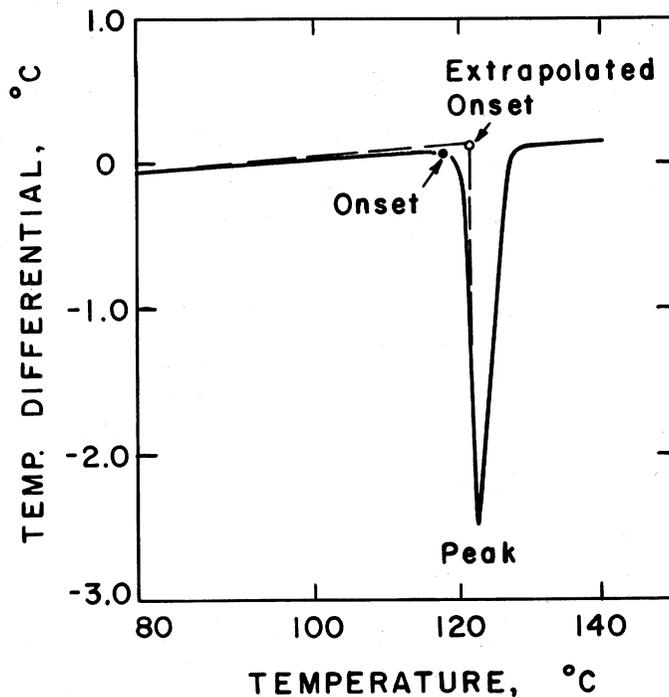


FIGURE 2.—DTA thermogram of benzoic acid.

In reporting temperature information concerning the peak on a thermogram the following temperatures are often of value:

(a) *Onset temperature*: The sample temperature at which the slope of the thermogram first departs from the base line on heating. This corresponds to the first indication that a change in the sample is starting to take place. Unfortunately, the exact position of the onset is often difficult to determine accurately.

(b) *Peak temperature*: The sample temperature at which the temperature differential between sample and reference is greatest. The transformation taking place in the sample is almost complete at this temperature. As previously stated, for compounds undergoing fusion, the temperature at this point is reported as the compound's melting point.

(c) *Extrapolated onset temperature*: The temperature obtained by extrapolation of the base line and the straight line portion on the low-temperature side of the peak. This point represents the starting temperature for the major portion of the transformation.

Inspection of Fig. 2 shows that for fusion of a pure crystalline compound the peak and extrapolated onset temperatures are within 1°C of one another. The onset temperature is somewhat less. The over-all transition takes place over a relatively narrow temperature range of about 4°C. Melting-point determinations by the capillary tube method would show a much smaller range because of the lack of sensitivity in observing the onset of melting.

With this background in mind, we decided to investigate the suitability of differential thermal analysis for measuring the transition that takes place on heating leather specimens. This communication describes DTA measurements conducted at atmospheric pressure on leather specimens immersed in water.

### EXPERIMENTAL

**Instrumentation.**—The instrument used in this investigation was the Du Pont 900 Differential Thermal Analyzer.† The block diagram in Fig. 3 illustrates the flow of thermocouple signals and the general plan of the apparatus (3). The cell assembly consists of an aluminum block with sample and reference holes placed symmetrically about a heater hole and a hole to accommodate the temperature-programming thermocouple close to the heater. One such cell assembly permits visual observations to be made on the sample as it is being heated. The temperature-programmer provides the means to set the rate of heating of the cell. The temperature differential signal from the sample and reference travels through a preamplifier and is subsequently fed to one axis of an x-y recorder. The sample temperature signal is sent through a preamplifier and is fed to other axis of a recorder.

For the reported measurements a visual cell was used; rates of heating employed were from 2.5°C/min. to 15°C/min.; the differential scale was set at a sensitivity of 0.1°C/in. and the temperature scale was set at 10°C/in.

**Sample preparation.**—The selection of the hide and leather samples was such as to afford a check on DTA performance for a wide variety of samples which had undergone many types of treatment and tanning procedure.

Two methods of wetting the samples were employed. In some cases a mechanical working of the leather samples in water was used. The leather samples were then allowed to wet for fifteen minutes and for one hour, respectively, before being subjected to DTA. Another more practical and less time-consuming method involves saturation under vacuum. A beaker of distilled water, contain-

†Mention of commercial products and firms does not constitute an endorsement by the U. S. Department of Agriculture over others of a similar nature not named.

ing the sample, was placed in a vacuum desiccator, and a vacuum was pulled and then released.

The DTA samples and reference holders are glass tubes 25 mm in length and 4 mm in diameter. A typical leather sample was 5 mm x 10 mm weighing approximately 30 mg and immersed in about 60 mg of water. Although 30 mg was the usual leather sample size, a sample weighing as little as 6 mg was also used. When the leather-water sample was placed in a glass tube, it was folded in half so that the flesh surfaces were touching. The thermocouple was placed in the center of the fold.

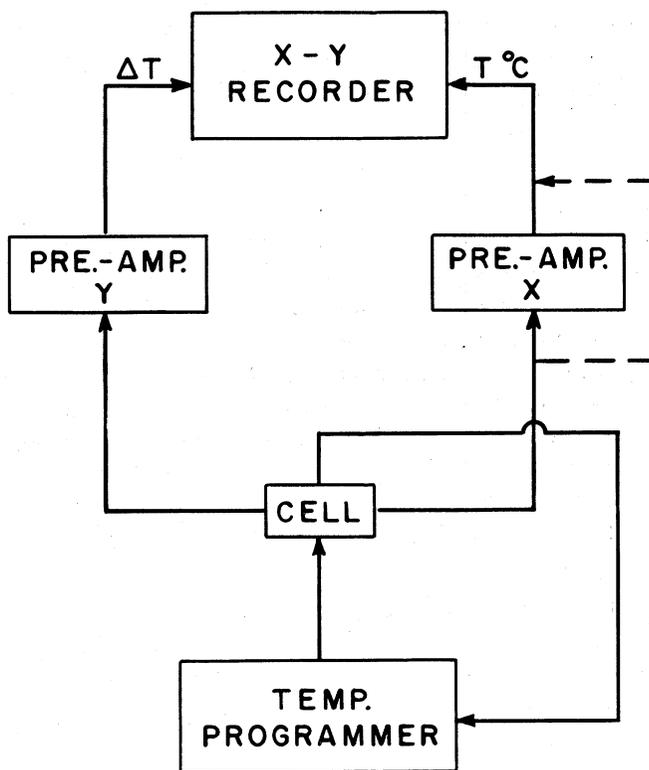


FIGURE 3.—Block diagram of differential thermal analysis components. Reproduction of Fig. 1 of reference 3.

The actual run was made in an air atmosphere, using a  $5^{\circ}\text{C}/\text{min}$ . heating rate, for reasons which will be discussed later. The length of time of a run varies depending on the leather sample, from about five minutes to about fifteen minutes. The temperature range investigated was from about  $30^{\circ}\text{C}$  to about  $100^{\circ}\text{C}$ .

**Conventional shrinkage measurements.**—For comparison purposes, an instrument developed in this laboratory (4) was used to determine the conventional shrink temperatures of the leathers in water by following the change in length on heating while immersed in water. The sample size for this determination is two inches long,  $\frac{1}{4}$  inch wide, and natural thickness. The strips were wet with water using the vacuum technique previously described immediately prior to the test. The heating rate employed was approximately  $1^{\circ}\text{C}/\text{min}$ . up to  $80^{\circ}\text{C}$  and slightly less for temperatures above  $80^{\circ}$ . All specimens were loaded with a 10-gram weight throughout the test to keep the specimen straight. The authors are well aware that any load retards contraction of the leather specimen and gives rise to somewhat erroneous shrink temperature results. However, for the majority of the leather specimens studied this effect was thought to be relatively minor. The shrink temperatures reported were obtained from length vs. temperature curves by extending the base line until it intersected with the extrapolated line obtained from the region of the curve in which the length of the specimen was decreasing most rapidly with temperature.

### RESULTS

**Typical leather-water thermogram.**—Shown in Fig. 4 is the thermogram of a vegetable-tanned calfskin immersed in water. The temperature range studied was from  $35^{\circ}\text{C}$  to  $100^{\circ}\text{C}$  using a heating rate of  $5^{\circ}\text{C}/\text{min}$ . The thermogram shows a pronounced minimum with a peak at about  $76^{\circ}\text{C}$  indicating a relatively large absorption of heat by the leather-water system. Visual observations made on the leather specimen during the heating in the DTA apparatus revealed that shrinkage was taking place in the temperature range of the minimum.

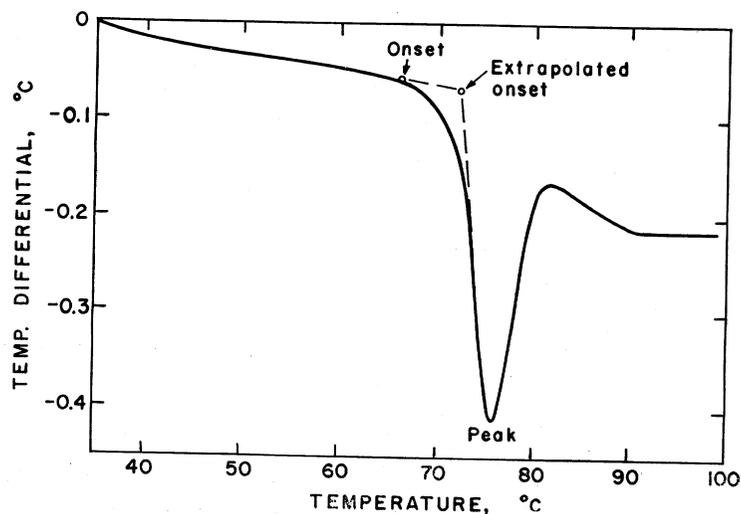


FIGURE 4.—DTA thermogram for a vegetable-tanned unfinished calfskin immersed in water.

It should be noted that the observed transition for the specimen investigated takes place over a ten-degree temperature range. The transition starts relatively slowly as indicated by the small amount of deviation from the base line for the first few degrees beyond the onset temperature and then proceeds to increase at a much more rapid rate until the peak temperature is reached. The over-all temperature of the transition is somewhat broader than that observed for a pure crystalline material, approximately twice that of benzoic acid. The thermograms of many semicrystalline polymeric substances which exhibit a first-order transition (melting) show similar endothermic peaks. For example, the melting of the crystalline regions in polyethylene gives rise to a comparable peak (5).

**Reproducibility of peak temperature.**—Shown in Table I are the results obtained with a vegetable-tanned, chrome-retanned finished upholstery leather. The reproducibility of the peak temperature for different samples of the same leather is excellent,  $\pm 0.5^\circ\text{C}$  when the same heating rate ( $5^\circ/\text{minute}$ ) and wetting out procedure were employed. Samples were cut adjacent to one another. Similar agreement was obtained for all the leather-water samples studied.

TABLE I  
EFFECT OF HEATING RATE AND WETTING-OUT  
PROCEDURES ON DTA PEAK TEMPERATURES

Heating Rate, $^\circ\text{C}/\text{min.}$	DTA Peak Temperatures, $^\circ\text{C}$ Wetting-Out Procedure		
	A <sup>1</sup>	B <sup>2</sup>	B <sup>3</sup>
2.5	90.7		
5.0	92.0	92.0	93.1
	92.9		
	92.0		
10.0	92.5	92.9	92.2
15.0	93.8		

1. Immersed in water; subjected to vacuum.

2. Immersed in water; mechanical working; conditioned in water for 15 minutes.

3. Immersed in water; mechanical working; conditioned in water for one hour.

**Heating rate.**—To determine the optimum rate, various heating rates were employed from  $2.5^\circ\text{C}/\text{min.}$  to  $15.0^\circ\text{C}/\text{min.}$  Generally, a slow heating rate (approximately  $2.5^\circ\text{C}/\text{min.}$ ) tended to shift the peak to a slightly lower temperature (Table I). The peak temperature of 90.7 reported for a vegetable tan-chrome retan finished hide at a  $2.5^\circ\text{C}/\text{min.}$  rate differs by  $1.3^\circ\text{C}$  from the  $92.0^\circ\text{C}$  value reported on a  $5.0^\circ\text{C}/\text{min.}$  rate. However, on some of the leather-water samples the difference in peak temperature occurring at the two rates was as much as

3.0°C. When 5.0°C/min. was employed as the heating rate, the peak was sharpened and lengthened. Little difference in peak temperature was observed between a 5.0°C/min. and 10.0°C/min. heating rate as far as reproducibility and peak sharpness were concerned. However, the length of the peak is considerably increased for a 10°C/min. rate of heating. Occasionally a fast rate of heating, for example 10.0°C/min., will obscure small details which otherwise would be presented in the thermogram. Heating rates above 10°C/min. shift the peak temperature to slightly higher values than those quoted for the 5° and 10°C/min. rates. The value of 93.8°C for a 15°C/min. rate given in Table I is characteristic. Therefore, 5.0°C/min. was chosen as the optimum heating rate.

**Wetting-out procedure and thermocouple contact.**—Observations on the two methods of wetting-out the samples are also given in Table I. In comparing the results shown for the peak temperatures of a vegetable tan—chrome retan finished leather, it can be concluded that the results obtained by the two techniques showed no significant difference. The length of soaking time after vacuum wetting had no effect. On some samples, especially vegetable-tanned specimens, however, long soak periods — 12 to 18 hours — resulted in erroneous results (peak temperatures were lowered). Vegetable tannin was undoubtedly extracted from the leather specimen during the prolonged soaking in water.

Comparison of runs with the thermocouple in direct contact with the flesh side of the leather sample containing excess water against those runs with the thermocouple in contact with the grain surface showed no appreciable difference. Flesh-side contact was adopted as standard for all runs reported. Hence, the standard experimental conditions adopted for this study were: vacuum wetting of the sample followed by immediate DTA at a 5°C/min. heating rate, the thermocouple contact being at the flesh side of the sample.

**DTA data for various leather-water systems.**—The thermograms obtained from ten different types of hide materials in the presence of excess water were similar except for the width and depth of the minima and temperatures at which they were observed. Their DTA data are summarized in Table II. Peak temperatures ranged from about 60° for untanned calfskin to about 96° for certain chrome-tanned leathers. Each has its own characteristic features. The DTA cell as presently constructed is suitable for carrying out measurements at atmospheric pressure only; therefore, peak temperatures greater than about 97°C cannot be reached. The boiling point of water gives rise to a large endothermic peak which starts at approximately this temperature. The kip specimen reported in Table II has a peak >97°C. We plan to investigate specimens with high peaks at some later date with a pressurized cell.

The temperature from the onset to the peak, which ranged from about 8° to more than 20° appeared to depend upon the type of leather. The extent of this transition range as previously discussed was not unexpected. At the present

time no attempt was made to correlate this range with type of tanning agent, source of skin, or any other variable.

TABLE II  
THERMAL BEHAVIOR OF LEATHER IMMERSSED IN WATER

Sample Description	DTA Data, °C			Conventional Shrinkage Temperature, °C
	Onset	Extrapolated Onset	Peak	
Calf-limed-bated-washed-acetone-dehydrated	51	56.5	62.5	57.5
Calf-veg. tan.-unfinished	66	72.0	76.4	73.0
Sheep-glutaraldehyde tan.	68	70.0	76.6	74.5
Cabretta-glutaraldehyde tan.	70	76.5	81.2	76.5
Hide-grain split-chrome-glutaraldehyde tan.	74	79.0	86.9	85.0
Hide-veg. tan.-chrome retan.-unfinished	79	85.0	90.0	88.5
Cabretta-chrome tan.-glutaraldehyde retan.	82	86.5	92.4	91.0
Hide-veg. tan.-chrome retan.-finished	77	86.5	92.5	87.5
Calf-chrome tan.-finished	81	90.0	95.3	92.5
Kip-chrome tan.-veg. retan.-unfinished	90	?	>97	>100

**Comparison of DTA data with conventional shrink data.**—If the minimum in the DTA thermogram is reflecting the shrinkage of leather, then a comparison of the shrinkage temperature as determined from the conventional change in length versus temperature measurements made on strips immersed in water should show a relatively good correspondence with the DTA data. Listed in the last column of Table II are the conventional shrinkage temperatures of the various leathers investigated. The shrinkage temperatures reported are between the extrapolated onset and peak DTA temperatures. The agreement is quite good considering the somewhat arbitrary manner in which conventional shrinkage temperature values are obtained and the fact that previous mechanical history (mechanical strains) can affect such measurements. There can be little doubt that the minimum in the DTA thermogram is a manifestation of the shrinkage of leather.

**Variation in thermal behavior (shrinkage in water) with location on a hide.**—Shown in Table III are the DTA data for chrome-tanned leather specimens which were selected from seventeen different areas (Fig. 5) from one

MEASUREMENT OF SHRINKAGE TEMPERATURE

TABLE III  
 VARIATION IN THERMAL BEHAVIOR (SHRINKAGE IN WATER)  
 WITH LOCATION ON A HIDE

Sample No.	DTA Data, °C		
	Onset	Extrapolated Onset	Peak
1	88	90.0	93.9
2	88	91.5	94.8
3	85	88.5	95.0
4	85	86.5	94.1
5	85	86.5	91.0
6	79	85.0	92.0
7	83	90.0	93.9
8	81	87.0	92.5
9	84	88.5	92.9
10	81	85.0	89.6
11	83	86.0	92.7
12	79	85.0	89.1
13	86	87.0	91.7
14	82	85.5	89.6
15	82	84.5	91.0
16	82	85.5	89.1
17	83	85.0	92.9

side of a hide. Examination of the peak temperature data shows that the leather specimens undergo shrinkage in a relatively narrow temperature range; all values were within  $\pm 3^\circ\text{C}$  of one another. Thus, at least for the hide investigated, these results indicated that tanning can produce a relatively uniform effect over the whole area of a hide.

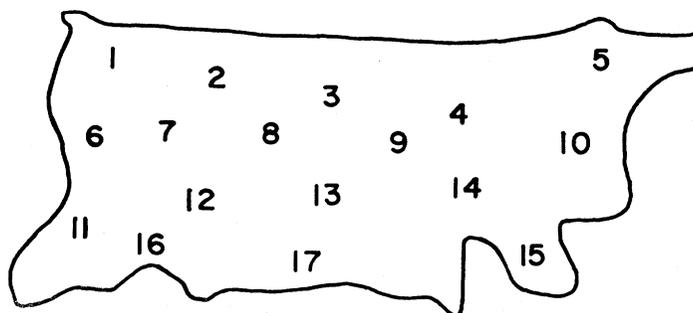


FIGURE 5.—Sample location on a side of chrome-tanned leather.

**Variation in thermal behavior with position relative to grain.**—Shown in Table IV are the DTA data for a vegetable tanned calfskin specimen that was split with a microtome into seventeen approximately equal layers. The original piece was 25 by 25 mm square. Each split weighed about 8 mg. The layers have DTA peak temperatures that show a spread of only 3°C for the extreme values. These results demonstrate the remarkable uniformity of tanning for this type of leather.

TABLE IV  
VARIATION IN THERMAL BEHAVIOR (SHRINKAGE IN WATER)  
WITH POSITION RELATIVE TO GRAIN

Split	DTA Data, °C		
	Onset	Extrapolated Onset	Peak
1 (grain side)	71	71.5	76.1
2	66	72.5	76.1
3	69	71.5	76.1
4	70	74.0	77.6
5	68	74.0	77.6
6	69	74.0	77.1
7	69	74.0	77.1
8	74	76.0	78.5
9	71	76.5	78.5
10	69	75.0	77.6
11	72	76.5	78.5
12	71	77.0	79.2
13	73	76.5	78.1
14	71	76.0	78.5
15	71	76.0	78.5
16	70	75.0	77.6
17 (flesh side)	71	74.0	77.6
Whole sample	66	72.0	76.4

#### ACKNOWLEDGMENT

The authors wish to thank E. I. du Pont de Nemours and Company, Wilmington, Delaware, for permission to reproduce Figure 1 of reference 3.

DISCUSSION

CHAIRMAN STUBBINGS: This paper will be discussed by Dr. Kanagy.

DR. JOSEPH R. KANAGY: DTA or thermal analysis is an example of one of the more recent and progressive types of analytical tools which are being introduced into industry by scientific research. It is also a more fundamental approach to a problem which is also characteristic of present-day scientific research.

I suppose that this could be called a sophisticated analytical tool.

But what we should remember is that the results from a sophisticated analytical tool would be difficult to interpret if it weren't for unsophisticated methods of analysis which form a foundation.

For instance, this work may be considered as a third stage of research on the shrinkage temperature.

First, the shrinkage was studied by measuring the change in length of a specimen or what you might call the temperature of curling.

Secondly, the forces exerted during shrinkage were measured. These, I suppose, are unsophisticated methods of analysis.

Now, in this work the energy involved is being measured. The measurement of the energy involved in any measurement is always considered the most fundamental and absolute measurement.

In view of this work, do you think that we should have a new definition for the shrinkage temperature of leather?

MISS WISNEWSKI: I think we have demonstrated with this work that melting in leather takes place over a broad temperature range. No one temperature therefore could be used exactly to define shrinkage temperature.

We feel that the leather's performance should be correlated with the shrinkage temperature range to determine which temperature, onset or peak, is the important one. In other words, a study is needed to arrive at a practical shrinkage temperature value.

DR. KANAGY: I notice that you and Dr. Witnauer have always expressed the idea of a melting point of leather. Do you think that this way of measuring it (the energy measurement) is a further indication that you have a melting point, that is, a real transition point rather than what has been known as a shrinkage temperature?

MISS WISNEWSKI: I think we probably have. We have shown that the first-order transition which takes place on heating every leather in excess water is very

similar to melting in benzoic acid and also to melting in polymer substances. The DTA measurement is a further proof of melting which occurs in leather when heated in the presence of excess water.

DR. KANAGY: Are there any questions from the floor?

DR. LUDWIG SELIGSBERGER (United States Army Natick Labs): We all have observed the dilation of specimens in the temperature just a few degrees before shrinking. Could it be possible that the onset temperature has anything to do with dilation or that the dilation could somehow be investigated by more sophisticated techniques? I see that Professor Gerngross who lately worked on studies in dilation will give a new paper in Vienna.

MISS WISNEWSKI: We haven't measured any dilation phenomena before the onset temperature.

It is possible for the specimen to absorb water as part of the shrinkage phenomenon, preceding the onset temperature, so that maybe a further investigation would be in order.

DR. R. BORASKY (University of Illinois): I would like to make a comment on the shrinkage of collagen. We noted many years ago at the Eastern Regional Research Lab when we measured the shrinkage temperature of collagen fibrils that shrinkage started at the end of the fibril and it was a swelling phenomenon. Then the swelling progressed right through the entire length of the fibril. Then it broke up.

Actually I think the phenomenon that you see in the shrinkage temperature measurement is just the same type that you see in the electron microscope. It is a gradual thing.

MISS WISNEWSKI: That is very true. We are trying to correlate our data with some electron microscope work being done at USDA. We will know more about that later. We have nothing to report at this time.

DR. KANAGY: I believe a measurement of the heat of shrinkage was made quantitatively many years ago. Since that time I think a number of us who have been working in this field have thought about measuring the heat of transition quantitatively in some way but have been too lazy to set up a calorimeter that would be accurate enough to do it. Now with the DTA analysis you can readily obtain a calibration with a material like benzoic acid, so that you can get a fairly good quantitative measurement of any material undergoing a transition.

Do you intend to do something like this with collagen?

MISS WISNEWSKI: We haven't made any quantitative measurements to date. However, with a tool such as DTA the work will be relatively straightforward and simple. We hope in the near future to make quantitative measurements of the heat effects observed in collagen transitions.

MR. JAMES M. CONSTANTIN (Merck and Company): I have two questions. The first is a very practical one. You talked of sample sizes of 30 milligrams. Do you want to tell us briefly how you do that sampling? That is pretty small as a piece of leather goes.

Secondly, the thing that I am interested in is, when you talk of hydrothermal stability, have you measured the effect of pH on your DTA data? This would be an important consideration too.

MISS WISNEWSKI: A small sample is cut with scissors from some section over the area of a hide. As I showed you on one of the slides, I sampled from various sections over the whole surface of a hide and didn't pick up any difference; therefore small samples apparently do not show deviation on the thermograms.

But the pH measurements are something else again because it depends on what you are using to control the pH.

Salts would affect the thermocouple, and also the transition points, so you would have to be cautious to measure the shrinkage temperature at known or controlled values of pH.

MR. CONSTANTIN: I am thinking that the pH of the stock you are sampling for DTA measurements will range across maybe two, three, or four pH units, and you will get a very different hydrothermal behavior if the pH changes across that wide a range. Perhaps this is not true in DTA measurements, but when you are measuring dissolution of hide substances you get an entirely different curve at pH3, at pH4, and at pH5.

MISS WISNEWSKI: You mean a differently shaped curve?

MR. CONSTANTIN: You get different rates of dissolution.

MISS WISNEWSKI: We started about one month ago following a hide as it was being processed through the tannery, our own tannery at USDA. We found no change as far as the shape of the thermograms is concerned. There were some changes in the transition temperatures at different pH, but I don't have the data with me.

MR. JOSEPH BASSETT (A. C. Lawrence Leather Company) : Could you give us a little information as to the type of thermocouple you used, the size, and whether it is commercially available, and also whether you have to use a cold junction reference?

MISS WISNEWSKI: Yes. The instrument itself is set up with cold junction reference thermocouple in the rear of an instrument. The thermocouples are constructed by DuPont. They are chromel alumel analytical thermocouples available with the instrument.

DR. KANAGY: Are there any other questions? If not, I want to thank Miss Wisniewski for giving a very fine presentation.

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