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Effect of Temperature on the Volume of Leather and Collagen in Water

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The coefficients of cubical expansion of 10 tannages of leather and tendon collagen have been measured by using water as the confining liquid. The results, calculated for dry leather of density 1.560 g/ml, show that an average coefficient of 540×10^{-6}/°C applies for collagen and all leathers except chrome-vegetable leather, the coefficient of this tannage being 340×10^{-6}/°C. These averages have a reproducibility indicated by standard deviations of 13×10^{-6}/°C and 37×10^{-6}/°C, respectively. The "shrinkage" or transition temperature is a band rather than a sharp point on the temperature scale. During apparent shrinkage, an increase in real volume of approximately 1 percent occurs. This increase in volume is irreversible, but the thermal expansion below the transition range is nearly completely reversible. The rate of expansion during transition of collagen follows the law of a first-order reaction. The results are interpreted as indicating that the shrinkage does not occur at a characteristic temperature but is a rate process. The transition may be pictured as a change of state possibly coupled with a reaction.

I. Introduction

Although the art of leather manufacture predates historical records, the physical and physicochemical constants, as well as the details of the chemistry of leather and its parent substance, collagen, are largely unknown. Published data for the ordinary physical constants of leather and collagen are practically nonexistent. This lack of data may be attributed directly to the extreme chemical and physical complexity of the system of tanned collagen fibers known as leather. Although it is accepted that leather is possibly not a pure substance and is subject to variations due to differences in the hide itself and introduced by nonuniformity of the tanning processes, it is a matter of practical and theoretical interest to determine either the physical constants or their order of magnitude.

The present experiments were designed primarily to measure the coefficient of cubical expansion of leather with full cognizance that information of a new nature would be obtained in the region of the shrinkage temperature. Using glass dilatometers with water as the confining liquid, it was found that the average coefficient of cubical expansion calculated for dry material is 540×10^{-6}/°C for collagen and all tannages with the exception of chrome-vegetable retan leather, which exhibited a smaller coefficient. This expansion is reversible below the shrinkage or transition temperature. If the leather-water system is heated in the neighborhood of the transition temperature, an irreversible expansion analogous in some respects to a fusion takes place. During this expansion in real volume, the apparent dimensions of the leather decrease, and the temperature at which this process occurs has heretofore been called the shrinkage temperature. The expansion in real volume occurs over a range of temperatures rather than at a sharp point on the temperature scale, and it appears that shrinkage is probably a rate process. The rate of expansion of collagen was found to follow the law of a first-order reaction. At temperatures exceeding the shrinkage temperature, the material formed during transition exhibits reversible expansion, the coefficient of which is essentially of the same order of magnitude as that of the original leather.

II. Apparatus

The dilatometer used is shown in figure 1. Two such dilatometers of the same dimensions were constructed with Pyrex ground glass joints to facilitate cleaning and inserting samples. The stopcock attached to the side arm was used for filling and to permit removal of liquid during the course of the measurement, so that the complete temperature range 25° to 75° C could be covered without using excessively long capillaries. The calibrated capillaries were capped with small ground tips containing a minute hole to permit expansion of the liquid but to retard evaporation of water from the capillary.

The two dilatometers were mounted side by side on a framework, to which was affixed a sheet of graph paper ruled in millimeters. The framework containing the dilatometers was placed opposite a triple-pane insulating window in a temperature-controlled airbath that maintained a temperature in the range 25° to 75° C to within ±0.001 deg C, as shown by preliminary tests with a Beckman thermometer. Experimental temperatures were measured with the desired accuracy by means of a thermometer graduated to 0.2 deg C, which was hung between the dilatometers so that it could be read through the window.

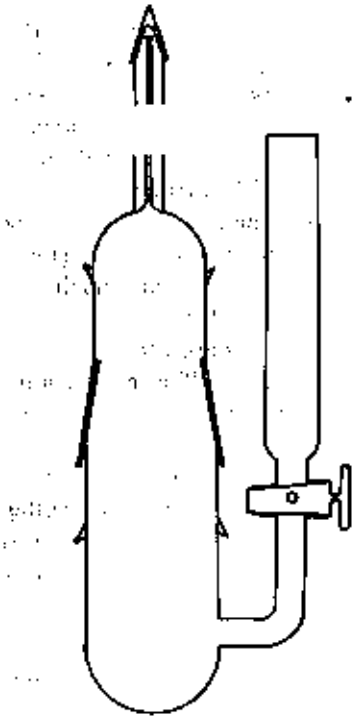

FIGURE 1. *Dilatometer.*

III. Experimental Procedure

1. Preparation of Specimens

Leather used in these experiments was in the form of strips 1 by 3 in. The strips were degreased with chloroform in a Soxhlet extractor for 24 hr washed in running water for 48 hr and then conditioned at 70°±1° F and 50±2 percent relative humidity for at least 7 days. Prior to use, the strips were weighed and immersed in distilled water in a suitable vacuum flask. The system was connected to a water pump and evacuated at approximately 30 mm of Hg for at least 48 hr. Sufficient leather was prepared to permit a moisture determination on conditioned strips not used for test.

2. Method of Measurement

The two clean, dry dilatometers were weighed. One dilatometer, hereafter referred to as the blank, was filled with freshly boiled distilled water by using the side arm and stopcock. Trapped and dissolved air was removed by attaching the dilatometer to a water pump by means of the capillary and pumping at a pressure of approximately 30 mm of Hg for several minutes, the stopcock being closed during this process. The water remaining in the side arm was removed by use of alcohol and ether, and this dilatometer was reweighed to obtain the weight of water in the blank.

The second dilatometer was packed with weighed strips of leather that were prepared as described, then filled with water in a similar manner and reweighed. From these measurements, the following necessary data were obtained: (1) the weight of water in the blank, (2) the weight of dry leather in the experimental dilatometer, (3) the weight of water in the experimental dilatometer (this figure includes the weight of the water in the leather obtained from a moisture determination on the conditioned strips).

The dilatometer assembly was placed in the air bath, which was adjusted to the lowest temperature at which both water levels in the capillary tubes were in the range of calibration of the capillaries and after attainment of equilibrium, the readings of the heights of the levels and the temperature were recorded.

The temperature of the air bath was then raised approximately 2 deg C and after attainment of

equilibrium (approximately 3 hr), the temperature and heights of the levels were again recorded. This procedure was repeated until the levels approached the top of the capillaries. At this point, after recording the readings, the stopcocks on the dilatometers were opened, and water was drained from the systems until the levels were again at the bottom of the capillaries. Since this procedure necessitated opening the air bath, it was necessary to permit temperature equilibrium to be reestablished before recording the height of the water levels. From a knowledge of the capillary calibration curves, and the recorded heights of the levels, the volumes of water removed were calculated. A knowledge of the density of water at the temperature of draining permitted calculation of the weight of water removed and consequently a correction of the weights of water in the dilatometers.

3. Calculation of Coefficients of Expansion

From a knowledge of the capillary calibration curves, all readings of heights of water levels were converted into increments of volume based on the initial height of the water level. The volume increment of the water in the dilatometer containing leather was calculated from the volume increment observed in the blank and the ratio of the wieghts of water in the two chambers. Subtraction of the calculated volume increment of the water for the dilatometer containing leather from the volume increment observed in this container, yielded the volume increment of the leather. The volume increments were plotted as ordinates with the corresponding temperatures as abscissas, and the slope of the line through the points was calculated by the method of least squares. The slope of the line, so obtained, was divided by the volume of the leather at the initial temperature to give the coefficient of cubical expansion of the leather.

IV. Results and Discussion

1. Coefficients of Cubical Expansion

The results of the individual measurements of the coefficients of expansion are given in table 1, and the chemical analyses of the leathers are given in table 2.

TABLE 1. *Expansivity of leather and collagen*

Type of material	Volume expansivity	Weight expansivity
TANNAGES ON WHICH DUPLICATE DETERMINATIONS WERE MADE		
	$1/°C$	$(ml/g)/°C$
Chrome	565×10^{-6}	382×10^{-6}
Do	496	320
Chrome-vegetable	396	276
Do	339	217
Vegetable	543	337
Do	503	322
Alum-vegetable	599	383
Do	590	379
TANNAGES ON WHICH SINGLE DETERMINATIONS WERE MADE		
Vegetable-chrome	497×10^{-6}	319×10^{-6}
Iron	592	380
Zirconium-vegetable	473	303
Formaldehyde	532	341
Uranium	532	341
Tendon collagen	538	345

TABLE 2. *Chemical analyses of leathers and collagen used for expansivity measurements*

All figures calculated on dry basis except those for moisture and acidity.

Type of leather	Moisture	Total ash	Grease	Oxide of metal tanning agent	Hide substance	Water-soluble material	Insoluble ash	Acidity
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	pH
Uranium tannage [1]	14.9	14.2			96.6			3.8
Vegetable-zirconium [1]	14.0	5.5	0.3		83.0	5.5	5.4	3.7
Alum-vegetable [1]	12.4	11.4	.4	2.1	62.2	1.8	2.0	3.6
Chrome-vegetable [1]	15.3	5.1	.4		74.4	2.2	3.3	2.7
Alum [1]	11.0	8.1	38.7	1.7	53.7			2.7
Vegetable-chrome [1]	15.1	5.4	0.3	5.0	80.9	3.7	4.5	3.4
Chrome [1]	13.8	4.8	10.4	3.9	73.7			3.2
Vegetable [1]	10.8	1.0	12.1		44.8	9.0	0.2	3.2
Iron [1]	13.4	12.8	5.9	11.0	60.9			3.4
Tendon-collagen [1]	15.7	2.4			96.5			6.0

[1] Analyses made on degreased, washed leather or collagen.
[2] Analyses made on untreated leather.

It is to be noted that the coefficients of expansion agree fairly well, with the exception of the coefficients obtained for chrome-vegetable leathers, which are lower. Statistical analysis of the data obtained from duplicate measurements on four different specimens shown at the top of table 1 yielded the following results:

a. The standard deviation of a single measurement of volume increment is 0.0065 ml, as estimated from the least-squares calculations.

b. The weighted average expansivity of leathers on which duplicate measurements were made, exclusive of chrome-vegetable leathers, is 540×10^{-6}/°C. The standard deviation corresponding to this value is 13×10^{-6}/°C.

c. The weighted average expansivity of chrome-vegetable leather is 340×10^{-6}/°C. The standard deviation corresponding to this value is 37×10^{-6}/°C.

d. The variations of expansivity shown by similar specimens of the same tannage are larger than those anticipated by the experimental errors. Therefore, it is probable that different specimens of the same leather have somewhat different expansivities.

e. The values obtained for chrome-vegetable leather are significantly lower than the average value for the other specimens. The over-all average coefficient of expansion of the samples, including collagen but excluding chrome-vegetable leather, is 540×10^{-6}/°C. The weighted average coefficient of chrome-vegetable leather is 340×10^{-6}/°C.

f. Since there is, in general, no more variation between different leathers than that found between duplicate specimens, there is no necessity for assuming that the expansivity varies appreciably with the tannage, except for chrome-vegetable leather.

Chemical analyses given in table 2 were made in accordance with methods described in Federal Specifications for Leather and Leather Products, KK-L-311, dated March 28, 1945. The analyses were made, in part, on specimens that had been degreased and washed in accordance with the method described for preparation of specimens for expansivity measurements. Such analyses are denoted by footnote 1. Analyses made on samples of leather before any treatment are denoted by footnote 2. All results, except those for moisture and acidity, are calculated on a dry basis.

The volume expansivities given in table 1 are calculated with the assumption that the density of dry leather, irrespective of tannage, is 1.560 g/ml at 70° F. This assumption was made necessary by the lack of data on the density of dry leather. The density figure of 1.560 g/ml was obtained from the data given by Kanagy and Wallace [1].[1] Their figures were calculated to a dry basis and averaged, assuming an average moisture content of 14.60 percent. The figures for the weight expansivities are included in the table, since these figures were measured directly and the volume expansivities involve the assumptions enumerated.

Despite the wide variety of leathers tested, it is seen that the expansivities are very similar and show much less variation than is exhibited by results of most physical tests of leather. In view of this agreement and the fact that variation of density with tannage is most probably a second order effect, the expansivity of 540×10^{-6}/°C is ascribed to leather in general. It must be remembered, however, that this expansivity applies only to leather in water, as evidence has been obtained that a smaller expansivity results if nonpolar liquids are used to confine the leather.

The analyses show a wide range of hide substance content that necessitates the assumption that the collagen itself is the substance reponsible for almost the entire expansion and that salts or tanning materials present contribute little to the expansivity. Since the expansivity is of the magnitude of that of a liquid, and the other materials present are, in the free state, solids, this might be expected.

The volume expansivity obtained from these measurements is not in agreement with a value for the linear expansivity reported by Mitton [2], who found a coefficient of linear expansion of 22×10^{-6}/°C. This value, which was obtained from measurements on dry fibers at elevated temperatures, is of a different order of magnitude than the values for cubical expansion and is typical of a solid. Aside from possible differences due to temperature and environment, the disagreement between the two values is to be expected on the basis of the present concept of the structure of collagen [3].

[1] Figures in brackets indicate the literature references at the end of this paper

Collagen is anisotropic and probably consists of layers of peptide chains oriented parallel to the fiber axis. The layers of chains are assumed to be held together by salt-bonds and hydrogen-bonds. In the direction of the fiber axis it is to be expected that the strong covalent chemical bonds will produce a structure resembling that of a solid and cause a low expansivity. At right angles to the fiber axis the weaker, less well-defined bonds are expected to yield a higher expansivity. Since the volume expansivity represents the sum of the expansivities along the three mutually perpendicular axes, the volume expansivity of collagen will therefore be typical of liquids, the contribution of the expansivity along the peptide chain being of a lesser order of magnitude.

2. Effect of Trapped Air

It has been suggested that reproducibility would be almost impossible because of uncertainties regarding removal of air from the interstices in the leather. The following calculation shows that the effect of trapped air on these measurements is not significant.

The maximum weight of leather used in any measurement was 35 g and may be considered to occupy 35 ml (density=1). Assuming the maximum percentage of voids found by Kanagy and Wallace [1] to be present, i. e., 60 percent, the void space is 21 ml. In the evacuation preparatory to test, a maximum pressure of 30 mm of mercury was used, of which, at 25° C, 24 mm is water vapor and 6 mm is air pressure. Assuming that half the void space is filled by displacement, 10 ml of air will be trapped at 6 mm air pressure. When atmospheric pressure is restored, this air will be compressed to 0.08 ml by relatively air-free water in which it may (and does) dissolve readily. If no solution takes place, this trapped air will undergo an expansion of less than 0.02 ml during a measurement in which the temperature is raised from 25° to 77° C. Since most measurements involve volume increments of 0.4 ml, the air would introduce an error of less than 4 percent in the final volume.

During preparation of dilatometers for test, it was observed that it was not necessary to remove the last traces of visibly trapped air, since small bubbles dissolved readily in the relatively air-free water and did not reform at the highest temperatures attained. The trapped air in the capillary system of the leather will also dissolve, and the resulting error from trapped air is probably negligible.

3. Expansion Curve and Transition

A series of typical expansion curves is shown in figure 2.

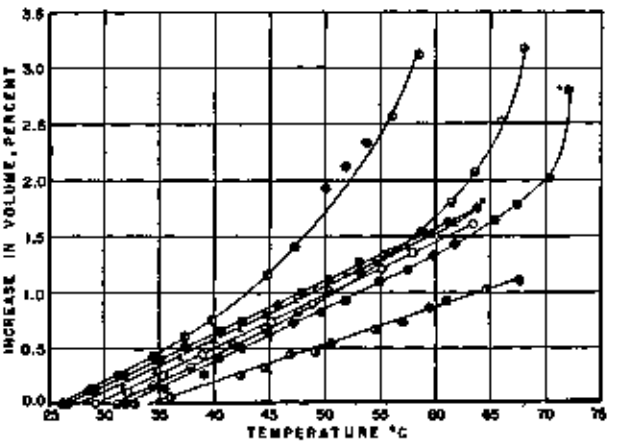

FIGURE 2. *Expansion curves for leather.*

●, Alum; ⊗, zirconium-vegetable; X, vegetable-chrome; ○, chrome; ⊖, alum-vegetable; ◉, vegetable; ◑, chrome-vegetable.

In this figure the percentage increase in volume is plotted against the temperature.

The initial portion of each curve is linear and was used for calculation of the coefficients. It will be noted that all the initial linear portions are parallel, save that of the chrome-vegetable leather. Along this portion of the curve, equilibrium was established rapidly, i. e., in 3 hrs. At an elevated temperature, depending on the tannage, a slow process set in that resulted in the excessive expansions seen in three curves. The total volume of leather and fluid in the dilatometer increased, whereas the apparent dimensions of the leather diminished. This discontinuity is identified with the shrinkage temperature, but the changes actually involve an expansion of the real volume of the leather. Although it is not certain that measurements in this region attained equilibrium, because of the slowness of the process involved, it is most probable that there is a progressive increase in volume, as shown by the figure, i. e., the expansion is not a change of state that occurs at a definite temperature, but is rather an analogous change that takes place over an interval of temperatures and may be considered to be a rate process.

The extent of the expansion at this transition has been evaluated roughly and is of the order of 1 percent. That the transition is not a simple fusion is shown by the observation that measurements conducted for long periods of time after transition occurred resulted in almost complete solution of the leather in the form of gelatine. One measurement on alum-vegetable tanned leather showed that two transitions were possible, one probably corresponding to transition of the central band of alum-tanned material and the other corresponding to the transition of the two external vegetable retanned strips. All samples tested showed this increase in volume on transition, with theexception of those for which the transition temperature was too high to be attained.

The increase in volume occurring in the transition process contradicts earlier predictions by Salcedo and Highberger [4], and by Wilson and Porth [5] that contraction should occur during shrinkage. The indication that transition is a process occurring over a temperature interval is at variance with a statement by Wohlisch [6] to the effect that shrinkage takes place above a sharply defined temperature.

Measurements of the shrinkage temperatures of some samples were made in accordance with the method described in Federal Specification for Leather and Leather Products KK–L–311, dated March 28, 1945. These measurements made on alum, alum-vegetable, and vegetable-tanned leathers gave shrinkage temperatures of 73°, 83°, and 68° C, respectively, whereas the transition temperatures noted on the curve as the departure from linearity are 35°, 48°, and 60° C, respectively. This also indicates that the shrinkage temperature is a function of environment and may vary by as much as 38° C, as in the alum-tanned leather.

The linearity of the graphical representation of the results is an argument against the formation of various hydrated leathers. Since there are no breaks in the lines, except for the transition process, if there is a hydrate present, it is stable over the temperature range of 25° to 75°C.

4. Reversibility of Expansion

In figure 3 are shown typical expansion curves in which measurements were made to determine the reversibility of the processes involved in the expansion.

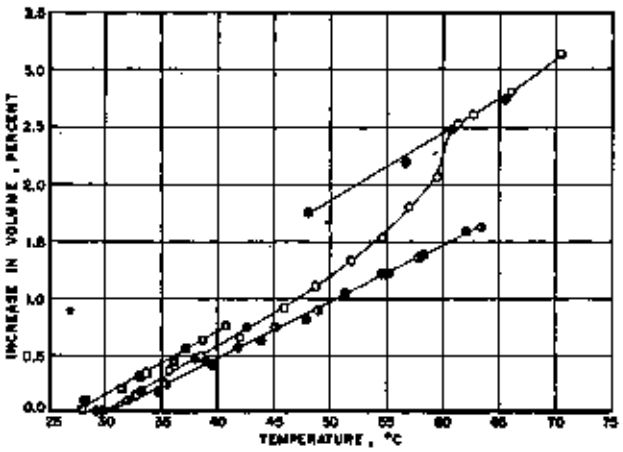

FIGURE 3. *Reversibility of expansion curves.*

□, Tendon collagen, increasing temperature; ■, tendon collagen, decreasing temperature; ○, alum vegetable, increasing temperature; ●, alum vegetable, decreasing temperature; ◑, chrome, increasing temperature; ⊘, chrome, decreasing temperature.

These measurements were made by increasing the temperature in 2 deg to 3 deg C steps until the liquid level approached the top of the capillary and then reversing the process and decreasing the temperature stepwise. After this one reversal, the temperature was again raised to the previous maximum, the volume was noted, the capillaries were drained, and the procedure was repeated at higher temperatures. Within the experimental error, the same volume was obtained at the maximum temperature before and after reversal. As shown by the figure, the linear portion of the curve is almost completely reversible. There is some indication from these and other measurements to be reported on the rate of shrinkage, that this reversibility is not complete even at moderate temperatures, but the divergence is very small. In this portion of the curve it appears, therefore, that the final volume is not influenced significantly by the time required for equilibrium to be established.

After passing through the transition, however, the process is not reversible, the contraction curve being displaced from the expansion curve by the increment in volume of the transition. This behavior was verified in every transition observed and represents definite evidence of the irreversibility of the transition process and further evidence that this is not a fusion unless the crystallization process be assumed to be extremely slow. It is very probable that a transition and a reaction with water take place and that even though the

reaction may be reversible, the formation of cross linkages is not because of deformation.

5. Rate of Transition

The measurements made on tendon collagen shown in figure 3 afforded a measurement of the rate of shrinkage. As shown in the figure, the temperature was raised to 41° C and then reduced to 28° C. It was not considered wise to exceed 41° C before reversing the process because of the possibility of transition. After the investigation of the reversal, the next higher temperature reached was 43° C, and after 2.5 hr at this temperature transition set in, and the rate of the process was measured. A graphical representation of the results is shown in figure 4, in which the logarithm of the volume change is plotted against the time.

This sample was essentially at equilibrium at 43° C when the transition ensued, and the increase in volume is measured from this pseudo-equilibrium value. It is noted that a straight line results, indicating a first-order reaction. Deviation from the line is to be expected after long intervals, since water is probably used up in the transition, and only a limited amount of water is available in the dilatometer.

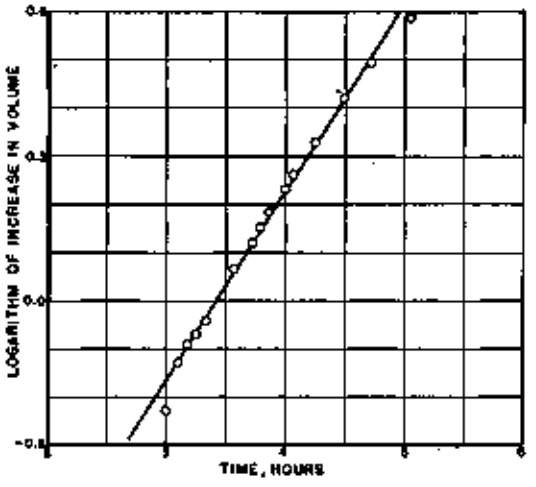

FIGURE 4. *Rate of transition of tendon collagen.*

A calculation of the velocity constant has not been made, since the variation of the constant with temperature may not be ascertained readily in this apparatus. Likewise the original and final volumes are not known, inasmuch as this transition produced an increase in volume sufficiently large to exceed the capacity of the capillary and render further measurements impossible. Further measurements are in progress on the rate of the transition and the temperature dependence of the velocity constant.

The author expresses his appreciation to John Mandel for the statistical analyses of the experimental data.

V. References

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