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STRENGTH INCREASES BY TENSION TANNAGES

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ABSTRACT

It is well known that tensile strength measurements, calculated for equal cross sections, give much higher results for individual collagen fibers than for mammalian hide in bulk, whether or not both are tanned or both are untanned. Also, it has been shown that when hide is forcibly pulled in one direction, a realignment of the fibers occurs, and this results in an increase in the tensile strength of the hide in the direction of the realignment.

A new and considerably improved technique of increasing tensile strength by mounting and tanning hide pieces under tension has been investigated, using bated or pickled cowhide and pickled sheepskin and various methods of tanning. Most of the pieces were chrome-tanned in a two-step process in which the chrome concentration was varied. Tension was applied during the first or second step or during both. An aldehyde-lignosulfonate combination tannage with stretching was also carried out. Characteristics of the stretched skins were compared with those of adjacent hide pieces that had been tanned in the same vessel but in a relaxed state. All the tannages under tension produced an increase in the parallel-direction tension strength (up to 12,000 lb/in^2 or more) but at the expense of elongation, which was lowered by as much as 80%. It is believed that tension-tanned leather has potential military and civilian application.

INTRODUCTION

Single collagen fibers and fiber bundles have been shown to be much stronger than hide or leather when the two are compared on the basis of equal cross-sectional area. Only a few data on the tensile strength of single fibers have been reported, namely:

Raw steerhide fibers (from forehead)	(in lb/in^2)	70,000	(1)
Vegetable-tanned leather (from forehead)	"	36,000–41,000	(1)
Vegetable leather	"	14,000–21,000	(2)
Kangaroo tendon	"	47,000–58,000	(3)

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Most workers (4–8) have found it more practical to determine *mean breaking length* because accurate measurements of fiber cross sections are difficult to obtain. As far as untanned dry fibers are concerned, both types of measurement are in close agreement. The results from tanned fibers, on the other hand, vary widely, with the lowest figures (8.8–14.8 km.) encountered after tannage with formaldehyde (4,5), benzoquinone at pH 9.1 (4), and unmasked chrome liquor (5). However, there is no difference in results when small pieces of hide are first tanned and then teased (gross-piece technique) or when the fibers are teased from commercially tanned leather (6, 7).

It is obvious that the higher strength of fiber bundles is due to their parallel alignment. Therefore, a similar alignment of the fibers in leather should result in a substantial strength increase. Mitton and Nattrass (9) have shown this to be the case. By applying tension to pieces of hide while tanning them with chrome, they obtained strength increases in the order of 50% more than with hides normally tanned. As would be expected, these increases were observed only when the force was applied in the same direction as the tension during tannage. When the force was applied at right angles, there was a 12% loss in strength, on the average. This held true both for chrome- and vegetable-tanned leather, with the vegetable leather showing the greatest strength increases (up to 100%).

Mitton and Nattrass point out that tannage under tension "clearly offers substantial advantages for the production of leather whose strength must be high, particularly if the strength is required for pulls in one direction only." They cite leather belts as an example. We could also mention laces, gussets, and rucksack and ski bindings. However, they are aware that more data must be provided before the optimum conditions for tension-tanning can be decided upon and operations on a commercial scale undertaken.

Two Russian workers (10) concerned with protein fibers in general rather than with leather in bulk have conducted a related investigation that at present is accessible to us only as a brief abstract. Chemical Abstracts summarizes the results as follows: "Depending on the amount of stretching applied to the tannery process it is possible not only to fix a structure of the raw fibers but to obtain additional orientation of the molecular chains with a corresponding increase in the tensile strength of the fibers." Positive evidence of such realignment of molecular chains by mechanical forces was uncovered for an amorphous protein many years ago when Bjorksten and Champion (11) found that the rhythmical stretching and relaxation of air-dried gelatin sheets raises their tensile strength in the direction of stretch when they are acetaldehyde-tanned but not when they are untanned. The strength increase they obtained is modest when compared with that obtained by Mitton and Nattrass. Yet, by improving the earlier improvised stretching techniques, it has been possible to obtain strength increases of a much greater magnitude. The experiments demonstrating this are the subject of this paper.

EXPERIMENTAL

Materials.—Adjacent pieces of bated or pickled cowhide and of pickled lambskin were cut into suitably sized pairs with one of each pair being used as a control. The bated hide was preserved with Merthiolate and was pickled in the usual way before tanning. All hide material was wrapped in a polyethylene bag and kept under refrigeration.

Equipment.—A brass stretching frame (Fig. 1) consisted of two cylindrical bars, *A* and *B*, each 5.5″ long and 0.75″ in diameter, with one third of

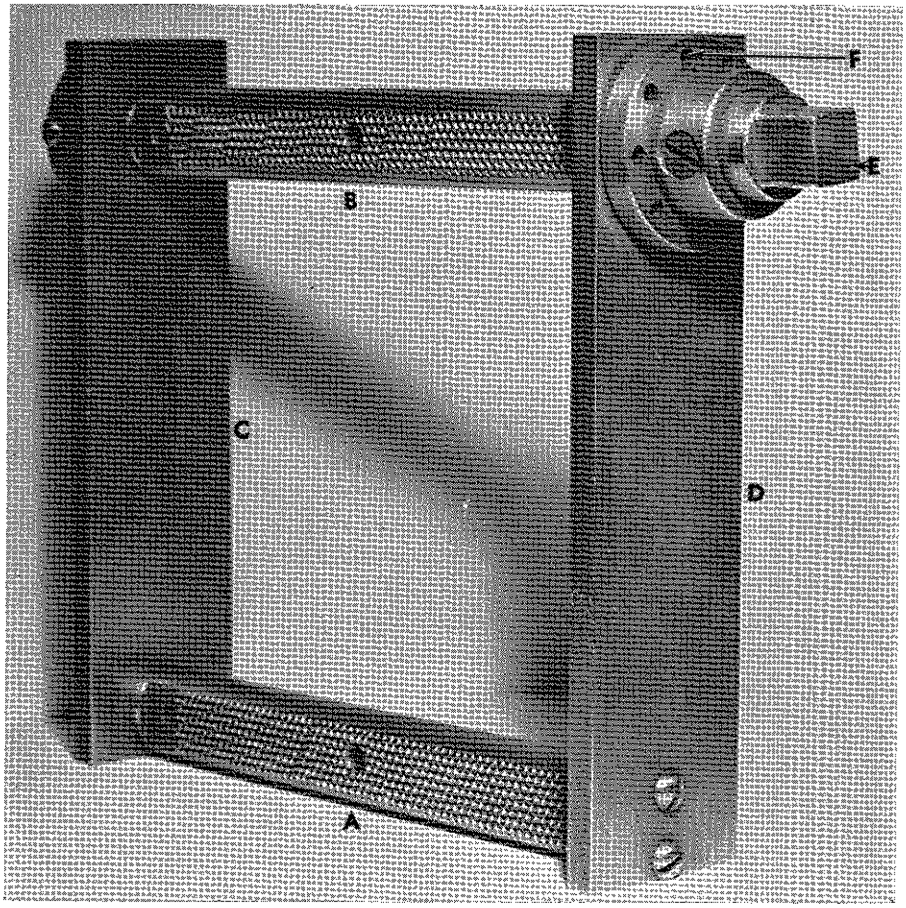

FIGURE 1.—Stretching frame.

A—Stationary bar
B—Rotating bar
C and D—Supporting plates
E—Turning knob
F—Hole for locking pin (Plate *D* has corresponding holes)

their surface flattened and knurled. Bar *A* was bolted securely between two plates, *C* and *D*. In a position 5″ from Bar *A* and parallel to it, Bar *B* was fastened between the plates but in such a way that it could be rotated by means of a 1½″ extension (*E*) beyond the plate. A series of small holes in Plate *D* and corresponding holes penetrating a ¼″ disc (*F*) attached to Bar *B* outside the plate, permitted a pin to be inserted through both disc and plate in order to lock the turning crossbar at regular intervals.

The hide pieces, cut so that tension would always be applied parallel to the backbone, were attached first to Bar *A*, being held against the knurled surface by means of a brass plate (not shown) and machine screws that passed through threaded holes in the plates and punched holes in the hide. The other end of the hide was attached in a similar fashion to Bar *B*. A hand wrench applied to the protruding end (*E*) of Bar *B* turned the bar and thus stretched the hide. By marking the holes that the pin occupied at the point of the greatest possible tension, one could apply the same amount of tension to other pieces. The force required to turn the bar was measured by a torquemeter and was found to be 600 inch-pounds. Under this force, the hides were elongated about 25%.

In many experiments the size of the hide pieces was doubled by first fastening them to Bar *B* of the stretching frame, then looping them around Bar *A* and returning them to Bar *B*, which in this way secured both ends.

Tanning procedures.—A series of chrome tannages were carried out using an aged stock solution of 33% basic chrome sulfate (Tanolin R) containing 100 g/l of Cr_2O_3. Each chrome tannage was carried out in two steps.

In the first stage no masking agent or tension was employed. All the hide pieces were tanned in revolving glass jars using 0.5% or 1.0% of Cr_2O_3, based on their pickled weight. There was one exception, Tannage Method A, in which tension was applied during this "pretannage" (but not to the control) and for which 3.0% Cr_2O_3 was used.

For the second tannage the hide pieces, under stretch on the frame, were placed in a laboratory rocker of 3-liter capacity and moved up and down at the rate of 28 times per minute. The control piece in a relaxed condition was hung in the rocker next to the corresponding stretched piece. Immediately before use, the tan liquors were masked by adding 3 moles of sodium formate to 1 mole of Cr_2O_3, at room temperature. Except for Method A, in which only 1.5% of the pickled weight Cr_2O_3 was used, the quantities were 4.5% or 3% Cr_2O_3. The prepared solutions were sufficiently diluted to cover the stretching frame in the rocker.

During both tanning procedures the pH was slowly raised by adding small amounts of $NaHCO_3$ until a pH of 3.3 was attained for the *pretannage*, which took 24 hr. and brought the shrinking temperature (Ts) to 76°–78°C., or a pH of about 4.5 for the *second tannage*, which took about 48 hr. and brought the Ts of the stretched pieces to about 100°–102°C. and of the controls to 103°–108°C.

After tanning, all specimens were washed for 10 min. in 25°C. running water and then air-dried.

While the same general procedure was followed for each tanning method, there were some exceptions, especially in fatliquoring. In all but Method A (in which there was no fatliquoring) the chrome-tanned pieces were fatliquored with 4% (of the pickled weight) of a mixture of equal parts of a cationic fatliquor and neatsfoot oil. The fatliquor was applied between the two tanning steps except in Method B, where it was applied after the retanning but before the air-drying.

An aldehyde and vegetable extract combination tannage, Method F, was also carried out, using a process similar to one recently developed for heavy leather by the Quartermaster Research and Engineering Laboratories (12). In this process one piece remained in the frame and the corresponding control piece hung freely in the tanning bath for 6 days. Equilibration with a solution containing Na_2CO_3 and $NaHCO_3$ in the ratio of 10 to 4 required 16 hr.; the aldehyde tannage using 3% technical formaldehyde (of the bated weight) required another 24 hr.; and the lowering of the pH to approximately 4.0 took 20 hr. more. A fresh liquor containing 20 parts liquid quebracho extract, 10 parts dry lignosulfonate extract, and 1.5 parts of a naphthalene sulfonic acid formaldehyde condensate (Leukanol ND) was used for the second tannage. This liquor was adjusted to 41° Bark. before being fed to the rocker, and was strengthened to 60° Bark. after 1 day, and to 80° Bark. the second day. For a period of 8 hr. out of the 24, the liquor was heated to 50°C.; thereafter it was allowed to resume room temperature. On the third day the pieces were rinsed and slightly fatliquored in a tumbling jar by the addition of 0.5% (of the bated weight) each of mineral oil, neatsfoot oil, and sulfonated cod oil.

Pieces of lambskin were also tanned under tension, using a single bath of formate-masked basic chromic sulfate and raising the pH to 4.5 with $NaHCO_3$. The liquor was rocked for 32 hr. and then left standing for 16 hr. before relaxation of the tension and fatliquoring in a revolving jar.

In addition, pieces of pickled cowhide and lambskin were fastened to a rectangular-type stretching frame that permitted them to be stretched in two directions (parallel and perpendicular to the backbone) as in a fabric stretcher. While subjected to such stretching, the pieces were tanned by the same method as C, D, and E.

These tanning procedures differed from those of Mitton and Nattrass in (*a*) employing cow or sheep skin rather than calf, (*b*) reducing the "exceptionally high" ratio of tanning bath to hide to about 10:1, (*c*) being more rapid—3 days instead of 8 for the chrome, and 6 instead of 28 for the vegetable tannage—and (*d*) producing chrome leather with a Ts of 100°–102°C. instead of 91°–93°C. A similar comparison cannot be made for the vegetable-tanned leather because of lack of data from Mitton and Nattrass.

Testing methods.—All pieces were air-dried and conditioned to 50% relative humidity and 73°F. before being tested for strength. Breaking load, tensile strength, elongation, and stitch tearing strength (when size of piece permitted including this test) were obtained in accordance with Federal Specification KK-L-311, except that the dumbbell specimen was only 4″ long and 0.25″ wide at the "waist". Bursting load was measured by means of a modified Scott Tester, using a ⅛″ plunger and a ⅜″ orifice. All strength measurements were taken in the direction of stretch. Ts measurements were obtained with a Transverse Shrinkmeter (13).

TEST RESULTS

Cattlehide leather

Tensile strength.—Physical data for the cowhides tanned under tension are given in Table I. Data for the unstretched control specimens are not given in order to keep the number of columns to the minimum, but they were used in computing the percentages of increase or loss. Strength measurements are given both in pounds and in pounds per square inch. This is because stretching causes loss of thickness to varying degrees. On an equal cross-sectional basis, the chrome tannages A and B, the latter conducted on flanky belly pieces, and the aldehyde-vegetable tannage F gave especially large strength increases.

Table I shows that the average strength of tension-tanned leather depends to some extent on thickness. Very thick pieces such as were used in Method D, which was carried out on particularly heavy shoulder pieces, may exceed breaking loads of 300 lb., or tensile strengths of 10,000 lb/in^2. Light pieces, on the other hand, such as were used for Methods C and E, may reach a breaking load of only 100 lb., or a tensile strength of only 6,000 lb/in^2; these pieces were thinner than the rest because they had been stretched after removal of a flesh split.

In Methods D and E, half of the control pieces, after having been tanned in the relaxed state, were mounted on the stretcher before washing and kept there for the same length of time (48 hr.) as the pieces that had been tanned under tension. As Table I shows, this "post-stretching," identified as Methods D_2 and E_2, is not as effective as the tension tannage.

Individual test results not shown in the table revealed that the greatest increases in strength were obtained from that part of the hide at the outer edge of the stretched part. There the fibers were subjected to a greater pull than in the center, and as a visible indication of this extra pull, all specimens

TABLE I

CHARACTERISTICS OF CATTLEHIDE LEATHER AFTER TANNING UNDER TENSION

(Force applied in same direction as tension)

Tannage Method	Chromic Oxide (% of pickled weight) First Stage	Chromic Oxide (% of pickled weight) Second Stage	Fatliquor Applied	Thickness oz.	Breaking Load lb.	Tensile Strength lb/in2	Elongation at Break %	Increase Breaking Load %	Increase Tensile Strength %	Loss Elongation %	Loss Thickness %	Av. No. Measurements*
A	3†	1.5†	None	6.7	325	12,200	—	207	294	—	21	3
B	1	3†	After retan	4.8	158	8,090	28	110	236	64	34	7
C	1	3†	Between pretan and retan	3.3	85	6,470	18	157	177	80	14	20
D_1	0.5	4.5†	" " "	7.6	303	10,100	29	106	148	76	22	7
D_2	0.5	4.5	" " "	8.8	284	8,610	32	93	111	74	10	7
E_1	0.5	4.5†	" " "	4.4	100	5,760	18	127	135	67	4	7
E_2	0.5	4.5	" " "	4.2	56	3,450	20	27	41	64	9	7
F	Aldehyde-extract†		After retan	8.9	300	8,020	24	124	210	nil	31	7

*Except for thickness where from 2 to 3 times as many measurements were made.
†Signifies tanning stage or stages where tension was applied.

assumed a slightly constricted form during tannage. Evidently, the fibers in that area had become not only better oriented but subject to greater extension. For instance, the peak tensile strength from Method B was 11,260 lb/in^2 at the outer edges. Two specimens from the same location exhibited tensile strength values of 10,070 and 6,950 lb/in^2 and breaking loads of 365 and 128 lb. respectively after Tannage Methods D_1 and E_1. This "edge" effect was evidently missing from the British experiments, which were conducted on pieces over 50% wider than ours, and its absence explains—at least partially—why the strength increases observed were more modest than those found in this study.

Mitton and Nattrass observed that breaking load and tensile strength taken at right angles to the direction of the applied tension are both considerably decreased in comparison with the controls. This observation was confirmed by a few tests not included in Table I.

Elongation.—The tension-tanned chrome leather pieces of Methods A to E broke at elongations varying from 18% to 32%, or at values from 64% to 80% lower than the elongations at break of the controls. The degree of elongation observed apparently is unrelated to the tensile strength. In Method F, the elongation at break was the same both for the tension-tanned and control pieces, a result that reflects the well known rigidity of leathers tanned with vegetable extracts.

TABLE II

BURSTING STRENGTH OF TENSION-TANNED AND CONTROL PIECES OF CATTLEHIDE LEATHER

Tannage Method	Bursting Strength		Degrees of Freedom	*F* Value
	Tension-tanned lb.	Control lb.		
A	190	184	1,7	0.20
B	125	119	1,4	0.36
C	43	44	1,16	0.62
D_1	112	125	1,6	1.7
E_1	90	73	1,14	9.9*
F	245	240	1,26	0.12

*Significant at the 99% level ($F = 8.9$); other F values not significant.

Bursting strength.—The results of the bursting strength tests are presented in Table II. An analysis of variance was performed on each of the tannages. As the table shows, the F values received are very low and not significant except in the case of Tanning Method E_1, carried out on grain splits. The bursting strength of the tension-tanned piece was more than 20% greater than that of the control. A second tannage of grain splits (*C*) showed no appreciable difference in strength between the tension-tanned and the unstretched piece. This inconsistency may have been caused by the degree of splitting or by positional differences.

Stitch tearing strength.—The results of the stitch tearing test (given to only three tension-tanned cowhide pieces and their controls) are given in Table III. The tension-tanned pieces were found to be considerably weaker than

TABLE III

STITCH TEARING STRENGTH OF TENSION-TANNED AND CONTROL PIECES OF CATTLEHIDE LEATHER

Tannage Method	Direction of Test	Stitch Tearing Strength: Tension-tanned X_1 lb.	Stitch Tearing Strength: Control X_2 lb.	Difference X	Deviation x
A	Parallel	61	90	29	1
	Perpendicular	62	106	44	16
D_1	Parallel	80	154	74	46
	Perpendicular	100	126	26	− 2
E_1	Parallel	62	45	−17	−45
	Perpendicular	46	58	12	−16
Total		411	579	168	0
Mean		68.5	96.5	28	

By statistical analysis, on a paired comparison basis (see G. W. Snedecor, *Statistical Analysis* [Iowa State College Press, 1948] page 44), a t value of 2.24 is obtained, which is significant at the 95% level.

the controls, with the exception of the grain splits tanned by Method E_1 and tested in the parallel direction. The number of measurements was too small for a statistical analysis of directional effect; however, a paired comparison between tension-tanned and control pieces can be made, and such a comparison indicates a very significant tendency toward loss in stitch tearing strength by tanning under tension. This was not unexpected in the light of previous work on the various types of tears (14, 15).

Neither stitch tearing properties nor bursting strength was studied by Mitton and Nattrass.

Chemical properties.—For the tension-tanned chrome leathers a minimum Ts of 100°C. was considered adequate. In order to obtain this Ts the control pieces tanned in the same liquor generally had a 2°–3°C. higher Ts. Occasionally, however, differences as much as 8 °C. were observed between the tension-tanned and control pieces. For the aldehyde-vegetable tension-tannage the difference was 14 °C., and for that reason this leather was fully analyzed, with results given in Table IV.

TABLE IV

CHEMICAL COMPOSITION OF ALDEHYDE-VEGETABLE TENSION-TANNED LEATHER

	Tension-Tanned	Control
Water solubles, %	6.4	12.1
Hide substance, %	70.0	55.3
Grease, %	1.7	2.5
Water-insoluble ash, %	0.3	0.3
Degree of tannage	31	54
Acidity (pH)	4.8	5.0

The difference between the stretched and unstretched pieces is shown to be considerable. The stretched showed fewer water solubles and less grease, which would be expected from the pulling of the fibers closer together, resulting in a markedly lower degree of tannage. These differences might have been minimized by extending the duration of the tannage and by using a more economical liquor-hide ratio.

New Zealand lamb.—The test results from the pieces of lambskin tanned under tension are shown in Table V. The breaking load and tensile strength were again found to be many times greater for the tension-tanned leather than for the controls. The differences are of the same order of magnitude as those obtained with cowhides of similar thickness, although single measurements of breaking load exceeded 140 lb. and 10,000 lb/in² of tensile strength.

Cowhide and lambskin subjected to two-way stretch.—Parallel and perpendicular (relative to the backbone) breaking loads of air-dried pieces of pickled cowhide and lambskin that had been stretched in two directions while being tanned according to Methods C, D, and E were compared with those of the control pieces, with the results (averages of 6 measurements per value) shown in Table VI.

TABLE V

CHARACTERISTICS OF CHROME-TANNED SHEEPSKINS AFTER TANNING UNDER TENSION

(Force applied in same direction as tension)

	Thickness oz.	Breaking Load lb.	Tensile Strength lb/in²	Bursting Strength lb.	Elongation %	Increase Breaking Load %	Increase Tensile Strength %	Loss Elongation %	Average Number Measurements
Tension-tanned	3.3	94	7,260	39	13	261	245	72	7
Control	3.1	26	2,110	30	47				7

TABLE VI

BREAKING LOADS

	Cowhide lb.	Lambskin lb.
Parallel direction		
Tension-tanned	13	15
Control	16	24
Perpendicular direction		
Tension-tanned	12	12
Control	17	19

These figures show that, without exception, two-way stretch failed to orient the fibers for increased strength and actually caused strength losses to varying degrees.

CONCLUSIONS AND RECOMMENDATIONS

The results of tanning under one-way tension clearly indicate highly significant strength increases in the direction of the applied tension. In unsplit chrome- or vegetable-tanned leather, tensile strength values of approximately 10,000 lb/in^2 are feasible. Cowhide split to 3 or 4 oz., and also pickled lambskin, can reach average tensile strength values of about 7,000 lb/in^2 and average breaking loads of about 100 lb. Tanning under tension, therefore, distinctly appears to be a possibility for upgrading inferior stock or for producing leather of exceptional strength.

The small-scale experiments reported in this paper were undertaken primarily to create new interest in tension tannage. The next step would be the construction of increasingly larger stretching frames in which hide pieces could be tanned under tension. It is believed that the building of a practical stretch-tanning unit would not be unsurmountable. The continuation of work of this kind in the Quartermaster laboratories is impossible, however, because of the curtailment of funds.

The future will determine whether the stretching technique can also be used in studies of a theoretical nature, especially in studies of those phenomena that depend mainly on weave and cohesion of fibers rather than on spatial changes in the protofibrils or molecular chains.

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