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Alum Retannage of Vegetable-Tanned Insoles* Improves Their Serviceability

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It has been shown in previous work [1, 2, 3, 4, 5] that alum retannage imparts valuable properties to vegetable-tanned leather. There is an increase in resistance to acid deterioration, to moist heat, to molds and an increase in area stability. This type of retannage was first used to give increased durability to leather of the bookbinding and upholstery types. Its use was later extended to insole leather for shoes. In tests made at Camp Lee by the Quartermaster Board of the Armed Services, it was found that the use of alum-retanned insoles in place of vegetable-tanned insoles reduced the number of failures in the normal wear test by 68 per cent. W. Grassman and P. Stadler [6] have examined the effect of alkaline perspiration solutions on insole leather. They report a "good perspiration resistance of leathers which have been treated with cationic tannins and favorable conditions with regard to shriveling of samples retanned with chromium and alum salts". Work by this Laboratory has demonstrated that the optimum concentration of Al_2O_3 required to give maximum protection with minimum changes in the desirable characteristics of the leather is from 2.5 to 3.0 per cent on a moisture-free leather basis. It has been shown that the penetration of an aluminum sulfate tanning liquor could be increased by the addition of sodium acetate as a "masking" or "stabilizing" agent. Later, it was found that this mixture of aluminum sulfate and sodium acetate could be conveniently replaced by basic aluminum acetate, and in tannery operation the retannage could be effected by the addition of aluminum acetate to the other materials usually drummed into the leather in the tanner's oil wheel. The retannage can also be carried out by a "dry dipping" method in which the dry leather is dipped into a solution of basic aluminum acetate, in which the concentration, temperature and time of immersion are so regulated that the leather will pick up the required amount of Al_2O_3.

The Camp Lee test gave definite evidence that alum-retanned insoles were superior to vegetable-tanned insoles in actual wear. The recent "Mailmen's" service test [7], conducted by this Laboratory to study the serviceability of canaigre-tanned outsoles, afforded also an excellent opportunity to confirm the results of the Camp Lee test on the relative serviceability of vegetable-tanned and alum-retanned insoles.

This paper reports results obtained when control vegetable-tanned and alum-retanned leathers, prepared as described below, were tested as insoles

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in shoes in which the serviceability of outsoles was being simultaneously studied.

Preparation of Test Leathers

Through the cooperation of the Middleburg Tanning Corporation, the alum retannage was carried out at their tannery at Middleburg, Pennsylvania. From regular vegetable-tanned bellies suitable for insoles, 3 lots of 15 bellies each were retanned by the "dry dip" method to contain approximately 2.5, 2.75, and 3.00 per cent Al_2O_3. Three lots of 50 bellies each were retanned by the oil wheel method to give leathers with approximately 2.75 per cent Al_2O_3. Except for minor variations, these bellies were all finished by the normal tannery procedure. Pieces of the leathers taken immediately after retanning contained the desired concentrations of Al_2O_3. However, when the leathers were finished, the concentration of Al_2O_3 in the outer layers had decreased considerably. This was attributed to subjecting the rough, dry leather to the action of a "sour dip" (a fermenting mixture of glucose and Epsom salts) for a rather long period. This removed from the outer layers some of the alum before it was firmly fixed. The alum was restored to the outer layers by dry dipping in an aluminum acetate solution of the required strength. When finished and dried, these alum-retanned insole leathers were entirely free from any indication of cracky grain.

To furnish leather for the control insoles, 16 vegetable-tanned bellies, not retanned, but in other respects as similar as possible to those used for retanning, were selected. From the center of each belly 5 to 7 insoles were cut. Each retanned insole was matched with a control vegetable-tanned insole of the same thickness and cut from the same location on the belly. Each pair of insoles was then used in the preparation of a pair of test shoes.

Wear Test

In the actual service test 61 pairs of shoes were worn until the original outsole and 2 resoles had been worn through. The periods of wear ranged from 9 to 12 months. When the second resoles were worn through examination of the insoles indicated that the test had progressed to such a stage that the relative serviceability of the vegetable and alum-retanned insoles could be evaluated. The wear test was then discontinued and the condition of the worn insole leathers compared.

Chemical Analysis of Test Leathers

Analyses of the original leathers before use and of the worn insole leathers are shown in Table I [8]. The analysis of the vegetable-tanned control leather was made on a sample composited from the belly leathers used. The analysis of the alum-retanned leather is a calculated average of the analyses of 12 separate bellies. The Al_2O_3 content ranged from 1.9 per cent to 3.8 per cent,

TABLE I

Analysis of Leathers Before and After Mailmen Service Test
(Results on Moisture-Free Basis)

		Before Test		After Test	
		Vegetable Control	Alum Retan	Vegetable Control	Alum Retan
Petroleum Ether Extract	%	6.6	5.0	8.2	7.2
Insoluble Ash	%	0.3	2.5	0.8	2.9
Hide Substance	%	30.5	31.0	41.8	40.0
Soluble Matter	%	39.7	28.1	28.5	18.0
Combined Tannin	%	22.9	33.4	20.7	31.9
Degree of Tannage	%	75.1	107.7	49.5	79.8
Soluble Nontannin	%	27.3	23.9	12.7	12.2
Soluble Tannin	%	12.4	4.2	15.9	5.8
Total Ash	%	9.4	8.0	4.7	6.0
Total Al_2O_3	%	——	2.8	——	2 5
Total Al_2O_3 on hide substance basis	%	——	9.0	——	6.3
pH*		3.1	4.1	5.1	5.1
Shrink Temperature, C°*		83.5	107.	82.	99.

*Not on moisture-free basis.

but of the 70 insoles cut from the bellies 60 had Al_2O_3 contents ranging from 2.4 per cent to 3.0 per cent, 5 contained 1.9 per cent and 5 contained 3.8 per cent.

Physical Tests and Evaluation of Leathers

Representative samples of the original control and alum-retanned leathers were evaluated for their resistance to perspiration and repeated flexing and drying by use of an insole testing apparatus[9]. This tester was designed to flex the leather while moistened with a synthetic sweat solution to hasten the deterioration and approximate, as nearly as possible in a laboratory test, actual wearing conditions. The conditions and specimens used in conducting this test were as follows:

Test specimen ..... 1 inch by 5 inches[9]
(with a dumbell specimen cut but adhering at its ends to the test specimen)
Temperature ..... 100° F. (38° C.)
Speed ..... 60 cycles per minute
Tension ..... 2.6 lbs.
Load on roller ..... about 4.0 lbs.

The synthetic perspiration solution was prepared by the method described in Federal Specification KK-L-311a[10] as modified by Kremen[11] and has the following composition:

For one liter of solution use:

NaCl	10 grams	
$(NH_4)_2CO_3$	4 "	
Na_2HPO_4	1 "	
Urea	240 "	(approximately 4 molar)

Adjust to pH 7.8 with lactic acid, then dilute to volume with distilled water.

The procedure was as follows: The thickness of each dumbbell specimen was determined and recorded. The specimens were then placed in the tester and

(1) Flexed 5 minutes dry at 60 cycles per minute (300 cycles).
(2) Three ml. sweat solution added while running and flexed for 30 minutes, equal to 1800 cycles.
(3) Two ml. sweat solution added while running and flexed for 120 minutes, equal to 7200 cycles.
(Total number of cylces—9300).

The specimens were removed from the tester and placed in an oven at 39–41° C. for one hour, and then conditioned at 23° C. and 50 per cent relative humidity overnight. This entire treatment was repeated on 2 suc-

TABLE II

Tensile Strength of Vegetable and Alum-Retanned Leathers Before and After Testing on EURB Insole Tester

Belly No.	Vegetable Control			Alum Retan		
	Before Kg/Cm2	After Kg/Cm2	Loss %	Before Kg/Cm2	After Kg/Cm2	Loss %
1	130	86		128	112	
2	173	68		161	143	
3	194	85		208	164	
4	198	84		211	126	
5	228	108		227	135	
6	230	56		231	178	
7	231	89		231	170	
8	239	39		232	180	
9	244	68		239	110	
10	250	109		263	161	
11	265	82		289	162	
12	269	97		305	154	
13	290	86		320	197	
Average	226	81	64	234	153	35

Strength remaining after test as % of original strength—Control	36
Strength remaining after test as % of original strength—Alum	65
Improvement by alum retannage $\frac{65-36}{36} \times 100$	81

sessive days. The dumbbell specimens were then cut loose from the large specimens and tested for tensile strength (See Table II) and for crackiness by bending around standard diameter mandrels as described in the A.L.C.A. Official Methods [8]. The results of the cracking test and the diameters of the various mandrels used are shown in Table III and Figure No. 1.

TABLE III

Crackiness of Vegetable and Alum-Retanned Leathers, by Mandrel Method. Before and After Testing on EURB Insole Tester

(Reported as diameters of mandrels required to produce cracks)

Leather No.	Vegetable Leathers		Alum-Retanned Leathers	
	Before Diam. Inches	After Diam. Inches	Before Diam. Inches	After Diam. Inches
1	0.45	2.00	0.45	1.63
2	0.38	2.00	0.38	1.50
3	0.38	2.00	0.38	1.25
4	0.31	2.00	0.31	1.13
5	0.31	2.00	0.25	1.00
6	0.25	2.00	0.25	1.00
7	0.19	1.88	0.19	0.88
8	0.19	1.39	0.13	0.88
9	0.19	1.00	0.13	0.88
10	0.19	0.88	0.13	0.75
11	0.13	0.88	0.13	0.56
12	0.13	0.75	0.13	0.50
13	0.13	0.75	0.13	0.31

The worn insoles were further evaluated and sorted for quality by inspection for crackiness, curling, discoloration and deformation. They were graded on a scale ranging from 0, the poorest, to 10, equal to the unworn leather. Ratings were made separately by four sorters and were highly uniform between individuals, None of the worn insoles were rated higher than six on the scale. The results of the ratings are shown in Table IV. It was the opinion of a shoe repairer that shoes containing insoles with ratings of 0 to 2 were unsuitable for repair and further use; while those rated 3 or above could still be used. Figure 2 shows the relative percentages of worn vegetable-tanned and alum-retanned insoles that were of quality that would justify resoling the shoes for further wear.

Breaking strength determinations were made on the original leathers and on the worn insoles. The breaking strength of the original leathers is the average of 15 determinations of fairly close agreement. Since the condition of the worn insoles did not permit strength determinations on every insole, determinations were made on several insoles from each rating as described above. The breaking strength apparently was in harmony with the rating

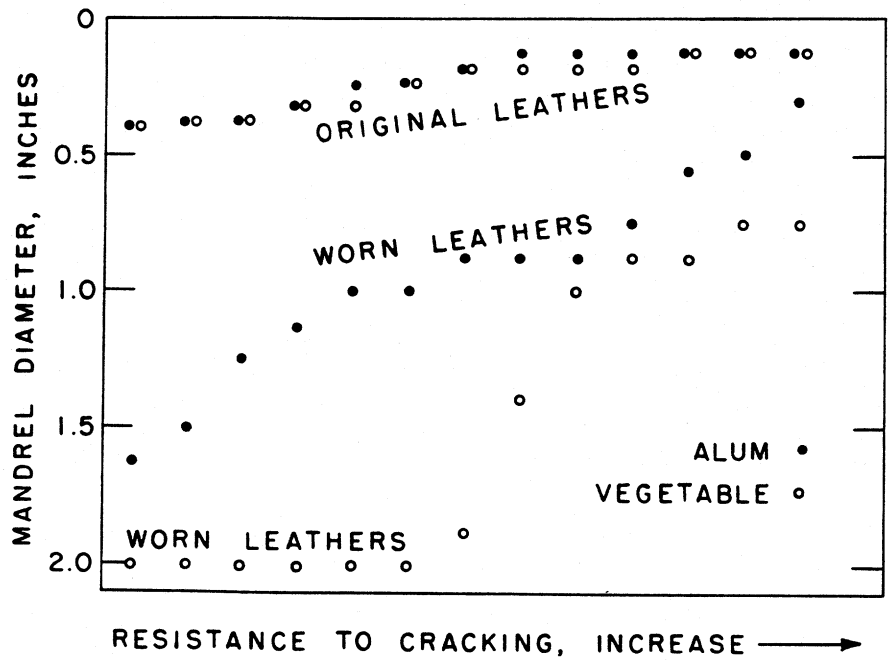

FIGURE 1.—Mandrel diameters at which original and worn leathers cracked on bending.

TABLE IV

Rating of Worn Insoles by Inspection

Number of Insoles

Rating Scale	0	1	2	3	4	5	6
Alum Retan	0	2	7	21	16	11	4
Vegetable	1	12	18	18	8	2	2

Soles suitable for repairing, 3 and above, Alum	—52	85%
Soles suitable for repairing, 3 and above, Vegetable	—30	49%
Improvement by alum retannage $\frac{85-49}{49} \times 100$		73%

given and was independent of the type of tannage, therefore, data from both tannages were combined to give the averages shown in Table V. The leathers in classes 0 and 1 were so badly deteriorated that samples often broke while being fastened in the strength tester and determination of breaking strengths was impossible. For this reason the arbitrary figure of 5 kilograms strength which has been used for this class is simply an estimated value. The figures in the second part of Table V are calculated from data in the first part of the table.

TABLE V

Deterioration of Insoles Based on Loss in Breaking Strength*

	Original Leathers			Worn Insoles			
	Vegetable	Alum Retan	Average	Classes 4, 5 & 6	Class 3	Class 2	Classes 1 & O
Breaking Strength in Kg.	92	96	94	70.5	58.2	29.6	5.**
Deterioration (loss in strength) %				25	38	69	95.
% of total vegetable insoles in various classes				19.7	29.5	29.5	21.3
% of total alum-retanned insoles in various classes				52.4	32.8	11.5	3.3
Total deterioration of vegetable-tanned insoles—%				57			
Total deterioration of alum-retanned insoles—%				37			
Strength remaining (100-Deterioration) vegetable insoles				% 43			
Strength remaining (100-Deterioration) alum-retanned insoles				% 63			
Improvement by alum retannage $\frac{63-43}{43} \times 100$				% 47			

*Since thickness measurements on worn insoles are not directly comparable with those made on the original leathers, breaking strength data instead of tensile strength data have been used.

**Since the condition of insoles in 1 and 0 classes was such that samples broke when being put in strength tester, an estimated average value of 5 kg. was used on these classes of worn insoles.

Discussion

The analyses of leather in Table I show the effects of alum retannage. The amount of combined tannin and the degree of tannage are increased; there is a corresponding decrease in the amount of soluble matter and soluble tannin. During wear the insoles have picked up a slight amount of oil and insoluble ash. There has been a decrease in soluble matter. In spite of this there has been a slight increase in the amount of soluble tannin and a decrease in the degree of tannage. This may indicate that wear has resulted in some detannage. If this detannage has some deleterious effect on the wear of the leather, the higher degree of tannage of the alum-retanned leather as compared with that of the vegetable-tanned leather would be beneficial.

According to the ratings in Table IV the alum-retanned insoles stood up in service much better than the vegetable-tanned insoles. Out of 61 insoles, 52 were included in ratings 3 to 6 thus showing greater resistance to service. In the case of the vegetable-tanned insoles only 30 of the 61 insoles were placed in groups 3 to 6. In Table IV it will be noted that about 85 per cent of the alum-retanned insoles are still serviceable while only about 49 per cent of the vegetable-tanned insoles are still serviceable. On this basis the alum-retanned leathers are 73 per cent better than the vegetable-tanned leathers.

A comparison of the data given in the tables shows that in every case there is a decided improvement resulting from alum-retannage. The figure of 73 per cent improvement shown in Table IV is probably the most valid as this indicates in a practical way the value of the insoles after being worn. This figure does not correlate with the value of 47 per cent improvement as obtained by breaking strength measurements on the original and worn leathers,

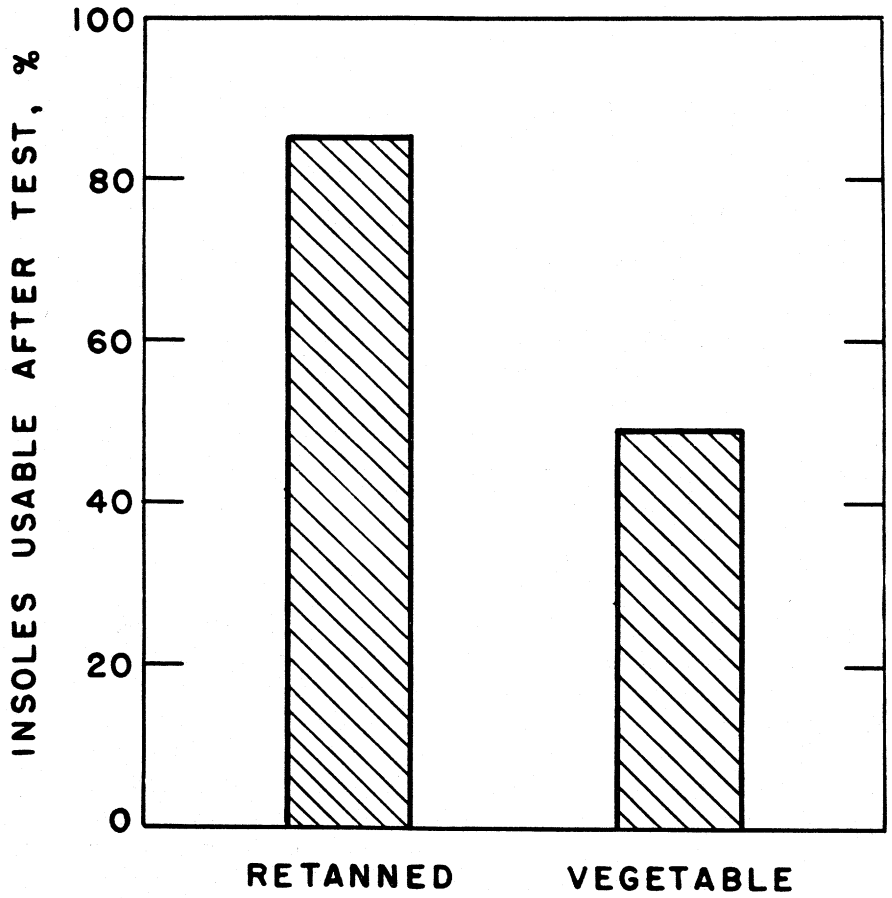

FIGURE 2.—Percentages of worn vegetable and alum-retanned insoles still serviceable after the test.

but does correlate quite well with the value of 81 per cent obtained with the insole testing machine based on tensile strength figures. The values for grain crackiness based on results obtained by bending specimens around mandrels of different diameters are not susceptible to simple mathematical comparison but Table III and Chart 1 show the superiority of alum-retanned leather to the vegetable-tanned leather.

It was mentioned that 5 alum-retanned insoles had considerably more Al_2O_3 than the average and that 5 had considerably less. It was hoped that these tests would give some further indication of the optimum amount of Al_2O_3 which should be present. However, it was found in each case that the number of samples was insufficient to rule out discrepancies due to the individual wear.

The wearers of the test shoes, in general, found them very comfortable. The only cases of discomfort were those usually attending the breaking in of new shoes and these were evenly divided between the two types of leather. Toward the end of the test, insoles which were badly cracked or deformed were uncomfortable irrespective of the tannage. There were no cases of discomfort reported that could be attributed directly to the use of alum-retanned insoles.

Conclusions

This series of tests demonstrates that the alum retannage process for making insole leather can be successfully applied in a commercial tannery to produce a satisfactory alum-retanned leather having an Al_2O_3 content ranging from 2.5 to 3.0 per cent.

The results of actual service tests in shoes and of laboratory testing of vegetable-tanned and alum-retanned insole leathers show that alum retannage increases the serviceability of insoles about 70 per cent and results in no noticeable deleterious effects on the wearer of the shoes.

Acknowledgments

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