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FOOTWEAR AND LEATHER SERIES
REPORT NO. 16

RAPID SOLE LEATHER TANNAGE
USING
DOMESTIC MATERIALS

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QUARTERMASTER RESEARCH & ENGINEERING CENTER
CLOTHING AND ORGANIC MATERIALS DIVISION

OCTOBER 1962

NATICK, MASSACHUSETTS

AD- Div. 14 Accession No.	UNCLASSIFIED	AD- Div. 14 Accession No.	UNCLASSIFIED
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In the storage tests, most experimental as well as conventional sole leathers, including those impregnated with rubber-resin mixtures, gained in fiber strength over a period of 1 to 2 years. However, all of them suffered serious losses in wet shrinkage resistance, indicative of a gradual hydrolysis of the collagen tannin combination. The losses are more severe in a hot-dry than in a hot-humid environment, and seem to differ also according to the aldehydes and other mineral or organic agents used for the tannage. The serviceability of the shoes worn in the field trial was not affected by these losses in wet heat (hydrothermal) resistance, although the leather was nearly 2 years old when the test was terminated.

The success of the new rapid-tanning process is explained in the light of the accumulated scientific knowledge which it uses.

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Natick, Massachusetts

CLOTHING & ORGANIC MATERIALS DIVISION

Footwear and Leather Series
Report No. 16

RAPID SOLE LEATHER TANNAGE USING DOMESTIC MATERIALS

Ludwig Seligsberger, Ph.D.

Functional Finishes and Leather Branch

Project Reference:
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Foreword

The present report is essentially a sequel to Report No. 11 of this series, "Tanning Heavy Leather with Aldehydes", since it brings the task set before the Quartermaster Research and Engineering Command to a successful conclusion.

This task was to explore the possibility of freeing the heavy leather industry from its dependence on imported vegetable tanning extracts. A stockpile of those materials is maintained by the U. S. Government mainly for the benefit of the sole leather manufacturers. A substantial part of their annual production is used in the footwear requirements of the Armed Forces.

In the Series Report No. 11, on the subject of heavy leather tannages, a way was shown to tan the heaviest steer bend within 24 hours by means of aldehydes, and to subsequently fill the leather with various high-molecular tanning or non-tanning compounds. The present report concentrates on using for this purpose large quantities of spruce extracts (or "lignosulfonates", as these waste products of the pulp and paper industry should rightfully be called).

The choice of aldehydes and their proper use was the main theme of the previous report; the subject of this report is the basic reasoning behind the use of lignosulfonates and the proper way of using them. The description of tanning trials is followed by discussions of two wear tests; the results of these tests show that leather made for Army purposes by the new tanning process with domestic materials is equal to, if not slightly superior to, the present standard leather for outsoles and innersoles.

The splendid cooperation of Armour Leather Company and Howes Leather Company in turning over their facilities to pilot-plant experiments is gratefully acknowledged.

S. J. KENNEDY
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Abstract

The problem of providing domestic replacements for imported tanning materials in the manufacture of heavy leather is discussed. Previous studies undertaken mainly to cover military emergency requirements are reviewed. A new approach taken by the Quartermaster Corps came after a thorough exploration of the tanning properties of aliphatic aldehydes. These studies culminated in the development of an original rapid-tanning process for sole leather using glyoxal and formaldehyde in fairly concentrated solutions of mild alkalies, followed by the fixation of lignosulfonates from heated liquors. Bleaching and loading operations were conventional, except that no imported extracts were used. The entire tanning process requires only 3 to 4 days if drums are used throughout (as for insole leather) and about twice as long if the fixation of lignosulfonate takes place in rocker vats.

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RAPID SOLE LEATHER TANNAGE USING DOMESTIC MATERIALS

INTRODUCTION

1. Dependence of tanning industry on imports

Vegetable-tanned leather is used by the Armed Services mainly as soling material. The men's dress oxford, for instance, uses a leather outsole and insole. The combat boot uses a leather midsole and insole.

The manufacture of this type of leather requires substantial quantities of vegetable extracts. Before World War II, less than half of them were of foreign origin, but today imports take care of almost the entire needs of the industry.

The magnitude of the imports may be seen from figures representing the three extracts which in modern tanning processes are most important. The U. S. imports of these extracts for domestic consumption were as follows (in long tons of 100% tannin) (1):

	<u>1950</u>	<u>1960</u>
Quebracho	57,000	27,600
Wattle	15,800	6,500
Chestnut	550	5,100

In order to alleviate the potentially dangerous dependence of this country on foreign sources, the U. S. Government, in the years 1951 to 1953, stockpiled all three of these tanning materials in substantial amounts (2).

In addition to this stockpiling program, the Munitions Board, fully aware of the serious problem existing in sole leather manufacture, also recommended "under a high priority, a research and development project for the evaluation and exploration of synthetic tanning materials."

2. Previous efforts to provide domestic replacements

Several agencies of the Federal Government have tried to develop domestic tannages for sole leather. The first successful project including a tanning and field trial was conducted by the Quartermaster Corps using Orotan, a domestic "exchange" sytan (3, 4). The performance of the outsoles and insoles made from Orotan was at least as good as that of soles produced by conventional tanning materials and probably somewhat better (5).

Another project, conducted by the Department of Agriculture, was concerned with the cultivation of canaigre, a tannin-bearing root of the American Southwest, with the preparation of a tanning extract from this plant and with the manufacture of heavy leather by a process using only this extract (6). The Quartermaster Corps supported this project by conducting a wear test which demonstrated the possibility of making sole and insole leather with canaigre extract (7).

At the present time the Department of Agriculture is working on a new project exploring the tanning potential of starch dialdehyde (8). Sole leather has already been manufactured using this oxidized starch product in conjunction with vegetable extracts (9a). In this project, domestic materials were not used in their place, and the resulting leather, therefore, does not represent a full substitution for imported supplies comparable to canaigre or Orotan-tanned leather.

Orotan is being used by many tanners today as a secondary ingredient of vegetable blends for the tannage of heavy leather. Up to the present, however, Orotan cannot be produced at a cost sufficiently low so that the tanner can be induced to use it on a wide scale or that the Army, in peace time, could justify a directive requiring its use for military items.

Similar conclusions were reached about canaigre (10a). At current market prices for importing vegetable tanning extracts, canaigre cannot be expected to attract investment capital. Canaigre shares this disadvantage with other projects aimed at replenishing domestic supplies of tannin-bearing plants or at using waste barks (2, 11, 12, 13). One very important reason for this is that these materials are not generally found near existing plants. On the other hand, because of high transportation costs, long hauls of cheap raw materials are not worthwhile (10b).

3. Present approach: lignosulfonate

The approach of the Quartermaster Corps, therefore, was different in this respect: the need for using an existing inexpensive substitute for vegetable extracts was recognized. The pulp and paper industry has actually offered the tanner such a raw material, ordinarily referred to as "spruce extract" or misnamed "sulfite cellulose extract" and consisting chiefly of water-soluble lignosulfonate. This product is well known for its high affinity for hide substance, although it is not considered in the strictest sense a tanning agent; but much of it is still going to waste in spite of many years of effort to introduce it into the tanning industry. At the most, only a small part of lignosulfonate is added to the sole leather blends now in use.

The producers of lignosulfonate offer several brands, which differ mainly as to the origin of the lignin or as to the degree of fractionation. In laboratory trials described earlier (9) the sodium salt of a fractionated hardwood lignosulfonate was selected for this study because of the consistently higher degree of tannage obtained by it.

In times of emergency, interest in lignosulfonate is aroused and attempts are made to increase its contribution to the tanning of heavy leather. But a search of the international literature did not reveal any systematic investigation of the serviceability of shoes soled with leather in which lignosulfonate had been used as either a major component or to the exclusion of any other vegetable extracts.

It was felt that the results of past experience could be used to advantage in conducting tanning experiments with lignosulfonate, but that these should be supplemented by wear trials in order to arrive at definite conclusions as to lignosulfonate's suitability. Furthermore, it was considered essential to apply lignosulfonates in a rapid tanning process in order to demonstrate their versatility. Studies cited above, using Orotan and canaigre as substitute tanning agents, did not combine their use with efforts to cut tanning time. However, in order to remain competitive, a speedier tanning process without a sacrifice in quality is probably the most urgent immediate problem for the sole leather industry.

PART I NEW ALDEHYDE LIGNOSULFONATE RAPID TANNAGE

1. Developments leading to new rapid tannage

The new type of rapid tannage described in this report will be later referred to as a "domestic tannage" in the sense that it uses only domestic tanning materials. However, the new process also uses three other significant advances in tanning methods:

1) The discovery of a new aldehyde tanning process in connection with the fundamental study on the tanning properties of aliphatic aldehydes undertaken by the Quartermaster Research and Engineering Center Laboratories (9b, 14, 15).

2) The introduction of a rubber-resin treatment for sole leather as a military requirement (16), based on Navy-sponsored work by the National Bureau of Standards (17). In field trials, outsoles impregnated with the proper materials gave up to 35 percent more wear than the oil-treated outsoles which had been standard until 1959 (18).

3) The improvement of insole durability by a retannage with chrome or alum, as demonstrated respectively in wear trials by the Quartermaster Corps (19) and by the U. S. Department of Agriculture (20). Although chrome is now used in preference to alum for military procurements under the insole specification KK-L-159, alum remains an alternate in case of emergency and, therefore, was considered the proper mineral tanning agent to be used for a purely domestic insole tannage. It was further decided to use the alum on shoulders and bellies in a drum process. This way of making insole leather appears to be the most rapid and most economical, especially by comparison with the dipping of racks of cut soles into chrome liquors which is widely practiced.

The double "dry dip" described by the USDA (20) is costly and impractical, although more effective than immersing cut insoles into alum solutions. In the latter process, very little alum was picked up by the insoles and consequently the good performance of earlier wear trials could not be repeated with this leather (19). The poor ratings were unexpected and are probably in part responsible for the fact that alum-retanned insoles have not been reinvestigated for their wearing qualities since 1956.

2. Principal features of new process

The salient features of the new tanning process as stated before (9c), are as follows:

1) The hides are conditioned in aqueous solutions of alkali carbonates and bicarbonates strong enough to give a normality of at least 1.0 after reaching equilibrium with the water volume inside the hides.

2) The hides tanned in these solutions with mono- or dialdehydes are rapidly "neutralized", not by rinsing, but by the gradual addition of dilute acids or acidic salts, until a pH of 5.0 or lower has been attained.

3) The neutralized hides are immersed in fairly strong ligsulfonate solutions, the pH of which is gradually decreased.

4) The hides are loaded and at the same time their pH is re-adjusted to slightly above 3.0.

3. Aldehydes used

The aldehydes which can be used in this process are formaldehyde and glyoxal; both are manufactured on a large scale by U. S. chemical companies. Formaldehyde is available as a 37 percent solution, glyoxal as the polymeric hydrate in 30 percent solution. Imported polyglyoxal in solid form has also become available.

Formaldehyde is, on the basis of strength, still considerably less expensive than glyoxal. Nevertheless, glyoxal was the preferred tanning agent for the following reasons as discussed earlier (9d), i.e.:

1) On the plant scale, glyoxal can be handled with ease, since it does not irritate the mucous membranes as formaldehyde does; on the contrary, it has a pleasant smell and no known toxic effects which would require the setting up of threshold limits in the atmosphere.

2) Glyoxal, being a somewhat larger molecule, appears to give fuller leather than formaldehyde.

Glyoxal imparts a pleasing buff color to the leather; the tanner is more accustomed to this than to the pure white color that would result from a straight formaldehyde tannage.

A small percentage of formaldehyde is used with the glyoxal for the following reasons:

1) A uniform cream color is obtained throughout all layers of the hide, whereas glyoxal alone leaves the center layer white.

2) A full tannage is secured even in the event that considerable amounts of glyoxal are destroyed because of lack of control over a temperature rise during the tannage. It has been pointed out that glyoxal undergoes the Cannizzaro reaction in alkaline solutions and that all possible precautions should be used to avoid heating-up of the stock (15).

Other aldehydes have been successfully used instead of formaldehyde or glyoxal, under precisely the same conditions, for instance, glutaraldehyde (9e) and dialdehyde starch (also called "oxy-starch") (9f). But for the time being these aldehydes cannot compete in costs with formaldehyde and glyoxal and there was no further work using them beyond the small-scale tanning experiments already reported.

4. Steps to maintain low temperatures

The required low temperature, 15 to 25°C (59 to 77°F) at the outset and a 30°C (86°F) maximum at the close of the tanning process, could be easily maintained in small-scale experiments, but presented some difficulties in the drum tannage of larger packs of hide. Practical steps that were used or could be used in this instance include:

Reducing the drum speed to 8 to 9 rpm,

Moving the stock intermittently,

Cooling liquors and stock to the same temperature, preferably below 21°C (70°F) before the start of the tannage.

5. Successful combination with rubber-resin impregnation method

The development by the National Bureau of Standards of a new and very effective impregnation method (with a rubber-resin mixture) for sole leather found industry-wide acceptance at approximately the time the Quartermaster Corps' domestic tanning process using aldehydes and lignosulfonate was tried out on a pilot-plant scale. A combination of these two methods was therefore possible. In the two tanneries where it was tried, it turned out to be eminently successful. Several factors played an important part in this success:

A rubber-resin impregnation determines wearability to such a degree that differences in the choice of materials and in the duration of the preceding vegetable tannage become irrelevant.

In rubber-resin impregnated sole leather, "color" has become immaterial. Such leather varies in shade from light to dark brown, regardless of the type of tanning materials used. Originally, efforts were made to restore the light color of conventional sole leather after the impregnation (21), but today the dark color typical of the rubber-resin treatment has been generally accepted.

Proper impregnation, (i.e., thorough penetration and sufficiently large pickup) is difficult to obtain on cut stock of conventionally-tanned leather; such stock, however, can be impregnated much more economically than entire bends. When the leather has been tanned with domestic materials, it is less dense and allows the impregnation to proceed faster and to deposit more resin and rubber than conventional leather does under the same circumstances.

6. Methods of validation

The new tanning process was explored in three directions by:

1) Manufacturing leather in plant equipment (i.e. pilot plant runs in two tanneries).

2) Periodic testing of such leather for storage stability in three Quartermaster climatic chambers simulating temperate zone, desert and tropical surroundings. The principal features of these storage chambers have been described (22, 23).

3) Wear-testing of low quarter shoes furnished with the domestically-tanned sole and insole leather. First, the cooperation of about 100 employees at the Quartermaster Research and Engineering Center was obtained for an informal test, using part of the production of one tannery. Later a larger and more comprehensive test was conducted by the Army's Field Evaluation Agency at Fort Lee, Virginia (24). In this test the outsole and insole leather produced in another tannery was used.

PART II PILOT PLANT RUNS

1. Scope of three tannery trials

The first tannages in tannery equipment were run on a very modest scale (9g). After the aldehyde tannages, a commercial vegetable blend was applied either in a drum or in rockers. The leather was used for storage stability studies only. In a previous paper (16) the changes in bursting strength of this leather over a 1-year period have been reported. In the meantime, these studies have been expanded to cover 3 years. At the same time, T_s (shrinkage temperature) measurements covering the same time interval (3 years) have been compiled.

In a second tannery (Lot A) a number of trials were run; this series was concluded by an experiment involving 20 hides which has been described in the above-cited paper (15). The resulting bends were used for storage tests and as outsole and insole components for the above-mentioned informal wear test. The insoles were not given any after-treatment; this was so that the perspiration resistance of a straight aldehyde-lignosulfonate tannage could be tested.

Finally, in the third tannery (Lot B) 25 hides were tanned by a very similar process. However, the bends alone were transferred to rockers to be "retanned" with lignosulfonate and then loaded with more lignosulfonate and some Orotan. The bellies and shoulders were drum-tanned with lignosulfonate and alum and finished out as insole leather. Both types were used for the previously-mentioned wear test at Fort Lee, and were also placed in the Quartermaster Climatic Chamber for storage stability studies.

2. Tanning process for two large tests

The two large pilot plant tannages are presented side by side in Table I, under the heading "A" and "B". Lot A was subdivided, as described in the original paper (15), with one half of each hide delimed to pH 6.8 by additions of small amounts of formic acid. Lot B was more fully delimed in a paddle by 1.0 percent ammonium chloride and 0.7 percent formic acid (90%), on the white weight. The next day, the pH of the paddle liquor was 4.3. The hides were pulled for stamping, and the paddle was drained, rinsed and filled with fresh water to the height of 1 foot. Then the required amount of soda ash was added, and dissolved with steam and air-plunging. Only then was the sodium bicarbonate added, together with just enough water to avoid any losses from overflow after adding the stock.

In the new tanning process for sole leather (as shown in Table I) the stock passes through four stages. These are listed and discussed immediately after Table I which follows.

TABLE I RAPID SOLE LEATHER TANNAGE PROCESS*

Procedures and Materials

		<u>Lot A</u>	<u>Lot B</u>
1. <u>Alkalizing (in paddle)</u>			
Ratio, hide to liquor, (approx.)		1:5	1:3.33
Ratio used, Na ₂ CO ₃ : NaHCO ₃		1:0.8	1:0.75
Na ₂ CO ₃ (per 100 gal.), lb.		52	76
NaHCO ₃ (per 100 gal.), lb.		42	57
Running schedule, hr.	run	2	4
	stop	4	
	run	2	
Paddles are left alone for 2 days:			
Lot A: turning 1/2 hr. each day			
Lot B: without turning			
Final Temperature, °C (°F)		21 (70)	-
Final pH value (liquor)		9.5	9.35
Normality (total alkali)		1.2	1.58
2. <u>Aldehyde Tannage (in drum)</u>			
Volume of alkalizing liquor transferred, gal.		80	120
<u>Glyoxal</u> (30%), diluted with 10 gal. water			
(in feeds), lb.		70	50
<u>Formaldehyde</u> (36% minimum), added with last			
feed of glyoxal, lb.		10	15
Running schedule, min.	run (1st feed),	30	10
	rest	30	15
	run (2nd feed),	30	10
	rest	30	15
	run (3rd feed),	60	10
	rest	30	30
	run (4th feed),	90	10
	rest	-	30
	run (5th feed),	-	10
	rest	over night	
	run (next a.m.)	5	5**
Drum speeds: 1st day, rpm		7-8	20
2nd day, rpm		17-19	20
Final shrinkage temperatures, °C (°F)		88(190.5)	87(189.5)

*Note: All quantities are based on 1000 lb white weight.
Actual white weight: 1280 lb in A, 1920 lb in B.

** Drum was not equipped with reducing gear to lower speed, heated stock up to 36°C (97°F).

	<u>Lot A</u>	<u>Lot B</u>
3. <u>Lowering pH Value (in drum)</u>		
Discard 1/3 of liquor or gal. (approx.)	50	55
Sulfuric acid, lb.	90	85
Total running time, hr.	2.5	4.0
Final pH value (liquor)	3.6	3.5
Final pH value (hide cubes, in water 1:20)	-	4.6
4. <u>Rocker Processing</u>	<u>Sides</u>	<u>Bends*</u>
Liquor prepared with sodium salt of hardwood lignosulfonate**		
1st day, Barkometer	44°	49°
temperature, °C (°F)	49(120)	50(122)
pH value	2.6	3.0
time rocked, hr.	24	16
Barkometer, after this time	44°	50°
2nd day, Barkometer	58°	60°
temperature, °C (°F)	49(120)	45(113)
pH value	2.2	2.9
time rocked, hr.	24	24
Barkometer, after this time	56°	60°
3rd day, Barkometer	56°***	65°
temperature, °C (°F)	49(120)	48(118)
pH value	2.2	2.6
time rocked, hr.	3****	2
4th day, Barkometer	-	75
temperature, °C (°F)	-	48(118)
pH value	-	2.6
time rocked, <u>days</u>	-	3****
5. <u>Subsequent Routine Operations</u>	stock is rinse- rocked for 1 hr. and pulled; bellies are cropped off; stock is bleached and wrung.	stock is pulled, bleached and wrung.

* For tannage of bellies and shoulders see table II.

** In Lot A partially consisting of leftover liquor from preceding runs, in Lot B initially 1350 lb. and for strengthening 600 lb.

*** Liquor from 2nd rocker, not strengthened.

**** Not reheated every 24 hrs. as before, therefore cooling slowly to room temperature.

6. Loading or extracting
(in oil wheel)*

	<u>Lot A</u>		<u>Lot B</u>
	<u>backs</u>	<u>bellies</u>	<u>bends</u>
Actual wrung weight, lb.	800	330	920
Orotan, lb.	25	25	30
Sodium acetate, anhydrous, lb.	6	6	10
Epsom salt, lb.	40	30	50
Corn sugar, lb.	36	30	40
Filler, lb.	30	25	60
Oil emulsion, lb.	12.5	15	12.5
Time running, min.	55	50	45

Stock hung over night to
sunny, set out and hung in
loft to dry, conditioned,
rolled, etc., in conventional
manner**

Finished weight, lb.	Actual	490	180	540 [est.]***
	Mean, per unit	12-1/4	4-1/2	10-3/4

*Per 1000 lb. wrung weight

**Except for alternate rights and lefts of Lot B which were impregnated
by rubber resin mixture

***Estimated on the basis of actual weight of 24 of 50 bends

The four stages of the new tanning process are as follows:

1) Alkalizing, which has the function of equilibrating the
hides with non-swelling alkalizing liquors as postulated in the original
paper (26) and in the patent (14), the suitable range as cited in the
latter to be preferably between 1.0 to 2.5 normal.

2) Aldehyde tannage, in a "short" liquor, by gradual addition
of small portions of glyoxal and/or formaldehyde, which raise the T_g of
the stock in a few hours to the vicinity of 90°C (194°F).

3) Lowering pH value or acidification in drum by the gradual
addition of strong acids; formic and hydrochloric acid have successfully
been used as well as sulfuric acid, for the purpose of obtaining a pH
of 3.5 to 4.0. This operation is the shortest of all, and routinely
should not take more than 2-1/2 hr.

4) Rocker processing, taking advantage of the affinity of
aldehyde-tanned hide for vegetable tanning extract, syntans and lig-
nosulfonate. In the above examples lignosulfonate was used by itself,
but blends with vegetable and synthetic tanning agents were used in
earlier trials (9h, 15). The rocker solutions were analyzed by the

participating tanneries which submitted the figures presented in Table III. Subsequent operations are routine except that the "extracting" or loading can be modified, as shown in Table I, to exclude any imported materials.

3. Possible variations of new process

The stock passed through all four operations in 9 days, but remained rather immobile for 2 days after alkalization and for 3 days after the rocker had been reheated and strengthened for the last time. These rest periods were dictated by convenience and not by necessity.

a. Alkalizing

The same is true of the use of paddles and drums. The use of drums for alkalizing the stock is more economical than the use of paddles (15), but was ruled out because, in general, heavy leather tanneries have no drums to spare. Drums, therefore, were used only for milling the alkalized hides in aldehyde solutions in preparation for immersing them in rockers in relatively strong extract solutions, thus hastening the tannage by many days or weeks. The only exception was the making of insoles from the bellies and shoulders of lot B in a drum, as outlined in Table II.

The relationships between the quantities of lignosulfonate used and the weight of the finished leather can be established for B only (Table II). As shown near end of Tables I and II, in this test, equal amounts of sole leather bends and of alum retanned shoulders and bellies were produced, i.e., 540 lbs. each. The manufacture of the bends required 1950 lbs. and the making of the insole stock 400 lbs. of lignosulfonate. It must be borne in mind also, that the two lignosulfonates differ: In the rocker a refined hardwood product and in the drum the unfractionated product (which costs only about 1/3 as much as the former), are used. Economy demands, therefore, that the rocker system be designed for circulating of lignosulfonate liquor, while the drum liquor is discarded. Since, however, in each tannery only one lot was tanned, strengthening served as a substitute for cycling. A tanner who wants to use similar liquors in a regular tan-yard can empirically arrive at the proper number of rockers for his purpose, which probably will vary from 3 to 6. An interesting system which may be adaptable to large-scale operations was developed in the laboratory for lignosulfonate blends with commercial vegetable extracts (25).

It should be pointed out that it is possible to re-use the alkaline bath in the paddle 6 to 8 times, as was done in unpublished small-scale Quartermaster experiments. In this case it is advantageous to delime the stock before by weak acids in place of ammonium salts. The latter, by forming additional compounds with aldehydes will inactivate them and therefore should not be allowed to accumulate in the liquor or hides.

TABLE II RAPID INSOLE LEATHER RETANNAGE (LOT B)*

(Drum retannage of bellies and shoulders** of Lot B after their separation from bands which are processed in rockers)

- | | |
|---|----|
| 1. Aluminum sulfate ($Al_2(SO_4)_3 \cdot 24H_2O$), lb., | 75 |
| in 3 feeds, 2/5, 2/5 and 1/5 of total *** (dissolved in water gals) | 18 |
| Sodium acetate, anhydr., lb. (dissolved in last feed of alum) | 15 |

Followed by:

- | | |
|---|----------|
| 2. Sulfite cellulose (added dry), lb., in 3 feeds, $\frac{1}{2}$, $\frac{1}{4}$, and $\frac{1}{4}$ of total | 480 |
| Running time (min.), 1st feed | 120 |
| 2nd feed | 75 |
| 3rd feed, next a.m. | 60 |
| 3. Oil emulsion, lb. ($\frac{1}{2}$ hr. after 1st feed of sulfite cellulose) | 31.5 |
| Temperature (all feeds), °C (°F) | 60 (140) |

Stock pulled, piled on truck, covered 3 days, set out and hung to dry.
Finished conventionally

Actual Finished weights (approx.), lb.	540
Mean finished weight per belly, lb.	5.4
Mean finished weight per shoulder, lb.	5.34

* All quantities based on 1000 lb. drained weight

** Actual drained weight 836 lbs.

*** 1st feed in drum before adding stock, 2nd feed after 10 min.,
3rd feed after 60 min. running time (20 rpm)

TABLE III ANALYSIS OF LIGNOSULFONATE LIQUORS IN RAPID SOLE LEATHER TANNAGE
DESCRIBED IN TABLE I

	<u>Lot A</u>	<u>Lot B</u>
<u>1st day (before adding stock)</u>		
Total Solids %	10.6	11.4
Insolubles %	.13	.18
Non-tannins %	5.55	5.18
Tannins %	4.95	6.05
Purity	47.1	53
<u>2nd day</u>		
Total Solids %	13.8	not
Insolubles %	.04	analyzed
Non-tannins %	7.60	
Tannins %	6.13	
Purity	44.6	
<u>Last day (before dumping)</u>		
Total Solids %	12.5	16.9
Insolubles %	0.0	0.2
Non-Tannins %	7.5	8.1
Tannins %	5.0	8.6
Purity	40.0	51.5

In order to restore the strength of the alkalizing bath, all that is needed is to add dry sodium carbonate and bicarbonate in the same ratio as in the original solution. No more than 24 hours seem to be necessary to reach equilibrium; this means that a tanner pressed for time can lob off 2 days in the first stage of the process.

In drums, alkalization of the stock can be accomplished by milling for 2-1/2 hours at 18 rpm, resting overnight and milling 1 more hour the next morning.

b. Aldehyde tannage

The mechanism of the aldehyde tanning process has already been discussed above, on the basis of previous papers on the subject (9, 15, 26). In the interest of economy, glyoxal should not be used when the temperature in the drum cannot be properly controlled and when it would rise unduly during milling. Formaldehyde, on the other hand, does not undergo decomposition by the Cannizzaro reaction as glyoxal does. When fed in small portions, 2 to 3 percent formaldehyde (36% minimum), on the white weight, may suffice to penetrate the heaviest parts of a hide and raise the T_g to 91-92°C. (196-198°F).

c. Lowering pH

In order to save time in acidifying the tanned stock, the spent tan liquor was drained and discarded. However, this step is unnecessary and probably uneconomical. Once the proper amount of acid for a given load has been found, the lowering of the pH proceeds rapidly, without interruptions for sampling at frequent intervals and should be accomplished within 2 hours. Another 30 minutes of drumming would assure the tanner that equilibrium has been attained. Slow feeding of acid in the final stage--not exceeding 1/4 of 1%, on the white weight per load--and cutting a hide sample from the butt area into small slices for the purpose of shaking them in a small volume of water for a few minutes and then taking the pH of the slurry, are recommended as means for standardizing the conditions at the end of this phase.

Technically important in this operation is the use of a drum which allows the rapid escape of the carbon dioxide gas evolving during the acidification of the stock. Drums open at both ends should be used. Otherwise, pressure may build up that can destroy the drum or cause losses in the hose or pipe line or in the tub from which the acid solution is fed.

d. Rinsing

Before the stock is transferred to the rockers, it may be rinsed or wrung out. Neither operation has been practiced in the tanning trials so far, but the advantages are obvious: The solutions in the rocker vats would more rapidly penetrate, and excess salts from the drum liquors would not accumulate in the saps. In a rocker system with circulating liquors, it would be very important to keep the concentrations of the salts low.

4. General principles in the use of lignosulfonates

Originally lignosulfonates were manufactured from spruce and popularly called "spruce extracts." Today this is a misnomer, since all trees, hardwood and softwood alike, are used in making paper and hence are a source of lignosulfonate.

a. Statement of Czech scientists

The high affinity of hide substance for the extract was discovered many years ago and has attracted the attention of leather technologists ever since. One of the most concise statements of prerequisites for the best use of lignosulfonates was formulated by scientists supervising large-scale experiments by Bata in Zlin, Czechoslovakia, (27, 28). They stressed meeting the following conditions:

- 1) Keeping the hides from swelling unduly during tannage,
- 2) Raising liquor densities above 1.06 (= 60° Barkometer),
- 3) Maintaining a pH lower than 2.5,

- 4) Maintaining purity by sewerage and strengthening cycled liquors generously.
- 5) Using lignosulfonates before (and not together with) vegetable extracts.

To insure rapid penetration, the first point above made by Wagner (28) is of paramount importance. A few years earlier Vogel (29) had already used formaldehyde (F) in an attempt to depress the swelling of hide before putting it in a lignosulfonate liquor. Gustavson states (30a) in general terms that a formaldehyde pretannage is used "to maintain the degree of swelling of the hide which has been attained by a given pretreatment". Evidently, if a flaccid state is desirable in contact with lignosulfonate, it is still better to keep the stock in a flaccid state throughout the preceding operations. The difficulty arose from the fact that one did not know how to avoid any osmotic swelling while taking advantage of the increase in aldehyde fixation at pH values above 8 (31). Here the new tanning process, as characterized briefly in paragraph 2, Part I, filled a long-felt need. The hides, after alkalizing, look and feel like pickled stock and undergo no change in thickness or plumpness while they are being tanned with formaldehyde or other aldehydes.

b. Preheating liquor

The other 4 points of the Czech scientists stated above are also reflected in the manner the lignosulfonate liquors was used. In addition, the liquor was preheated and kept for 3 days at an elevated temperature. The use of heat did not seem to cause any detrimental effects while it was speeding up penetration, but heat is probably not essential for the success of the tannage.

c. Blending with vegetable extracts

In the United States lignosulfonate is mostly used in conjunction with vegetable extracts. A blend of this sort, containing 30% lignosulfonate, has been used by the author in a test reported earlier (15). A 60% degree of tannage was obtained. It may seem surprising, in the light of this result, that the Bata scientists are opposed to the practice. Apparently they are skeptical whether vegetable extracts are preferentially taken up from blends containing large quantities of lignosulfonate of one kind or another.

On this point, American research workers presented evidence in favor of the assumption that the materials are taken up by the hide at the same ratio as they are offered (25). Japanese technologists, on the other hand, showed (32) that above pH 4.0 the tannins of chestnut are taken up faster than lignosulfonate, and concluded that differential absorption can be controlled by adjusting the pH of the liquors. It can be argued, of course, that the poor use of lignosulfonate at higher pH values can be tolerated in view of its low cost. It would be much more serious if the take-up of the vegetable tan were impaired. The other point of view also has merit: If the optimum for lignosulfonate fixation is

below 2.5 pH--a fact for which the evidence is overwhelming (33, 30b)--every effort should be made to profit from it.

The quantities of mineral acid needed to lower the pH to about 2.5 are not excessive. In a rocker vat for 50 bends with about 2,000 lb lignosulfonate, a total of 50 lb of concentrated sulfuric acid was required. Bleached and transferred to the oil wheel, this stock needed 9 lb anhydrous sodium acetate to acquire a pH of 3.4, representing a rise of about 0.3 pH units; after finishing the leather as usual, physical tests (table IV) showed, as expected, that the low pH of a lignosulfonate liquor is no more harmful to a hide than a strongly acid pickle solution.

The feeding of acid to the rocker vats does not represent as much of a problem as the dosage of the sodium acetate in the oil wheel. About 40 to 50% of the acid was present in the rocker before the bends entered. The rest was added the next day for lot A and within 3 days for lot B. Such differences in technique do not seem to influence the quality of the leather. However, the slightly lower degree of tannage of lot B can be traced back to the pH of the vat liquor for it which was never lower than 2.6, whereas the pH of the vat for lot A for several days was as low as 2.2 (table I).

d. Degree of tannage and pH

The connection between degree of tannage and pH was illuminated by the following experience in a laboratory tanning trial. Because of a poor estimate of the quantity of sodium acetate needed for a number of specimens, these specimens had, after drying out, a pH of 3.6 to 3.7, and so they were rewetted and milled with dilute sulfuric acid. When dried out again, their pH was 3.0. The chemical analyses before and after this pH adjustment for the 2 experiments are as follows:

	<u>% Water Solubles</u>		<u>Degree of Tannage</u>	
	Exper. 1	Exper. 2	Exper. 1	Exper. 2
Before pH adjustment	39	37	43	47
After pH adjustment	35	31	52	58

The improvement in the degree of tannage, as a consequence of lowering the pH, is obvious. The pH reached is considered the borderline below which the stability of leather may be imperilled.

e. Loading procedures

The time-honored practice of loading the sole leather with epsom salt and sugar was not changed. Filler and "oil mix" were used as prepared by the respective tanneries. As is the custom, the liquor volume was sufficiently small to allow for nearly complete exhaustion. However, the operation differed from the ordinary loading in that less of the "oil mix" and no vegetable extract or lignosulfonate were used. Instead, a

small percentage of Orotan, a domestic sytan derived from phenol, was used, in view of the objective that no imported materials be used.

The impregnating process used on half of the bends from lot B was not supervised. Nor was the nature of the impregnants determined by differential analysis. However, as far as the distribution of the extractable matter between chloroform and acetone is concerned, the resulting leather conforms to the requirements.

5. Testing methods for finished leather

Most of the tests on the finished leathers were made by the methods described in Federal Specification KK-L-311. The leather specimens required for these tests were taken from the locations designated in the Methods Book of the American Leather Chemists Association (page 115). Six matching backs of lot A and seven bends and seven shoulders of lot B were sampled. The exceptions are density, bursting force, shrinkage temperature and water absorption which were determined on specimens from the butt area which also served for the storage tests.

Three of the last-named test methods are not described in Federal Specification KK-L-311a. Density was obtained by dividing the weight of the die-cut specimens for compressibility by their volume before compression. The burst figures were obtained with the 1/8" plunger (34,38) on a converted Mullen Tester. Correct shrinkage figures were obtained only after extracting 1/4"-wide strips of leather with chloroform and soaking them subsequently for 16 hours in individual test tubes while applying a vacuum (35).

6. Properties of finished leather

a. General qualities

Probably the most remarkable property of the finished backs and bends was their flexibility, which is about the same as that of the flexible-type sole leather currently in demand. Color of the grain was rated "good" to "very good" by experienced tanners, but its looseness and openness were criticized. No drawing and wrinkling was evident in the bend area, and only a relatively small amount in the shoulder region.

Finishers' comments on the bends of lot B showed a slight concern over their tendency to wet in more quickly than regular leather. However, they did not cause trouble in rolling and behaved normally in all other respects. Assuming the weight of finished bends to be 52% of the white weight, the yield was 54.3% as against 61.4% for regular leather of the same weight class (12 to 12.5 lb). The weight of the shoulders and bellies, on the other hand, was reported to be normal. The bellies wetted with difficulty, evidently because of the presence of aluminum oxide, but once they were properly wetted they behaved normally. Shoulders "wet in" the same as regular stock.

b. Appearance of insole leather

The color of the insole leather from lot B was lighter than that of the usual alum retan made by the same tannery. This leather also smelled of lignosulfonate, while the sole leather did not. The reason for this is probably that the water solubles in the shoulders and bellies were above 40%, as compared with approximately 25% for the two lots of sole leather.

Also, the insole leather was not noticeably cracky and appeared to be tanned through uniformly. Surface stains were visible on bellies, but are not considered of critical importance, since insole leather is always degraigned. The superintendent of the tannery where lot B was made summed up his evaluation of the leather in these words: "It is quite evident that leather can be made by means of a tannage using domestic materials only" which was "the prime purpose of the experiment".

c. Chemical and physical qualities

The measurable chemical and physical properties are presented in table IV. On the whole they are no different from those of regular leather of the same type and also conform to the few requirements of the respective specifications (36).

d. Straight sole leather

Straight sole leather deviates only in hide substance (which should be 44% or lower) and in degree of tannage (which should be 61% or higher). It also passes the test for compressibility (16% maximum), the only physical test that is required at present (besides thickness, which is a part of every purchase description).

In order to raise the degree of tannage from slightly below 50 to a bit higher than 50, it is necessary only to aim at a pH closer to 3.0 in the finished leather instead of ending up with leather of pH 3.3 to 3.4, as lots A and B of table IV did. Probably a little more acid in the rockers or a little less acetate in the oil wheel would have accomplished this: the example cited in paragraph 4b above illustrates the point. On the other hand, laboratory tests designed to substantiate published claims that still higher degrees of tannage can be reached with lignosulfonate (37) were unsuccessful. In the exhaustive Czech study mentioned earlier (27) one finds the statement that lignosulfonate leathers usually have a degree of tannage of 40 to 50. Gustavson confirmed these results in numerous experiments conducted at various pH values ranging from 1 to 8 and sometimes higher (30b, 33). By blending with vegetable extracts it is, of course, easy to reach the minimum figure of the specification for "degree of tannage."

e. Impregnated sole leather

Impregnated sole leather passes in all respects the requirements listed for type III in amendment 1 of the original sole leather specification (36); this type represents a chrome-free impregnated sole leather. Not only

is the minimum requirement for hide substance very much lower than the figure given in table IV for this leather, but the requirement for a certain degree of tannage has been dropped and the upper limit for compressibility has been slightly raised (to 18% as compared to 7.3% in table IV). The three new requirements (for shrinkage temperature, acetone solubles and water absorption) are met. In the case of shrinkage temperature, the result did not exceed the minimum value of 75°C (167°F), since lignosulfonates alone do not elevate the shrinkage temperature of untanned collagen as vegetable tans do. Only the residual amounts of aldehydes still present from the "pre-tannage" caused the shrinkage temperature to be as high as it was, which however is 12 degrees (C) lower than the maximum reached, according to table I. Impregnation does not decrease the shrinkage temperature of any leather. A study by the Quartermaster Corps (35) showed that most impregnated vegetable leathers may have a shrinkage temperature

TABLE IV PROPERTIES OF LEATHER PRODUCED IN RAPID SOLE LEATHER

TANNAGE DESCRIBED IN TABLES I AND II

<u>Chemical Analysis</u>	<u>Lot A*</u>	<u>Lot B</u>		
	<u>Untreated</u>	<u>Untreated</u>	<u>Rubber-Resin treated</u>	<u>Insole</u>
Water solubles, %	24.3	26.3	22.8	41.9 **
Hide substance, %	48.4	46.9	38.6 ***	41.5
Grease, %	3.2	4.5	23.8	3.7
Insoluble ash, %	0.3	0.2	0.1	0.8
Degree of Tannage	49.2	47.8	38.0	31.1
pH	3.3	3.4	3.4	3.4
<u>Physical Tests</u>				
Compressibility, %	9.8	16.4	7.3	
Density	0.93	0.93	1.06	0.97
Shrinkage temperature, presoaked in water, °C	78.5	75	75	87
Thickness, irons	9.5	10.5	12.5	8.5
Bursting force, lb.	255	260	115	275
Water absorption ($\frac{1}{2}$ hr.), %	47.4	53.0	7.9	41.0

* Mean of data used in Table II, column a and b, of reference (15) of this report.

** Includes 11% inorganic matter (mostly aluminum oxide)

*** 66% of which is acetone-soluble

of 82-84°C (179.6-183.2°F), if properly tested. The pitfalls surrounding the shrinkage determination have also been described. The importance of properly rewetting the specimens is not sufficiently stressed in the amendment describing the test. Recent papers of the National Bureau of Standards (17, 18) do not explain why shrinkage temperature was introduced as a requirement and also do not discuss procedure or significance. However, it is conceivable that collagen could be filled with impregnants without gaining in hydrothermal stability, and would then shrink in water of 60-65°C (140-149°F). Furthermore, sole leather many years old which has perhaps become dark or cracky by age, or otherwise unsalable, could be impregnated and sold as "new". The decrease of shrinkage temperature in storage is a well-known phenomenon (15,23) which will be discussed below in more detail. The present minimum of 75°C (167°F), therefore, is a proper safeguard protecting the Government against misuse of the impregnation process while, at the same time, permitting the production of a purely domestic sole leather by the aldehyde process.

Strength properties of sole leather seem to bear no direct relationship to wearability and have not been investigated by the National Bureau of Standards in connection with the impregnation process. It was tacitly assumed that they would not be weakened by the treatment. In recent Quartermaster Corps projects, bursting force has been used as an indicator of the strength properties of the hide fiber, in accordance with the practice established in observing the strength losses of the so-called USXL series during storage (23). When the same property was tested on freshly-impregnated bends of lot B, the figures obtained (as table IV shows), were less than half the amounts for their untreated counterparts. Apparently the fiber had been weakened by the technique used.

The severe loss in strength did not betray itself in the appearance of the leather and in its performance as soling material (Part III, paragraph 3a). However, this strength loss need not occur, as was shown in a simultaneous investigation of commercial impregnated sole leather and of domestically-tanned sole leather impregnated on a laboratory scale. Data obtained in this study are presented in table V. Evidently the force required to puncture treated leather with a 1/8" plunger can vary within limits, but is definitely too low in the impregnated leather analyzed in table IV (approx. 120 lb as compared with 170 lb minimum in table V).

TABLE V
BURSTING FORCE OF IMPREGNATED VEGETABLE SOLE LEATHER

<u>Tannery</u>	<u>Thickness</u> (irons)	<u>Bursting Force</u> (lb)
X	10.9	177
Y	11.3	229
Z	12.5	170

NOTE: Mean values of 48 measurements, one-third taken on each of 3 cut soles submitted by the respective tanneries. Same soles served for study of influence of test methods on shrinkage temperature (35).

f. Insole leather

Insole leather deviates from specification requirements in water solubles (which should be 26% or lower) and, as a direct consequence of being high in these, it does not quite reach the required degree of tannage, i.e., 35. It also contains no chrome, since aluminum was used instead. Other properties shown in table IV, but not spelled out in the Federal Specification are similar to those of the sole leather, for example: grease, pH, density and strength. It is apparent that the latter did not suffer from the long milling during tannage. The T_g was higher than that of the various sole leathers, thanks to the presence of aluminum. On the basis of the figures in table IV, it was predictable that in serviceability and storageability this insole leather should compare favorably with that in the standard insoles now used in Army footwear.

PART III - STORAGE STABILITY

1. Procedures and criteria

Storage stability of regular sole leather in the cool warehouses of Germany was studied during World War II (39). Even though the Quartermaster Climatic Chambers came into existence under the impact of the same war, no similar investigation has ever been carried on in the United States, until the inauguration of the project reported here. In 1958, results with various standard and experimental sole leathers were reported for a storage of 1 year (15). These leathers have now been investigated after 3 years of storage. Others, whose tannage is outlined in tables I and II, have been aged 2 to 3 years. The climate in the Chambers has already been described (22,23).

For various upper leather tannages, fundamental differences in the aging characteristics, depending on climatic factors, were discovered (23). There were sharp contrasts between continuous exposure to a hot-dry (desert) or hot-humid (tropical) environment, while the climate of the temperate zone stands somewhere between these extremes in its effect upon upper leather.

Principal criteria used were bursting force and shrinkage temperature. They indicate two basically unrelated properties of leather:

- 1) Fiber strength
- 2) Hydrothermal stability, i.e., bond strength between collagen chain and tannin compound used in making the leather.

Freshly-tanned leather may rank high in both properties (e.g., chrome leather) or in only one (chamois is high in fiber strength, low in resistance to hot water). Defective tanning, overheating in the dye-bath and other events, sometimes difficult for the tanner to elucidate, result in a weak fiber, although the shrinkage temperature remains as high as in undamaged stock.

No other characteristics of sole leather have been re-examined while it was aging.

2. Bursting force

a. Changes

The result of a puncture test can be expressed as "pound bursting force" or as "pound/square inches bursting strength". The latter term was used in the early report (15). In the present report the actual reading on the instrument in pounds is used throughout as a means of following the aging process on the same specimen or comparing specimens representing various tanneries or tannages. Since they were all taken from butt areas and since outsole as well as insole leather

of nearly the same thickness was produced throughout, the direct readings of the force used should be more meaningful than figures computed for a 1-square-inch cross-section of leather.

The results of all measurements so far conducted by the Quartermaster Corps on various sole leathers are given in table VI. Only the leathers coded 1, 2, and 3 are sole leathers produced by industry in the conventional manner. All others are experimental leathers tanned under the auspices of the Quartermaster Corps by the rapid aldehyde process. The leathers coded 6 to 9 are 100% domestically tanned as shown in tables I to IV and are the main subject of this report. The leather No. 10 was retanned with chrome as shown in Appendix A. The leathers No. 7 to 9 have been stored only 2 years. The others have been stored 3 years.

b. General observations

The following three general observations can be drawn from the figures presented in table VI:

- 1) In conventional sole leather, a bursting force of 300 pounds is normal, but values up to 400 pounds may be encountered.
- 2) In aldehyde-tanned sole leather a bursting force over 300 pounds occurs less frequently than in conventional sole leather. For example, the grand average of all values listed for No. 4, 5, and 6 (from 0 to 3 years storage) is 278 pounds, compared with 345 pounds for No. 2 and 3 tanned in a conventional slow process in the same tannery.
- 3) The highest bursting force values occur most frequently on leather stored from 1 to 2 years, and not on freshly-tanned leathers.

In table VI the highest bursting force values found for each leather and in each chamber are underlined. Many of them occur more than once when strength reaches a "plateau". By assigning to the original bursting force the figure 100, the peaks may be expressed by the following figures:

<u>Leather Code</u>	<u>Peaks</u>
No. 1 - 3 (conventional)	<u>116</u>
No. 4 - 7 (aldehyde tannage with lignosulfonate)	<u>111</u>
No. 11-16 (same, but with vegetable extracts)	<u>112</u>

The peaks occur mainly after 1 and 2 years of storage, rarely after 3 years, indicating that the decline in fiber strength, usually associated with storage, develops late. It is probably significant that only a few types of leather in the temperate chamber are still at peak strength after 3 years. The other two climates are too severe for maintaining maximum fiber strength over equally long periods.

TABLE VI
BURSTING FORCE IN LB¹⁾ OF SOLE LEATHER BEFORE STORAGE AND AFTER 1 TO 3 YEARS OF STORAGE UNDER
VARIOUS CLIMATIC CONDITIONS

Code No.	Tannery ²⁾	Aldehyde (where used)	Other components	Temperate Summer				Moist Tropical				Moderate Desert			
				(y e a r s)	(y e a r s)	(y e a r s)	(y e a r s)	(y e a r s)	(y e a r s)	(y e a r s)	(y e a r s)	(y e a r s)	(y e a r s)	(y e a r s)	(y e a r s)
				0	1	2	3	0	1	2	3	0	1	2	3
1	B	-	Regular*	305	380	380	345	290	310	300	290	315	415	400	400
2	A	-	Regular*	315	375	330	325					325	285	340	355
3	A	-	Blend**	355	335	390	350					350	310	380	390
4	A	Formaldehyde	Blend**	345	380	370	335					330	335	390	375
5	A		Blend**	260	275	295	250	255	265	245	210	350	310	290	290
6	A		Lignos.	260	275	225	215	245	230	200	150	255	275	230	210
7	B		Lignos.	285	300	260		235	190	200		275	255	275	
8	B	Glyoxal and Formald.	Lignos. & Impreg.	125	150	160		115	120	125		110	170	185	
9	B		Lignos. & Alum	295	225	230		270	220			270	220		
10	A	Glyoxal and Formald.	Lignos. & Chrome	235		190	170	190		135	100	230		235	195
11		Formaldehyde		240	285	280	275	270	270	275	240	235	275	265	260
12		Glyoxal		250	280	285	260	235	250	245	240	255	270	280	265
13	C	Glyoxal		225	265	265	255	225	235	205	200	225	260	260	245
14		Glutarald. (alkaline)	Regular*	230	240	250	250	275	235	225	220	240	275	265	240
15		Glutarald. (acid)		235	275	280	265	215	220	195	150	215	290	305	290
16		Dialdehyde starch		250	300	305	280	230	240	240	235	265	285	265	270

* Regular* regular vegetable tannage.

** Blend= vegetable extracts blended with 30% lignosulfonate.

1) Mean values to nearest 5 lb of 1b measurements in butt areas of bend or back (one per chamber, except for No. 6 where butt pieces of 6 bends per chamber were placed in storage).

2) Same code identifies tanneries in this table and lots produced in these tanneries in preceding tables.

3) Leather squares of No. 11 to 16 sprayed with paranitrophenol solution to prevent mildew. For statistical comparison between treated specimens and controls of leather No. 6 stored side by side see Appendix B.

NOTE: Highest values for each type of leather are underlined. Figures in parentheses must be disregarded as being too low.

c. Aging characteristics

In the impregnated stock No. 8, the original strength is suspiciously low. This was the subject of an earlier discussion (Para. 6.e., Part II) and can be substantiated by a comparison with impregnated stock prepared from regular sole leather. For several years, such stock has been commercially available from a number of sole leather tanneries. Three brands on which the QM Leather Laboratories demonstrated the correct method of taking the shrinkage temperature (35) were stored in the climatic chambers. Their strength properties, by comparison with those of No. 8, are considerably better, as shown in table VII below.

TABLE VII
BURSTING FORCE IN LB. OF IMPREGNATED SOLE LEATHER
BEFORE STORAGE AND AFTER 1 OR 2 YEARS STORAGE

Code	Tanned With	Temp. Summer (years)			Moist Tropical (years)			Moderate Desert (years)		
		0	1	2	0	1	2	0	1	2
X*	Vegetable blends	240	255	230	205	245	225	240	290	240
Y*		180	230	200	155	225	215	175	210	170
Z*		175	175	170	175	175	165	185	180	165
No. 8**	Glyoxal, formald. and lignosulfonate	125	150		115	120		110	(170)	

* Mean Values (to nearest 5 lb) of 2 measurements at each end of cut soles, using 2 to 4 cut soles of each brand per chamber.

** Mean Values (to nearest 5 lb) of 12 to 16 lb measurements in butt areas of bend or back (one per chamber).

Individual differences among the 3 commercial products are considerable. Only brands X and Y show the same distinct maxima in bursting force after 1 year of storage, as do most of the untreated upper leathers of table VI. Brand Z is remarkably uniform in strength, independent of storage time and also regardless of storage conditions, while at the same time, on the whole, showing lower bursting force figures.

d. Characteristics of insole leather

Among insole leathers, of which two are shown in table VI, No. 9 represents alum-tanned insole leather of tables II and IV; No. 10 is a small lot of 4 chrome retanned backs of the following composition:

	Position			
	<u>A</u>	<u>C</u>	<u>J</u>	<u>All</u>
Water Solubles, %	4.2	5.0	5.1	4.8
Hide Substance, %	68.4	61.8	64.7	65.0
Grease, %	2.9	5.0	2.8	3.6
Insoluble Ash %	6.1	5.7	5.8	5.9
Chrome Oxide, %	4.2	4.2	4.5	4.3
Degree of Tannage*	27.0	36.0	33.0	32.0
pH	4.7	4.9	4.9	4.8

*Disregarding chrome complex

This insole leather (No. 10) had been tanned with glyoxal and formaldehyde, as had lot A of table I, and then chrome-retanned without the benefit of lignosulfonate or foreign extracts; for details of the procedure see Appendix A.

Table VI offers strong evidence that the use of mineral tanning agents in sole leather causes the same slow degradation in the leather fiber; this has been observed before on upper leather. However, even after 3 years, under all storage conditions tested, the loss of strength would not interfere with wear; burst figures listed for No. 9 and 10 are higher than most of the figures recorded on the lot No. 8 which was impregnated and when worn in the field, gave no indication of being weak or low in puncture resistance (see Part IV, para 3).

3. Shrinkage temperature

a. Problem and purpose

Three factors established some time ago motivated the considerable research the Quartermaster Corps did on the shrinkage temperature of its sole leather production tests:

- 1) Vegetable soles suffer considerable losses in shrinkage resistance while aging, as reported first by the National Bureau of Standards (40).
- 2) Lignosulfonate fixation does not materially raise the shrinkage resistance of untanned hide, as pointed out earlier (par. 6.e., Part II).
- 3) Fixation of lignosulfonate by aldehyde or vegetable-tanned leather causes a loss in its shrinkage resistance (15).

b. Results of tests

Examples underscoring these 3 points are to be found in table VIII; here are shown the mean values for the shrinkage temperature in water of all the leathers for which bursting forces have been recorded

TABLE VIII
SHRINKAGE TEMPERATURE IN °C. 1) OF SOLE LEATHER BEFORE STORAGE AND AFTER 1 TO 3 YEARS OF
STORAGE UNDER VARIOUS CLIMATIC CONDITIONS

Code No.	Tannery	Aldehyde (where used)	Other Components	Temperature Summer (y e a r s)			Moist Tropical 2) (y e a r s)			Moderate Desert (y e a r s)		
				0	1	2	0	1	2	0	1	2
1	B	-	Regular**	89	82	82	89	85	82	89	82	76
2	A	-	Regular*	90	89	90				90	88	83
3	A	-	Blend**	85	85	84				85	86	84
4	A	Formaldehyde	Blend**	90	90	88				90	91	83
5	A		Blend**	91	88	88			92	91	80	72
6	A		Lignos.	79	73	71	91	91	69	79	70	65
7	B		Lignos.	75	69	68	75	69	66	75	67	62
8	B		Lignos. & Impreg.	75	70	68	75	70	67	75	68	64
9	B		Lignos. & Alum	87	80	80	87	75	75	87	78	79
10	A	Glyoxal and Formald.	Lignos & Chrome	100+		92	100+	100+102		100+		79
11		Formaldehyde		89	87	85	89	88	86	89	78	78
12		Glyoxal		90	88	84	90	84	80	90	79	72
14	C	Glyoxal	Regular*	93	86	81	93	78	71	93	79	73
15		Glutarald. (alkal.)		91	88	85	91	90	87	91	81	72
16		Glutarald. (acid)		91	84	79	91	86	85	91	77	69
		Dialdehyde starch				78			83			65

*Regular = regular vegetable tannage.

**Blend = vegetable extracts blended with 30% lignosulfonate.

1) Mean values to nearest full degree Centigrade of 2 or 3 measurements in water of specimens from butt areas of bend or back.

2) Leather squares of No. 11 to 16 sprayed with paranitrophenol solutions to prevent mildew. In instances of unprotected controls being aged side by side with treated specimens (as in No. 6), the T_s differed on the average no more than 1 degree (C).

in table VI with the exception of No. 13. The origin of the stored leather samples has been discussed in para. 2 above.

Table VIII shows that:

1) The same leathers which suffered no strength losses in storage suffer serious losses in shrinkage resistance.

2) Losses in shrinkage resistance are high in a hot-dry climate and moderate in a hot-humid climate.

3) Losses are slowed up by time, reaching "plateaus", depending, it seems, not only on the kind of tanning agents used, but even on the manner of their application.

c. Comparison of 3 groups of leather

To illustrate points 2 and 3, the results for the main groups of table VIII (representing conventional leathers, and combinations of aldehydes with lignosulfonate and with vegetable tans respectively) have been averaged for presentation in table IX. First, the losses in shrinkage temperature are shown, instead of the actual readings, and in another column the increases over the shrinkage temperature of untanned hide are presented.

The arrangement of table IX permits at a glance a comparison of the behavior of the 3 groups in various climatic surroundings. It also shows that the temperate climate is more closely related to the tropical than to the desert climate.

Conventional sole leather (Code Nos. 1-3) shows the smallest losses in shrinkage temperature, even in the hot-humid climate, while the aldehyde/lignosulfonate combination (Code Nos. 4-7) shows the largest losses. Yet after 3 years in the desert chamber, the 100% domestic sole leather shrinks in water a few degrees higher than untanned hide does.

d. Tannages with glutaraldehyde No. 14 and 15

Of special interest, in view of more recent investigations by the Eastern Regional Laboratory of the U. S. Department of Agriculture (43) are the aging properties of the 2 sole leather tannages with glutaraldehyde No. 14 and 15 conducted in the alkaline or acid medium respectively.

When the aldehyde was used on the alkaline side (No. 14), the decline in shrinkage temperature in the three chambers was (in °C):

	<u>Temperate</u>	<u>Tropical</u>	<u>Desert</u>
After 1 year	7	15	14
After 3 years	<u>11</u>	<u>21</u>	<u>25</u>
Loss in 2 years	4	6	11

The second leather (No. 15) is hydrothermally nearly stable in a tropical climate, while the first leather (No. 14) is less stable in this climate than in a temperate climate.

Chemically and physically, both leathers were very much alike (9). The difference, therefore, can be explained only by assuming that the bonds between collagen and glutaraldehyde differ in kind, depending on pH, being less subject to hydrolytic separation when formed in the acid than in the alkaline range. This hypothesis seems to be confirmed by the observation reported recently (41,42) that a more acidic tanning medium is superior to alkaline tanning solutions in developing perspiration resistance in glutaraldehyde leather.

In conclusion, it should be pointed out that the poor shrinkage resistance in a hot-dry environment does not come as a surprise; in the large Quartermaster Corps study on the degradation of upper leather in storage quoted earlier (23) the picture was much the same for almost every kind of tannage investigated.

It may be stated parenthetically that, as will be shown later on, this decrease in shrinkage resistance does not affect serviceability in the field test conducted in the rather hot summer climate of Virginia, at the end of which the leather coded No. 8 was about 2 years old.

e. Comparison of impregnated sole leather (No. 8) with similar commercial leathers

Omitted from Table IX is the impregnated domestic sole leather No. 8 which has the same wet heat stability as No. 7 that served for the impregnation. The question of how the shrinkage resistance of No. 8 compares with that of commercial sole leather brands impregnated with rubber and resin is answered in the following table which complements table VII, comparing bursting forces of the same brands.

Table X shows that, as expected, commercial impregnated sole leather is more resistant to wet heat than the domestic leather No. 8, that is, that the picture is the same as before impregnation. There are, of course, distinct differences between different brands. It should be noted, for instance, that the hydrothermal properties of Z are not affected with time like those of X, Y, and No. 8. Lot Z also had uniform, although not the best, strength properties, as has been noted following discussion of Table VII.

TABLE IX FACTORS INFLUENCING LOSSES IN SHRINKAGE RESISTANCE OF SOLE LEATHER
(3 groups of leather in 3 storage conditions)

Leathers, coded in Table IX	Avg. decrease ($^{\circ}\text{C}$) in shrink- age temperature at end of:						Rise of shrinkage temp. above that of untanned hide ¹⁾ after 3 yrs. of storage.		
	1st year			3rd year			Temp	Trop	Des
1 - 3 (Conventional)	3	*	3	2	*	4	22	*	19
4 - 7 (Aldehyde with lignosulfonate)	4	*	7		*			*	
11 - 16 (Aldehyde with vegetable tan) ²⁾	5	7	12	5	5	13	19	22	4

NOTE: 3 storage conditions: temperate summer (Temp), moist tropical (Trop),
and moderate desert (Des).

* Indicates deleted because of lack of complete records.

¹⁾ Assuming it to be 62°C

²⁾ With the exception of No. 13, see text, par 3b above.

TABLE X SHRINKAGE TEMPERATURE (°C)* OF IMPREGNATED SOLE LEATHER
 COMPARED WITH COMMERCIAL BEFORE STORAGE AND AFTER 1 TO 2
 YEARS OF STORAGE
 (Under 3 Climatic Conditions)

Code	Tanned With	<u>Temperate Summer</u>			<u>Moist Tropical</u>			<u>Moderate Desert</u>		
		(years)			(years)			(years)		
		<u>0</u>	<u>1</u>	<u>2</u>	<u>0</u>	<u>1</u>	<u>2</u>	<u>0</u>	<u>1</u>	<u>2</u>
X	Vegetable Blend	82	80	78	82	84	79	82	74	69
Y		84	82	79	84	84	72	84	78	72
Z		82	80	81	82	80	83	82	78	78
No. 8 Glyoxal formalde- hyde and lignosul- fonate		75	70		75	70		75	68	

*Mean values to nearest °C of 2 to 4 measurements on each cut sole or square specimen at each storage period.

Desert storage again is more severe than the other storage conditions in affecting wet shrinkage; that is, here too the impregnated sole leather reacts in the same way as the untreated one.

f. Mineral tannages (#9 and #10)

Also omitted from Table IX are the two tannages No. 9 and 10 in which a mineral tannage is combined with aldehyde and lignosulfonate. They exemplify the great difference between alum and chrome in maintaining hydrothermal stability. After a 2-year storage period, the difference in shrinkage temperature between chrome and alum retannage amounts to: 12 degrees (C) in the temperate and 25 degrees (C) in the tropical chamber. There is no difference in the desert chamber.

Upper leathers comparable to these sole leathers in their composition are also much more susceptible to wet shrinkage after storage in desert climate than after storage in more humid climates, as can be seen from the following figures obtained on shrinkage temperature (°C) before and after 3 years of storage (23) in 3 climatic chambers.

	Before Storage	After 3 Years Storage		
		Temperate Summer	Moist Tropical	Moderate Desert
Chrome retan (at 60% level)	101	85	83	77
Chrome Orotan	104	100	99	87

g. Straight aldehyde leather

The hydrothermal properties of the domestically-tanned sole leather in storage are principally determined by the presence of aldehyde, since lignosulfonate does not raise the wet shrinkage resistance of hide. Straight aldehyde leathers show a very pronounced decline of the shrinkage temperature with time, according to Quartermaster laboratory observations which have been summarized in Table XI.

The first part of this table shows the behavior of the most important aldehydes in all 3 climatic chambers. Apparently it is during the first year of storage that aldehyde leather is most affected by a loss of hydrothermal stability; only in the desert climate, however, does 2 years of storage suffice for the T_s of the leather to dip below that of raw hide.

TABLE XI SHRINKAGE TEMPERATURE ($^{\circ}\text{C}$) OF STRAIGHT ALDEHYDE LEATHER BEFORE STORAGE AND AFTER 1 to 3 YEARS OF STORAGE UNDER VARIOUS CLIMATIC CONDITIONS

Aldehyde	<u>Millimoles per lg collagen:</u>		<u>Temp. Summer</u>				<u>Moist Tropical</u>				<u>Mod. Desert</u>					
	<u>Applied</u>	<u>Fixed*</u>	<u>(years of storage)</u>													
			<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>		
a. <u>Conventional amounts of aldehyde</u>																
Formaldehyde	0.8		90	69	69	68		90	75	73	74		90	62	59	56
Glyoxal	0.8		89	72	69	67		89	--	70	72		89	62	60	53
Glutaraldehyde	1.0		86	74	70	70		86	80	77	77		86	63	62	59
b. <u>Excessive amounts of aldehyde</u>																
Formaldehyde	33	1.7	88			47**										
Glyoxal	17	1.9	85			57										
Succinaldehyde	1.2	0.43	82			57										

* Balance remaining after determination of hide substance, grease and ash, except in the case of formaldehyde which was determined directly by the well-known method of Highberger and Retzsch (44).

** 0.24 millimoles per 1 g formaldehyde remaining.

In the second part of the table, shrinkage temperatures are given for 3 aldehydes stored 3 years in the temperate zone. In two instances, by tanning with large excesses of the aldehydes, the fixation was raised to a level presumably representing the maximum that can be reached in aqueous solutions. Surprisingly, the decline is so sharp that after 3 years in the temperate summer chamber the shrinkage temperature was many degrees lower than that of rawhide. Yet, the leather felt soft and full and still possessed a bursting force of over 40 pounds, as against 62 pounds before storage.

The detanning action of heat and humidity seems to depend, at least in part, on the volatility of the aldehyde. The 3 compounds listed in the first part of the table compare as follows in their boiling point:

formaldehyde	-21°C
glyoxal	+50°C
glutaraldehyde	+188°C

The higher the boiling point, the less of the aldehyde will escape in storage. Consequently, glyoxal-tanned leather should be more stable than formaldehyde-tanned leather, but not as stable as glutaraldehyde leather. The figures of table XI give indications that this is so, especially under moist-hot conditions.

h. Importance of shrinkage temperature

In the past, shrinkage temperature has never been of any particular concern to the sole leather tanner. This property, however, can be of great significance for military footwear, since it is stored for many years before issue. It seemed necessary, therefore, to prove that sole leather - regardless of tannage - is sufficiently stable under all climatic conditions. The tests described above allow us to state with confidence that the new 100% domestic tannage provides the necessary hydrothermal stability.

PART IV WEAR TRIALS

1. Leather used in shoes of two trials.

All shoes worn in the trials were low quarter men's oxfords, conforming to MIL-S-13192A.

The leather tested in these shoes was obtained in the two production tests A and B as described in table I. The leather of test A was worn in the shoes of individuals working at the Quartermaster R&E Center; the purpose was to gain first-hand information about the wearing qualities before issuing the next lot to troops. When the returns were favorable - as will be discussed further - more shoes were fabricated with outsoles and insoles of lot B for a wear trial under the auspices of the Field Evaluation Agency, Fort Lee, Va., as described later.

Both wear trials tested essentially the same type of leather, i.e., a glyoxal formaldehyde lignosulfonate combination sole leather, which was crossmated with conventionally-tanned soles at the shoe factory. However, the following differences existed:

Lot A 1. Outsoles. All outsoles of lot A as well as all out-
(QMREC) soles on the standard shoes crossmated with them, were dipped in a treating compound in accordance with the specification valid at the time of this test (45).

2. Insoles. The insoles manufactured from lot A were worn without receiving a post-treatment, but the insoles of the standard shoes crossmated with them were retanned with chrome by a conventional method (36, 46).

Lot B 1. Outsoles. One-half of the outsoles of lot B were oil-
(FEA) dipped by the shoe factory; the other half were rubber-resin treated by the tannery. The two kinds were crossmated with conventionally-tanned oil-dipped soles.

2. Insoles. One-half of the insoles were cut from the shoulders tanned by the aldehyde alum lignosulfonate combination described in table III; the other half were vegetable insoles, post-treated with chrome, as is mandatory for all military insoles. Hence, the crossmating of outsoles in one-half of both trials was the same, and the regular insoles used in the 2 trials were also the same. Rubber-resin treated outsoles, on the other hand, and 100% domestic insoles were tested only in the 2nd trial which was the "official" field trial and will therefore be discussed in more detail than the first trial.

2. Informal wear test (Lot A, at QM Center)

a. Size of test

The shoes were issued to nearly 100 individuals. After 9 months, shoes that had been worn extensively during this time were recalled until 45 pairs had been collected, including 10 that had been returned earlier because they had become unserviceable as the outsoles and insoles were separated.

b. Test results

The thickness of the outsoles was measured 1) at the arch where no wear had taken place, and 2) at the thinnest point. The unit for the measurements was 1/1000 inch or 1 mil, with holes scoring zero.

Results are presented in table XII..

TABLE XII

WEAR TEST A : THICKNESS LOSSES OF DOMESTIC AND CONVENTIONAL SOLE LEATHER

	<u>Thickness, 1/1000 inch</u>		<u>% Loss</u>
	<u>Arch</u>	<u>Thinnest Point</u>	
Domestic	235	79	66
Conventional	234	97	59

The size of the holes was estimated to the nearest 1/10 inch for the purpose of establishing 3 categories related to the approximate size of the holes. The results are shown in table XIII.

TABLE XIII

WEAR TEST A: HOLE COUNT (NUMBER OF SOLES WITH HOLES) OF DOMESTIC AND CONVENTIONAL SOLE LEATHER (45 subjects)

	<u>Number of Holes</u>			
	<u><0.5 inch</u>	<u>0.6 to 1.5 inches</u>	<u>>1.6 inches</u>	
Domestic	3	9	3	15
Conventional	-	6	1	7

According to table XII there was a difference in wear resistance between the 2 soles; the conventional one wore through about 10% slower than the domestic sole. Table XIII shows that by the time the individuals returned the shoes, holes in the domestic soles were not only more frequent, but also larger.

The results of the inspection for curling brought out another difference. The number of soles which were subjectively considered "slightly" and "considerably" curled, was as follows:

	<u>Slightly</u>	<u>Considerably</u>
Domestic	13	27
Conventional	21	7

The tendency to curl did not affect wearability, according to the individuals' testimony, and therefore should not be considered either a major defect or a cause for withdrawing shoes from wear. Cracking of soles - which would be a serious matter - was not observed.

c. Innersoles

The innersoles were examined for cracking and curling. The results are presented in table XIV. The conventional tannage, which includes a chrome post-treatment, emerged as superior to the domestic leather. This result came as no surprise and in the second production test led to the development of a new insole tanning process which added alum to the ingredients of the leather. The chrome-retanned aldehyde lignosulfonate leather identified as No. 10 in tables VI and VIII was not tested for serviceability.

TABLE XIV

WEAR TEST A: WEAR OF INNERSOLES TANNED BY RAPID DOMESTIC OR CONVENTIONAL PROCESS (45 Pairs)

	<u>Domestic</u>	<u>Conventional</u>
<u>Curling:</u>		
Considerable	13	3
Moderate	15	6
Slight	12	5
None	5	21
<u>Cracking:</u>		
Moderate	2	0
Slight	8	1
None	35	44

3. Field evaluation agency test on lot B: (24)

a. Size of test

Altogether, 116 individuals completed the test, wearing the shoes on garrison duty until both the original outsole and the sole replacing it failed, or until the test was terminated. The first failures occurred after 60 to 70 days, and when the test was terminated after 260 days, all but 47 pairs of the original crossmated combinations had been fully replaced by new half-soles.

The types of soles crossmated have already been discussed (Part II, Paragraph 1 seq.). All shoes were code-marked and inspected, as well as fluoroscoped, before being issued to the troops. No manufacturing defects were found. Each test subject was interviewed about acceptable appearance and fit of the shoes at the following times: at time of issue, each month thereafter, as long as he wore the test shoes, and when the shoes were withdrawn.

b. Subjective findings: Comfort and appearance

Comfort: When asked about comfort, most participants did not express any preferences. Only 9 to 12 responded to the question of whether they perspired less or felt cooler wearing one or the other insole, and these men responded only the first 6 months. Some consistently preferred the chrome retanned standard insole as being cooler and causing less perspiration. The returns, however, were too few to be considered reliable.

Appearance: For 9 months 75% of the participants found no difference in appearance between the 3 types of shoes worn by them; but in the final months of wear, they reported that the standard shoes began gradually to look better than either of the experimental types, mainly because the former held their shape better; this was because there was less curling and spreading of the standard outsoles in comparison with the domestic ones. It will be recalled that the very same tendency was characteristic of the innersoles of production test A, which were not alum retanned.

The observations of the test subjects were supported by the evaluation of the inspecting test supervisors. Table XV shows the findings of both (toward the end of the test).

TABLE XV

WEAR TEST B: SHAPE RETENTION OF SHOES MADE WITH DOMESTIC AND STANDARD SOLE LEATHER AFTER WEAR TEST

Domestic Tannage treated with:	Same as standard by judgement of:		Poorer than standard by judgement of:	
	wearers	supervisors	wearers	supervisors
Rubber resin	14	11	10	13
Oil compound	16	16	6	6

According to the FEA report (24), only 19 test shoes inspected at the end of the test were considered poorer than the standards to which they were crossmated. Earlier in the test, the number was somewhat higher (before drop-outs); for example, after 6 months 21 experimental shoes with rubber-resin treated outsoles and 20 shoes with oil-treated outsoles were judged to be poorer in shape retention than the standard shoes. At

this time there were still 93 pairs being worn (out of 116 pairs) as compared with 46 pairs represented in table XVI.

TABLE XVI WEAR TEST B: OUTSOLES DEFECTS* ON WORN TEST SHOES

(worn 6 or 13 months)

Leather	Spreading				Curling				Cracking			
	6 mos.		13 mos.		6 mos.		13 mos.		6 mos.		13 mos.	
	mod.	sev.	mod.	sev.	mod.	sev.	mod.	sev.	mod.	sev.	mod.	sev.
a. Standard, oil-treated	28	1	13	6	13	1	11	5	0	0	4	0
b. Domestic, oil-treated	19	5	7	6	17	1	6	5	0	0	5	0
c. Domestic, rubber-resin-treated	18	11	6	6	18	3	9	4	2	0	2	1
d. Total of both domestic (b & c)	37	16	13	12	35	4	15	9	2	0	7	1
d - a	9	15	0	6	22	3	4	4	2	0	3	1

*Outsoles were rated "moderate" (mod.) or "severe" (sev.)

c. Subjective findings, outsoles: cracking and curling

Shape retention was admittedly influenced by curling of outsoles. However, separate observations on curling were recorded 4 times during the test. At this time all soles were also inspected for signs of spreading and cracking. The detailed findings of the original report were condensed to table XVI showing the more pronounced defects in the middle and at the end of the wear test.

As a rule, spreading and cracking were less frequent than curling. However, table XVI shows that each of these defects was often considered quite severe and that their total number was larger with the domestic than with the standard outsoles (d - a). Nevertheless, it was noted that the defects were not serious enough to affect durability and wearability. It must be concluded that a certain allowance should be made for leather to spread and to curl and even to crack slightly during prolonged wear and that the present treatment (with a rubber resin mixture) cannot prevent these occurrences any more than the oil treatment.

d. Subjective findings, insoles: cracking and curling

At the same time when the outsoles were inspected for signs of curling, spreading, and cracking, the insoles were also inspected for these defects. Partial results obtained in the middle and at the end of the test are condensed in table XVII. Only the number of instances in which the defects were rated "moderate" or "severe" are presented. The conclusion of the inspecting team was that the cross-mated types of insoles did at no time show differences in curling, cracking or spreading. The table, on the other hand, indicates that after prolonged wear, defects were more frequent in insoles tanned with "domestic" material than in standard insoles. This finding is based on the calculation of the difference (b - a) in table XVII and is comparable to the result of a similar calculation for outsoles in table XVI.

TABLE XVII - WEAR TEST B: INSOLE DEFECTS* ON WORN TEST SHOES

Leather	Spreading				Curling				Cracking			
	6 mos		13 mos.		6 mos		13 mos		6 mos		13 mos	
	mod.	sev.	mod.	sev.	mod.	sev.	mod.	sev.	mod.	sev.	mod.	sev.
a. Standard	31	0	21	16	5	0	22	5	0	0	12	7
b. Domestic	37	12	17	28	6	0	24	14	0	0	19	11
b - a	6	12	-4	12	1	0	2	9	0	0	7	4

* Note: Insoles were rated "moderate" (mod.) or "severe" (sev.)

Outsole and insole degradation, of course, are not the same since insoles suffer from the action of perspiration, outsoles from abrasion under changing terrain conditions. Nevertheless, what has already been said of outsoles, i.e., that a certain degree of deterioration in wear must be expected, especially from a tannage coming new from the laboratory, is also true of insoles. It is generally conceded, for instance, that the stability of insoles is more improved by a chrome retannage than by any other means (46-48) and it is quite conceivable that only a small quantity of chrome, in addition to aluminum, is needed to make the insoles produced in the Quartermaster tests as perspiration-resistant as standard vegetable chrome insoles.

e. Objective findings: hole count of outsoles

Actual measurements expressing wear characteristics consisted of:

- 1) Counting holes that would require withdrawal of shoes from test.

2) Comparing outsole thickness before wear and at the time of withdrawal because of failure or termination of test.

The first method of evaluation (hole count) is represented by the figures of table XVIII.

TABLE XVIII - WEAR TEST B: HOLE COUNT (NUMBER OF SOLES WITH HOLES) ON OUTSOLES OF SHOES MADE WITH DOMESTIC AND CONVENTIONAL SOLE LEATHER

Crossmated Pairs		Crossmated Pairs*	
<u>Standard</u>	<u>Domestic</u>	<u>Standard</u>	<u>Domestic</u>
<u>Oil-Treated</u>	<u>Oil-Treated</u>	<u>Oil-Treated</u>	<u>Rubber-Resin Treated</u>
<u>With Holes</u>			
34	17	16	16
<u>No Holes</u>			
24	41	40	40

*Two pairs were not available for inspection

The table shows that, judging solely from the hole counts:

1) Oil treatment substantially increased the wear resistance of the domestically-tanned soles, as compared with that of standard treated soles.

2) Rubber-resin treatment of the domestically-tanned bends did not improve the wear resistance of soles cut from them, as compared with oil-treated standard soles.

Size of holes was not estimated, as it was in the informal wear test A above (Table XIII). It may be assumed, of course, that bigger holes occur more frequently in the type of outsoles which give less wear.

f. Objective findings: loss of leather (thickness)

The second method of evaluation measuring the loss of leather (i.e., outsole thickness) during wear, seems, therefore, fairer and more meaningful. Results are given in Table XIX.

TABLE XIX - WEAR TEST B: ORIGINAL THICKNESS AND THICKNESS
LOSSES (IN 1/1000 INCH) OF SHOES MADE WITH
DOMESTIC AND CONVENTIONAL SOLE LEATHER

Location of Losses	Crossmated Pairs				Crossmated Pairs			
	Standard		Domestic		Standard		Domestic Rubber	
	Oil-Treated	Oil-Treated	Oil-Treated	Oil-Treated	Oil-Treated	Oil-Treated	Resin-Treated	Resin-Treated
	Orig.	Loss	Orig.	Loss	Orig.	Loss	Orig.	Loss
Inner Ball	232	181	250	151	232	159	238	132
Outer Ball	235	168	250	147	235	146	240	137
Average	234	175	250	149	234	153	239	135
Loss %		75		60		65		56

Average values for the loss of leather during wear are based on:

- 1) Original thickness of 6 outsoles.
- 2) Residual thickness of 51 pairs of outsoles, i.e., 29 pairs in which the standard soles were crossmated with one experimental type and 27 pairs in which they were crossmated with the 2nd experimental type.

The thickness measurements were taken in 3 locations: toe area, outer ball and inner ball. Only the losses of leather in the ball areas are shown in table XIX, since the loss in the toe area was small and in only a few instances caused holes to form.

Table XIX permits the following conclusions:

- 1) The losses in the two ball areas are nearly the same. Therefore, they were combined to calculate the percentage losses shown in the last line.
- 2) The percentage losses for standard soles on the one hand and for domestic soles on the other hand can be combined.
- 3) The new averages for loss of leather are $70 \pm 5\%$ for standard and $58 \pm 2\%$ for domestic soles (regardless of treatment).
- 4) On the basis of these averages, the domestic soles seem to wear $70-58/58 = 21\%$ better than the standard soles.
- 5) By comparison with this difference in wear, the difference of 10% between standard soles and of 4% between experimental soles worn by two groups of test subjects are without significance. In other words, both experimental soles wore out to the same degree, but (as shown in 3 above) considerably slower than the standard oil-treated type soles crossmated with them.

6) These results differ from those of the hole count in only one respect, namely in that the rubber-resin treatment was now equal to the oil treatment, a fact which was obscured by the hole count. Actually, it was expected that it would be superior, but it appears that the rubber-resin impregnation damaged the domestic soles and lowered their fiber strength, as shown in table VI. The damage occurred because of the high temperature used in the process and in the future can be easily avoided by taking the lower heat resistance of lignosulfonate leather into consideration.

4. Conclusions

The field test representing the final phase in the project proved even more conclusively than the informal wear test that a new type of domestic sole leather produced by a rapid process is fully as satisfactory as the standard sole leather now used. It was fortunate that the new leather could be tested after impregnation with oil, as well as with rubber and resin, reflecting the progress which had been made since the initiation of the project in the related field of extending the wear of leather.

PART V - BACKGROUND DISCUSSION ON NEW TANNING PROCESS

Earlier in this report we described a new domestic sole leather process as it was developed by the Quartermaster Corps. In view of the many other attempts to introduce faster and simpler sole leather tannages, the advantages of this particular process will now be examined.

1. The three conditions for accelerating tannages

The conditions necessary for accelerating the tannage of large hides are well-known:

1) a good separation of the fibers allowing the rapid entry of high-molecular organic extracts

2) increased agitation

3) elevated temperatures

a. Facilitating entry of organic extracts

Previous suggestions on how to facilitate the entry of organic extracts (condition No. 1 above) include pickling (27) and a pretreatment with sodium metaphosphate (49m, 50, 51). These methods merely suppress swelling, but do not exercise a true tanning action. For this purpose tanning agents of low molecular weight - principally alum, chrome or formaldehyde - have been recommended. The use of chrome in particular was investigated by several authors (51-54). Although the most popular pretanning agent, it was not considered in this investigation because of its foreign origin. A very informative discussion on the subject of pretannages is found in Gustavson's book on the Chemistry of Tanning Processes (30c and d). A review of the technical aspects was recently presented by Herfeld (55).

b. Increased agitation

Increased agitation (condition No. 2 above) is usually applied to the pretreatment only. The shortage of drums in most sole leather tanneries creates a serious bottleneck. It is difficult to visualize the introduction of any rapid-tanning process deserving the name without the use of drums at the pretanning stage. In some tanneries it may be possible to use the drums ordinarily used for the loading operations, by introducing additional work shifts; in other tanneries, investments in a few new drums may be the only solution.

The use of elevated temperatures (condition No. 3 above) is restricted to the vegetable tannage or its substitution by lignosulfonates or syntans. The lignosulfonates may be heated by circulating them once a

day through storage tanks fitted with steam pipes or by installing heating elements and mixers right in the pits. These were used in the production tests A and B respectively. The effect of temperatures between 30° and 36°C (86 and 96°F) is considered conducive to strength in a number of combination tannages using wattle (50, 56) or other vegetable tans (54).

c. Elevated temperatures

Temperatures of 40°C (104°F) or higher are believed to damage the stock. Therefore the use of lignosulfonates heated at around 50°C (120°F) in the present investigation may be considered a new departure. No incipient wet-shrinkage or hardening effect was observed nor were any strength losses noted. This was true not only of the factory trials of the present report, but also of the many laboratory tests conducted before the semi-production tests (only a fraction of these were included in the preceding Series Report (9)). Maintaining the solutions at the recommended temperatures is admittedly a difficult engineering problem in today's tanneries and requires a considerable investment. In conjunction with pretreatments which amount to a real tannage such as those with aldehydes, heating of mixtures consisting of vegetable extracts and lignosulfonates probably offers greater advantages than the heating of pure lignosulfonate liquors. The reason is that the lignosulfonates have a clarifying action when they are added to vegetable tanning solutions, and the particle-size of fractionated lignosulfonates is more uniform than that of the natural tannin.

2. Successive versus simultaneous tannages

When two or more successive tannages or treatments are applied, it is very important not to use any which could be mutually exclusive. Basic studies of Gustavson brought to light many instances where the tanning agent used first acts to lower or prevent the pick-up of a second tanning material (30, 33). After a lignosulfonate pretreatment, for instance, the fixation of vegetable tannin is sharply reduced (30e). The same happens when vegetable tannins are used first and are followed by lignosulfonate (30f). In this case a considerable amount of the vegetable tannin originally fixed is displaced. Probably for this reason, the tanner who uses lignosulfonate in vegetable blends uses them both at the same time. As has been mentioned before, the pick-up from such blends is either in proportion to or even favors the more valuable vegetable tannins (25, 32).

The forces which explain these affinities are either the ionic bonds located in the acid and basic groups of the collagen molecule or the weaker hydrogen bonds across suitably-located peptide groups. Lignosulfonate is fixed by the basic amino groups, but vegetable tannins are mainly attached to the non-ionic peptide groups; hence they do not interfere much with each other when used at the same time. However, to some extent, vegetable tannins occupy the same groups as lignosulfonate and therefore influence each other when used in turn. Here many factors, such as type of tanning material, pH. or concentration come into play.

3. Type of tanning material: aldehyde and syntan

Formaldehyde (and also glyoxal) attaches itself primarily to the epsilon amino group of only two amino acids, lysine and hydroxylsine. A pretannage with these aldehydes seems to lower the affinity of the hide for vegetable tannins, but the evidence presented is meager (30a) and has not prevented widespread experimentation with such a pretannage. Interference with a subsequent fixation of lignosulfonate cannot be expected and, probably because of the poor prospects of discovering any, has never been closely studied.

Syntans, on the other hand, compete with lignosulfonates in occupying basic groups. Consequently, if they are used first, they prevent the fixation of lignosulfonates, and if used second, they are prevented from being fixed (30g). No basic facts are known as to how they react when present together. It may be assumed, however, that the picture is somewhat similar to that of a mixture of lignosulfonate and vegetable tannin which can be used together with reasonable expectation of being picked up in equal proportions. In the case of the domestic tannage developed at the Quartermaster laboratories, small quantities of phenolic syntan (Orotan) are given, together with lignosulfonate, in the "loading" of the leather. They are fully taken up by the stock, since no appreciable amount of spent liquors remains in the drum after this operation. At the same time, the affinity of the collagen for lignosulfonate is lowered by the necessary adjustment of the pH to above 3.0. Formerly-blocked basic groups are now free to combine with the syntan, while the excess of lignosulfonate remains in the leather as water-soluble matter.

4. pH adjustment

The pH adjustment should be made carefully so as to stay around 3.0; otherwise too much lignosulfonate is released by the active groups of the hide, increasing the water solubles beyond the limits acceptable in the trade or set by various specifications. The case in point is the insole leather produced by a drum tannage which, according to data on table IV, contained at pH 3.4 about 42% water solubles. Although this is much more than the 26% allowed by Federal Specification KK-L-159 (as pointed out in paragraph 6f, Part II), the storage tests and wear trial (FEA) did not uncover any deleterious effect.

5. Corrective steps

In making leather by a new method for the first or second time, deviations like those discussed above occur frequently and are excusable, especially when they do not detract from the usefulness of the finished item. Nonetheless, it should be the aim of any tanner interested in these tannages to correct these deviations at the source. For example, he can lower the pH to 3.1-3.2, in case of the shoulders and bellies for insole leather; also he can use in place of the high molecular sulfite cellulose, the same fractionated lignosulfonate as was used for the bends.

Conclusions

A new domestic tannage has been developed, based on a new procedure of tanning with aldehydes such as formaldehyde or glyoxal, whose peak tanning action lies above pH 8.0. The new process developed from small-scale experiments described in an earlier Leather Series Report (9) and has now been carried out on a semi-production scale in two tanneries. Leather produced in the course of these tests was worn in a Quartermaster field trial. The results showed that serviceable leather can be made by the new tanning process which uses more of the strategic or critical materials now stockpiled for the making of vegetable tanned leather.

Other practical benefits that could derive from the acceptance of the new process by the industry are:

- 1) A great shortening of the tanning process to a mere 8 days which allows for a more rapid delivery of finished stock.
- 2) A considerable simplification of laboratory control and supervision, since the number of rockers is drastically reduced and lay-aways are eliminated.
- 3) The favored use of inexpensive lignosulfonate, facilitating subsequent impregnations by rubber-resin solutions (these determine wear properties and water absorption).
- 4) The cheapness of lignosulfonate compensating for the use of aldehydes in the tanning process and for the expenses of the impregnation process.

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APPENDIX A

RAPID ALDEHYDE CHROME TANNAGE FOR INSOLE LEATHER

(All quantities based on 1000 lb white weight)

1. Alkalizing and aldehyde tannage: See Table IV in body of report
2. Chrome retannage and simultaneous lowering of pH (in drum):

Discard 1/3 of liquor and add: (lb):

		Running times, after feeding:
a. Sodium bichromate (technical) (dissolved in equal weight of water)	50	60 minutes
b. Sodium bisulfite (dissolved in 30 gal of water)	80	1/2 for 15 min; 1/2 for 15 min
c. Sulfuric acid, lb. (prepared one day before as a 4 lb./gal. stock solution)	110	Each of 10 feeds 15 min; 11th feed 90 min.
d. Formic acid, lb.	10	With third last feed of sulfuric acid

NOTE: Drum temperature 50°C (122°F)

pH (finely cut pieces) 4.4

T_s (glycerin/water) 110°C (230°F)

Next morning: Run 15 minutes. Wash 15 minutes at 35°C (95°F). Add to float 400 lb. Filler dispersion. Milling continued for 3 hours but could probably be considerably shorter.

APPENDIX B

TABLE XX BURSTING FORCE (LB) FOR 2 ADJACENT POSITIONS OF MATCHING SIDES OF DOMESTIC SOLE LEATHER * TESTING EFFECT OF FUNGICIDAL TREATMENT (Before and during moist tropical storage) **

Years Storage		Untreated (position 6)				Treated (position 7)				Ratio of 6 to 7
		#1	#2	#3	Avg	#1	#2	#3	Avg	
0	left	229	242	273	248	264	220	286	237	1.05
	right	261	246	273	260	246	220	280	249	1.05
1	left	265	238	257	253	242	214	245	234	1.08
	right	260	242	257	253	227	202	253	227	1.12
2	left	244	228	240	237	185	186	230	200	1.19
	right	223	208	234	222	188	172	244	201	1.11
3	left	180	168	170	173	154	133	163	150	1.15
	right	165	154	163	161	154	131	175	153	1.05

Note: Figures at column heads represent hide number 1, hide number 2 and hide number 3.

* Code No. 6 of table VI.

** Each figure represents the mean value of 16 separate burst measurements obtained on 1 sq. ft. specimens corresponding to position 6 and 7 respectively of the cattlehide sides in the National Bureau of Standards work on the influence of positional difference upon physical properties (38). Half of the measurements on the fresh specimens were made in a row along the edge parallel to the backbone, the other half in a second row 6 to 7 inches away from it. After each storage period 2 new rows of measurements, about 1 inch below the previous one, were made. Hence the original measurements are about 3 and 9 inches away from the backbone, with the distance increasing about 1 inch with each storage period.

The burst measurements disclose two trends:

- 1) Values are 1.05 to 1.19 times higher in position 6 than in position 7.
- 2) They gradually diminish with length of time in storage.

None of these phenomena is in any way influenced by the presence or absence of a fungicide. The first observation parallels the results by the National Bureau of Standards presented below. In fact, N. B. S. figures

supplement these earlier findings on upper leather tannages which demonstrated the marked strength difference between positions 6 and 7.

The second observation supports the data of table VI, underscoring at the same time the known fact that a fungicidal treatment does not slow up strength losses (in leather) caused by exposure to tropical conditions.

Bursting Force (in lb.) for Adjacent Positions 6 and 7
of Cattle Hide Leather

	Position		Ratio of po- sition 6 & 7
	6	7	
Vegetable Retan Cow*	84	73	1.15
Vegetable Retan Steer*	87	67	1.30
Chrome Sides, Split**	122	82	1.49
Chrome Sides, Unsplit**	73	56	1.30

* Source: J. Amer. Leather Chemists Assoc. 47, 731-32

** Source: J. Amer. Leather Chemists Assoc. 47, 409, 411

APPENDIX C

PREDICTION OF WEARABILITY ON THE BASIS OF THE SATRA WEAR INDEX

A new concept of using the analytical characteristics of sole leather to predict wearability has recently been advanced by SATRA in England (57). The wear index thus obtained was compared statistically with the results of actual wear tests. The conclusion was reached that the index "provides a useful indication of what the durability of the sole leather is likely to be" and "a useful means of comparing tannages".

The wear index can be formulated to include compressibility or to exclude it. If including compressibility, the following formula, rearranged from the formula on top of page 352 of reference(57), is applied:

$$\text{Wear index} = \text{density. } (3.16. (\text{hide substance \%} + \text{fixed tan\%}) - 34) \\ \text{minus } (54.5 + 1.036. (\text{compressibility \%}))$$

In defining "fixed tan", the figures for fat, water solubles, insoluble ash and moisture are all subtracted from 100 and the result is then added to the figure for hide substance, also obtained at the moisture content prevailing in the conditioned leather. In short, if one wishes to calculate the wear index for the domestic sole leather discussed in this report, the figures of table IV cannot be used directly, but must be recalculated for the leather with its given moisture content. The density and compressibility figures, on the other hand, can be applied to the formula since here the SATRA way of estimating them is considered close enough to the methods used in arriving at the values of table IV.

In the test for compressibility, the pressure of 3000 lb/sq in. applied by SATRA is the same as in the Federal Specification method, but it is applied to a disc, 3 inches in diameter (hence about 7 sq.in), instead of a 2 x 2 inch piece, and this piece is compressed at an estimated water content of 20% instead of being simply in equilibrium with the atmosphere of a conditioning room. No explanation for conducting the test on a moist sample is given. In view of the enormous pressure applied, the difference in compressibilities obtained by the two methods must be rather modest.

Originally the Wear Index formula was derived from data collected by the Bureau of Standards (58) on a representative group of U. S. sole leather for which an average value of 100 was calculated. The validity of the index was confirmed by sampling a great variety of British sole leathers (on the part of SATRA) which found virtually the same value, i.e., an overall bend average of 101. If a bend had a higher wear index, for example 130, it would follow that soles cut from it would have, on the average, a 30% longer service life than the average of the tannages so far investigated.

It is of great interest to test the validity of the wear index on special tannages evaluated in field trials like the domestic tannages of the report. In attempting this the following figures for the sum of hide substance and combined tannin in % of conditioned leather will be used:

Lot A	65.5
" B, untreated	62.4
" B, rubber-resin treated	47.2

Entering these figures and the necessary values of table IV into the formula given earlier, the following figures are obtained as the wear indices:

Lot A	104
" B, untreated	74
" B, rubber-resin treated	83*

*Obtained by adding the acetone insolubles of the chloroform extract to the combined tan.

A tannage conducted parallel to Lot A, using vegetable extracts and lignosulfonate in the proportion 7 to 3 (15), shows a wear index of 106.

Since all these sole leathers are of the flexible variety, one could expect, in accordance with the finding of SATRA, that their wear indices would be significantly lower than 100. However, this was the case of only Lot B, where it was plainly caused by the fairly high figure for compressibility (16.4%). The same Lot B, when impregnated, gives a creditable wear index only after the rubber it contains is added to the fixed tan. Otherwise the wear index would be a mere 60 which, of course, is absurd in view of the fact that rubber resin impregnants improve wear. It also should be remembered that the wear indices of the other lots refer to the leather as it came from the tannery, i.e., before it was oil-treated for the wear trials according to Military Specification MIL-C-1829 (then valid). Existing evidence that this oil treatment increases wear by as much as 18% (18) would justify raising the wear indices by that much, which would make them almost identical for both types of Lot B. The fact that they also gave nearly the same service in the field trial (see Part IV, par. 3) could be taken as proof of the validity of the concept of a wear index.

It is obvious, on the other hand, that any wear index in the 80's does not reflect the finding of the wear test that both these lots were as good as, or even slightly better than standard leather and that Lot A was definitely inferior to it, notwithstanding the fact that its wear index before the oil treatment was 104, suggesting an index of at least 120 after it. Since the difference between Lots A and B stems mainly from their compressibilities, it is apparent that in the case of tannages as flexible as A and B the wear index stresses low compressibility more than it should.

It is also difficult to conceive of a wear index in whose formulations hide substance and combined tan share equally, i.e., a wear index indicating that - provided the other two characteristics are the same - a leather with 50% hide substance and 15% fixed tan and a leather with 40% hide substance and 25% fixed tan would wear alike.

Turning to impregnations, it seems necessary to allow for not only the acetone insoluble (rubber) fraction, but also for a part of the acetone soluble (resin) fraction to be added to the fixed tan in order to arrive at reasonably high wear indices for impregnated leathers.

SATRA calculates the wear index for each and every bend in one lot (preferably no less than 10) and then computes means and standard deviation. Work of this magnitude probably is justified in establishing the index, but was dropped in favor of using average values for all bends in a single lot (necessitated by the use of composite samples for the chemical tests). In this respect the foregoing attempt to introduce the wear index to a U. S. field test on a special sole leather tannage may stimulate further work. It should be added that in the course of such studies, thought should be given to changing the formula itself to:

- 1) allow for the use of the "degree of tannage" which is independent of the moisture content of the leather sample and also reflects the ratio and not simply the sum of hide substance and combined tan,

- 2) adopt the conventional method of testing compressibility without any moistening of the specimen as now required.

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