

A RAPID SOLE LEATHER TANNAGE WITH ALDEHYDES*

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ABSTRACT

A new method of tanning with aldehydes (1) pointed a way toward the making of sole leather by a rapid process in which conventional vegetable extracts could be partially or fully replaced by domestic materials.

After adjusting the stock to the proper pH in the manner described previously, it is possible to reach a shrinkage temperature of 90°C. or higher in less than 24 hours by tanning with a mixture of glyoxal and formaldehyde. Afterwards, it takes only a few hours to ready the hides for immersion in rockers. Here the pretannage with aldehyde allows the use of rail liquors that are over 40° Barkometer strong and also heated to 120°F. In pilot-plant experiments, it took only 3 to 5 days to obtain full penetration. The largest of these experiments in which liginosulfonate alone was employed is discussed in detail. Chemical and physical data concerning the finished leather are also presented, together with some observations concerning storageability of leather produced in earlier tests.

The new rapid tannage produces a flexible but sufficiently firm type of sole leather such as is in demand today, without a sacrifice of color or heat resistance.



INTRODUCTION

In a previous paper describing new methods of tanning with aldehydes (1) the idea was advanced of employing these in combination tannages using either vegetable extracts or their substitutes and replacement materials. Experiments of this kind have been conducted mainly on heavy leather which is consumed by the Armed Services in large quantities as soling material. Since conventional leather of this type is for the most part tanned

*Presented at the Fifty-fourth Annual Meeting, Swampscott, Mass., May 27, 1958.

with imported tanning materials, the U. S. Quartermaster Research & Engineering Center has a strong interest in developing alternate tannages which would reduce the reliance of our leather industry on imported tanning materials. However, unless a new domestic tanning process offers immediate advantages, for instance by accelerating the tannage or by imparting new properties to the leather, prospects of arousing interest in it in peacetime are dubious. Fortunately, these prerequisites seem to be fulfilled in the present case.

A number of tannery trials exploring the possibilities of starting the making of sole leather with an aldehyde tannage have been reported in *Footwear and Leather Series Report No. 11*, published recently (2). The experience gained by this test series and by subsequent laboratory experiments served as the basis for a new set of pilot tests. This paper will describe only the final experiment, the largest of the four, made on 20 hides. It will stress the incidental benefits of the new tanning process to the tanner and also give a full account of the physical and chemical properties of the resulting leather. Preliminary data in regard to aging properties will be presented for sole leather produced in earlier tannery trials described in the report already mentioned (2).

EXPERIMENTAL

An outline of the pilot-plant test is given in Table I. The tannage can be defined in short as a mixed aldehyde tannage followed by filling and loading with lignosulfonate only. The aldehydes employed were technical solutions of glyoxal and formaldehyde, in the ratio 6 to 1 which corresponds approximately to 5 to 1 for the pure aldehydes. The stock consisted of ten

TABLE I

OUTLINE OF RAPID SOLE LEATHER TANNAGE

(All quantities, unless otherwise stated, are based on 1000 lb. white-weight.)

Alkalizing (in paddle)		
Ratio, skin to liquor		1:5
Temperature		70°F.
NaHCO ₃ (per 100 gal.)		42 lb.
Moles per liter		0.6
Na ₂ CO ₃ (per 100 gal.)		52 lb.
Moles per liter		0.6
Running schedule:	run	2 hr.
	stop	4 hr.
	run	2 hr.

TABLE I (Continued)

Tannage (in drum)		
Volume of alkalizing liquor transferred		80 gal.
Temperature		70°F.
pH Value		9.5
Normality (total alkali)		1.2
Glyoxal (30%), in 10 gal. water at 75°F. (in 4 feeds)		70 lb.
Formaldehyde (36%), minimum (added with last glyoxal feed)		10 lb.
Running schedule	run (1st feed)	0.5 hr.
	rest	0.5 hr.
	run (2nd feed)	0.5 hr.
	rest	0.5 hr.
	run (3rd feed)	1.0 hr.
	rest	0.5 hr.
	run (4th feed)	1.5 hr.
	rest	overnight
	run	0.75 hr.
Drum speeds	1st day	7-8 rpm
	2nd day	17-19 rpm
Final shrink temperature		190°F.
Lowering pH Value (in drum)		
Discard one third of liquor		
Sulfuric acid		90 lb.
Total running time		2.5 hr.
Final pH value (liquor)		3.8
Retannage (in rockers)		
Tanning material		Sodium salt of hard-wood lignosulfonate
1st Rocker		
Barkometer		45°
Temperature		120°F.
pH value		2.6
Days in rocker		1
2nd Rocker		
Barkometer		60°
Temperature		120°F.
pH value		2.2
Days in rocker		1
3rd Rocker		
Temperature (at start, falling to room temperature)		120°F.
Barkometer		Liquor from 2nd rocker, not strengthened
Days in rocker		3

sides taken after dehairing and fleshing, ten sides after bating, and the matching sides after further delimiting in dilute acid.

In the new tanning process the hides, according to Table I, pass through four stages. The first stage has the function of equilibrating the hide with a non-swelling alkalizing liquor as postulated in the original paper (1). In a sole leather tannery, because of the scarcity of drums, paddles were used for this treatment. The liquors were made up from sodium bicarbonate and soda ash in the ratio that they are present in sodium sesquicarbonate, i.e., 1 mole NaHCO_3 to 1 mole Na_2CO_3 . This latter compound may, of course, also be used. Other ratios of the two alkalies have been tried only experimentally. As Table I shows, the quantities employed corresponded to an initial normality of 1.8 with respect to total alkali and gave a pH of 9.5 and a normality of 1.6 as determined by titration after equilibrium with the hides was reached. However, in the interest of economy a normality of 1.2 has been successfully used.

In laboratory experiments the alkaline bath was reused 6 to 8 times without materially reducing the pH or impeding the tanning action. Its strength was brought up by simply adding dry sodium bicarbonate and soda ash, in the ratio 4 to 5, which is the same as in sodium sesquicarbonate.

The buffering capacity of bicarbonate prevents the glyoxal from undergoing decomposition by the Cannizzaro reaction, which becomes prevalent at pH values above 9.5. For the same reason good lime removal by washing the dehaired or even the bated stock is beneficial. Since in the pilot-plant test under discussion some hides were more thoroughly delimited than others, the lime content of the glyoxal tanning bath was probably lower than it would have been in the presence of only unbated stock. Maintaining a temperature of less than 85°F. in the tan drums is essential for the success of the tannage. In the light of evidence in the literature (3) it is not surprising that heating-up of the drums to 95°F. or more should be avoided. Practical steps to assure this included keeping shelves and pegs in the drums at a minimum and moving the stock intermittently at low speed, as Table I shows.

The length of pretreatment required in a tannery (in paddles) for full penetration of the hides with alkali has not been investigated systematically. Instead, the alkalizing operation always was started on Friday, with occasional agitation over the week end. In laboratory tests, however, some intermittent paddling at night was sufficient to reach equilibrium within 24 hours. On the other hand, this goal could be obtained in drums, in laboratory as well as in tannery tests, by moving the stock at about 18 rpm for only 2½ hours on the first day and another hour the next morning.

In earlier experiments with glyoxal the hides assumed a yellowish color in the outer layers but stayed cream-white in the center even though the shrinkage temperatures rose to 190°F. It was found, however, that by the addition of 1% formaldehyde a uniform light color can be obtained throughout the heaviest part of the hide.

Other acids besides sulfuric acid, notably formic and hydrochloric acid, have been used successfully during the third stage of the process for lowering the pH after the tannage. In earlier trials the spent liquor from the tannage was discarded before lowering the pH of the stock, and a freshly prepared sodium chloride or other salt solution was added prior to neutralizing the hides. It was found, however, that this step was unnecessary. The evolution of carbon dioxide during acidification can be better controlled in drums which are open on both sides. Caution is required to avoid losses in the tub or damage to the drum.

It is desirable to bring the pH down to the vicinity of the range prevalent in the rocker retannage, which is about 2.6. If the pH of the hides is lowered to 3.5 to 4.0, the pH of the rockers will not rise unduly. Exclusive of necessary steps to make the measurements, this pH can be reached within 2 hours. Another half hour of drumming has essentially the purpose of making sure equilibrium has actually been attained. Once the proper amount of acid for a given load has been found, the sampling for pH measurements at frequent intervals can be dispensed with. In the final stages a single feed of acid must be no larger than ¼% on the white weight. It is also necessary to cut a sample taken from the butt area of a hide into little cubes and to shake them in a small volume of water for several minutes in order to determine the pH of the stock more correctly than by taking the pH of the liquor in the drum.

Rinsing of the stock before placing it in the rocker vats is favored in order to avoid the accumulation of salts in the retan liquors but has not been practiced in most tannery trials. Wringing-out under high pressure has been found very effective in removing excess salts and also in promoting penetration of the tan liquor in the vats.

Laboratory trials showed that under a given set of conditions, as in a rocker system, the type of lignosulfonate employed determines the degree of tannage obtainable. On the basis of a number of small-scale tests the sodium salt of hardwood lignosulfonate was selected for the 4 pilot-plant tests of which this paper describes the last one, in preference to the sodium salt of softwood lignosulfonate and to the magnesium salt. All 3 types, incidentally, form viscous pastes when mixed with water in equal proportions, in contrast to the unfractionated spruce extracts which give very fluid solutions. The low affinity of these raw, unfractionated liquors for hide substance is well known.

Since the final experiment was twice as large as the preceding three, it required two rocker vats. The lignosulfonate liquor left over from the earlier tests was strengthened by fresh material until a barkometer reading of 45° was reached. It was heated to 120°F. and at the same time adjusted to pH 2.6 by additions of sulfuric acid, and then fed to the vats which had a capacity of 400 gal. each. The next day the liquor was returned to the

storage tubs and strengthened with 300 lb. fresh lignosulfonate to read 60° Bk. The pH which was now 3.2 was lowered to 2.2 by the addition of about 20 lb. concentrated sulfuric acid per 1000 lb. white-weight. The liberal use of sulfuric acid for lowering the pH in the rocker vats has the purpose of increasing the degree of tannage. Maximum fixation of lignosulfonate, according to many investigations, can only be attained in the vicinity of pH 2 (4) or at most pH 2.5 (5). In order to avoid acid deterioration of the resulting leather, the pH must be raised again in the oil wheel. As Table II shows, the 3 sides retanned with a blend of spruce and vegetable extracts acquired a higher pH than the lignosulfonate-retanned sides when oil-wheeled together, because of the initial pH difference.

TABLE II
ANALYSES AND TESTS ON RAPID-TANNED SOLE LEATHERS

	Beamhouse Treatment			
	a 3 backs, dehaired and fleshed	b Matching backs to (a), bated and delimed	c 1 back each, dehaired, bated, delimed	d Matching backs to (c), with same beam- house treat- ments
Domestic extract (lignosulfonate) in rockers, %	100	100	100	30
<i>Analyses of composite samples*</i>				
Water solubles, %	24.7	23.9	21.4	24.3
Hide substance, %	47.8	48.9	50.1	44.4
Grease, %	2.9	3.4	3.2	2.6
Insoluble ash, %	0.3	0.3	0.3	0.2
Degree of tannage	50.8	48.0	50.0	64.2
pH value	3.3	3.3	3.4	3.7
<i>Physical tests</i>				
Compressibility, %	9.7	9.9	10.9	9.5
Density	0.93	0.93	0.94	0.97
†Shrink temperature				
in water	78°C.	79°C.	81°C.	92°C.
in glycerol—water (3:1)	85°C.	87°C.	—	—
‡Thickness, in irons	9.6	9.5	9.6	10.1
†Bursting strength, lb. per in. thickness	1250	1300	1220	1300
†Water absorption, %	47.8	47.0	45.9	41.3

*From A, C, and J locations (Fed. Spec. KK-L-311a). All analyses and all physical tests except density, shrink temperature, and bursting strength were made by methods of KK-L-311a.

†Initial values, obtained on butt areas selected for aging tests.

On the third day, the liquor was reheated, its temperature having dropped 20°F. overnight, but no other adjustments were made. Rocking was continued for 2 more days, while the liquors assumed room temperature and their tannin content dropped from 5.35 to 5.0%.

Three sides were retanned separately in a blend consisting of 70% vegetable extracts and 30% lignosulfonate. Here, too, the liquor was 45° Bk. strong, but the pH was lowered only to 3.9. Heat was applied as in the other rocker vats. The length of the retannage was the same so that these sides could be reunited with the others for the subsequent operations.

After rinse-rocking for 1 hr. in water of 120°F., the bellies were cropped off. The backs and bellies were bleached and wrung in the usual manner, oil-wheeled, and loaded separately. Conventional loading materials were employed, except for Orotan, which replaced the imported vegetable extract. Only 2.5% of the syntan on the wrung weight was employed. In order to raise the pH of the leather above 3, an addition of 1% of anhydrous sodium acetate on the wrung weight was given. The oil was reduced to 1¼% on the wrung weight in order to compensate for the greater softness to be expected as a result of the aldehyde pretannage. All subsequent operations were conventional.

ANALYSES AND TESTS

The leathers were analyzed and tested, with the results reported in Table II. All the tests except for density, bursting strength, and shrink temperature were made by the methods prescribed by Federal Specifications 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 (6) on a converted Mullen Tester. Correct shrinkage figures were obtained only after soaking ¼"-wide strips of leather for 16 hours in individual test tubes while applying a vacuum. Water absorption was determined on 6" x 1" specimens by allowing them to dry out in a conditioned room between each of the 3 half-hour immersions of which the test consisted. Table II shows only the percentage of water absorbed during the first immersion, since the subsequent immersions did not cause the figures to rise materially. In some instances, they even declined somewhat.

RESULTS AND DISCUSSION

Probably the most remarkable property of the finished leather was its flexibility, which is on the order of the flexible-type sole leather currently in demand. Color and appearance of the grain are rated good by experienced tanners. No drawing and wrinkling was evident in the bend area, and only a relatively small amount in the flanks and shoulder region. Most of the figures for chemical and physical data, shown in Table II, conform to accepted standards for sole leather. Compressibility, for instance, is near 10%. The exception is the low degree of tannage for the leather produced with purely domestic materials. Many investigations in the past have

indicated that high degrees of tannage are, as a rule, unobtainable (4, 5, 7) with lignosulfonate alone even under optimum conditions. When the blend containing only 30% of lignosulfonate was used, the degree of tannage rose a full 14 points, accompanied by a marked increase in density. However, as demonstrated in laboratory tests, the degree of tannage can easily be raised with lignosulfonate alone. A value of 64 has been reached by strengthening the rocker vat on the third day to 80° Bk. By comparison, the blending of more syntan (Orotan) with the unfractionated type of lignosulfonate usually employed for loading was less effective. In the leather the composition of which is reported in Table II, the small percentage of the syntan that was used cannot have raised the degree of tannage more than 2.8%.

Another difference between the group retanned with lignosulfonate alone and the sides retanned with a blend is apparent in the higher water absorption of the former. However, as Table II shows, this difference between the matched sides (c) and (d) was no more than 10%.

On the other hand, the water absorption was higher by comparison with conventional tannages, which confirms observations by earlier workers (8, 9). Since all soles for military footwear have to be oil-treated (10), it was of interest to observe the effect of this treatment on the water absorption. We found that a pickup of about 12% of a commercial product suitable for this treatment resulted in lowering the water absorption to about 15%, which is within the range for conventional sole leather.

The claims that have been advanced for the oil treatment mentioned were of a modest nature as far as longer service of treated soles is concerned (11). Impregnation of soles with blends of polyisobutylene or butyl rubber and resin is said to extend wear much longer (12). These treatments were developed by the National Bureau of Standards for crusted stock only, because finished sole leather ordinarily is too dense for an effective impregnation. We have found that this is not the case with the leather tanned by the new process, using lignosulfonate as the only rocker material. Impregnations were carried out on pieces or cut soles, which gained 15 to 35% in weight after immersion for 1 hour in solutions of different resins like those derived from southern pine wood. One of these, Vinsol*, which is insoluble in the petroleum solvents customarily used, could be dissolved in tetrahydrofurfuryl alcohol, except for a very small residue. After impregnation with these resins water absorption was drastically and permanently reduced, but the flexibility was not affected.

For the stability of leather in storage, no two properties are more important than resistance to thermal shrinkage and fiber strength. In the past, sole leather has been studied for aging effects under favorable conditions, as in cool warehouses (13), but not under conditions closely corresponding to various environments in which leather footwear would be stored

*Hercules Powder Company

for issue to military personnel. Such warehouse conditions simulating three different climates have been created in the climatic chambers of the Quartermaster Research & Engineering Center (14).

Specimens of the sole leather represented by the figures of Table II have already been stored in these climatic chambers. Initially, as can be seen in Table II, the shrinkage temperature in water of the fully domestic leather was approximately 80°C. and was 7°–8°C. higher in the presence of 75% glycerin. This difference recalls recent observations (15) that the T_s of chrome leather in pure glycerin was 12°–22°C. higher than in water. With conventionally tanned vegetable leather the difference is more modest; the regular product of the factory where the tannery trials took place had a T_s of 92°C. by the glycerin-water method prescribed by Federal Specification KK-L-311a, and a T_s of 90°C. in plain water. Evidently T_s measurements in the glycerin-water mixture do not reflect the true heat resistance of any kind of leather, although the increases in T_s in presence of glycerin differ from tannage to tannage. Proper wetting-back of heavy leather presents additional difficulties. Since the Federal Specification is not, as a rule, applied to sole leather, it does not suggest that these pitfalls exist. Once an effective method of wetting finished sole leather had been found, the results obtained were consistent. Table II shows that increasing the quantity of lignosulfonate in the rocker from 30 to 100% caused a marked decline of the T_s in water. By comparison, the small differences in T_s among the beam-house treatments are probably without significance. Neither did the beam-house treatments seem to influence the other chemical and physical properties listed in Table II.

Aldehyde-tanned and vegetable-retanned sole leather produced in earlier tannery trials has been retested after one year in the storage chambers. The tannages in question have been described in the report mentioned earlier (2). Regular sole leather obtained from two different tanneries was aged under the same conditions.

The results for bursting strength are compiled in Table III. Most of the leathers showed moderate to large gains. Since 16 specimens were tested before and 16 after aging, and since the distances between the test sites were only about 1 inch, it seemed highly improbable that the strength increases could be attributed to positional variations. In order to prove this point, an analysis of variance was conducted. The F values, also shown in Table III, indicate a high degree of probability that most gains in strength are indeed "real"; statistically insignificant gains and losses occurred only with a few leather specimens aged under temperate summer conditions and with all 5 aldehyde leathers aged in the tropical chamber. Interestingly, the 3 leathers of tannery B lost significantly in strength under desert conditions. Other trends, especially differences among the various aldehydes used, may appear after more extended storage. Observations showing that

TABLE III
BURSTING STRENGTHS OF HEAVY LEATHERS BEFORE (1) AND AFTER (2) STORAGE FOR ONE YEAR
(Bursting strength, lb. per in. thickness)

Test No.	Tannery	Aldehyde Used before vegetable Retannage	Storage Conditions											
			Temperate Summer			Moist Tropical								
			(1)	(2)	F Value	(1)	(2)	F Value						
1	A	None	1400	1900	36	69.0	1500	1680	12	10.2	1430	1970	38	6.8
2	B	None	1280	1590	24	42.9	1500	1300	13	18.9	1500	1300	-13	18.9
3	B*	None	1590	1600	1	0.3†	1460	1280	12	8.5	1460	1280	-12	8.5
4	B*	Formaldehyde	1640	1800	10	2.2†	1560	1480	5	13.3	1560	1480	-5	13.3
5	C	Formaldehyde (1a)‡	1320	1630	23	87.9	1420	1460	3	0.3†	1240	1530	23	33.3
6	C	Glyoxal (1b)	1350	1510	12	13.0	1210	1310	8	2.6†	1290	1440	12	7.2
7	C	Glyoxal (5)	1340	1490	11	10.2	1280	1340	5	1.7†	1290	1490	16	36.3
8	C	Glutaraldehyde (3a)	1290	1270	-2	0.2†	1220	1250	2	0.4†	1300	1540	8	56.8
9	C	Oxystarch (4)	1290	1560	21	39.3	1240	1280	3	2.9†	1470	1580	7	6.7

*Used a vegetable extract blended with so-called spring extract.
†Not statistically significant. The 90% level is 5.6 at the 91.5% level (30 degrees of freedom).
‡Figures in parentheses refer to experiments reported in Reference 1. The 50% level is 5.6 at the 91.5% level (30 degrees of freedom).
§The bends that matched those used in experiment 4 were used in an experiment not reported in the above table.

maximum strength may not be reached for some time after leather has been finished have been reported previously, for instance by Stather and Herfeld (13).

CONCLUSIONS

The unusual emphasis on shrinkage properties of vegetable leather may not appear to be an important point to many tanners. However, military footwear is sometimes stored for years before issue, and, during this time, vegetable soles can suffer losses in shrinkage resistance which are considerable (16). Therefore, leather that possesses a low T_s to begin with may, on occasion, not stand up in use after storage, especially when storage conditions have been particularly unfavorable. It is also well known that lignosulfonate alone cannot materially raise the T_s of untanned hide. Therefore a retanning blend containing lignosulfonate will cause a greater drop in the shrinkage temperature of the aldehyde-tanned leather than a blend containing no lignosulfonate. We found that a blend containing 30% lignosulfonate lowered the T_s of the aldehyde-tanned leather by about 5°C. However, the T_s of the aldehyde tannage is so high that the decline in T_s resulting from the use of lignosulfonate in the retan can be tolerated. Even if lignosulfonate only is employed in the retannage, to the exclusion of vegetable tannins, the T_s of the final leather is still near 80°C., and by varying the proportion of lignosulfonate in the retannage blend the hydrothermal stability can be tailored to suit the requirements and wishes of the user. It is worth noting that conventional methods for facilitating the rapid entry of such blends into heavy hides, for instance by pretreatment with sodium metaphosphate (17), would not have the same effect as aldehyde pretannage in raising the shrink temperature.

For reaching the high T_s desirable at the outset, glyoxal was preferred to formaldehyde mainly because it requires less care in handling; probably it also is less likely to cause a drawn grain. These advantages appear to justify the higher expense of using glyoxal, which in fact, by the standards of the tanning industry, is a low-priced chemical.

The practical benefits of the new tanning process may be summed up as follows:

1. The tanning process is speeded up, requiring no more than 7-8 days from the dehairing to the bleaching operations.
2. The resulting sole leather represents the flexible type which is so much in demand today.
3. The number of rockers needed is drastically reduced and layaways are entirely eliminated. Hence, changes and readjustments, if necessary, are greatly simplified.

4. The cheapness of lignosulfonate compensates for the cost of the pre-tannage.

5. The number of hides in the process of being tanned and the extract requirements are smaller, resulting in considerable savings.

6. Because no liquors are weaker than 42° Bk., laboratory control work is less complicated.

The findings in this report are presented before final evaluation of the leathers in shoes, in order to give the tanner an opportunity to familiarize himself with the process in peacetime and to adapt it to present needs. This is expected to aid in demonstrating the feasibility of the process and to make it available in case of an emergency when reliance on domestic materials becomes imperative.

ACKNOWLEDGMENTS

Thanks are extended to the personnel of Armour Leather Company, Williamsport, Pennsylvania, especially to Messrs. Jack F. Wagoner, George L. Somer, and J. Stemoski, for the encouragement and willing cooperation received during the conduct of the pilot-plant experiments.

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Received July 12, 1958.

DISCUSSION

A. N. KAY (Howes Leather Company, Inc.): I always feel privileged to be asked to lead the discussion of what I may term a "practical" paper, for the ultimate purpose of all our studies is to help the tanner make better and cheaper leather more quickly. Unfortunately, though of understandable necessity, the results of most of our practical work cannot be published, and it is usually only when someone like the Q.M.C. or one of our suppliers tackles such problems that we have the opportunity of equating in public our science with practical leather-making. The excellent paper we have just heard is one such opportunity, and I hope we will make the most of it.

Those of us who have had the privilege of studying the earlier report referred to, realize very clearly that the deceptively casual simplicity of the present work is the result not of happy chance but of a tremendous amount of careful experimentation and study. In addition to the aldehydes listed in Table II many others were investigated, with and without vegetable, chrome, and zirconium retannages. Perhaps more important is that the conditions required for proper leathering (as distinct from mere combination) were also worked out. The success obtained is clearly evident in the data here presented and, what is more important, in the leather available for inspection. It is not surprising that the leather has such a delightful flexibility; conventional leather, analyzing 45-50% hide substance, would be equally flexible and show an equally high water absorption. What is surprising and important, I feel, is the low compressibility figure.

The work can be criticized on the grounds that the leather will not meet Federal specifications. To the extent that the water absorption is far too high, such criticism has a certain validity, but as Dr. Seligsberger has shown, such leather would be a "natural" for impregnation treatments.

The inability to meet the chemical specifications merely points up the dilemma facing the user and producer of sole leather. Lacking a reliable laboratory performance test, as the Bureau of Standards and the Q.M.C. are the first to admit, chemical testing (plus water absorption and compressibility) is the only way we now have of maintaining quality, and the specification limits are necessarily based on those obtained on good-quality conventional sole leather. If these leathers perform as well as might be inferred from the compressibility figures—and I hope Dr. Seligsberger will publish the performance results as soon as they become available—I have little doubt that provision will be made in the specifications to accommodate this type of tannage.

It is interesting to note that Dr. Seligsberger finds that lignosulfonates lower the shrink temperature. In blends with conventional materials one has tended—at least I have—to assume that this is largely due to a sort of “dilution” effect combined with the lack of “bridging” characteristic of lignosulfonates. Yet, here we have the same effect on an already stable tannage and one which is about as close to being covalent as one could hope for.

There is some evidence that, while lignosulfonates (in conventional tannage) do not fix in great amount, that quantity which is, is fixed very firmly indeed. Is it possible that the lignosulfonate has some special power of stripping off even covalently fixed tanning agents? I wonder if Dr. Seligsberger has any thoughts on this?

DR. SELIGSBERGER: I don't think there is any stripping off of covalently fixed formaldehyde. As we know, the formaldehyde leather does not have to contain even 1½ or 2% to shrink at 88° to 90°. It is remarkable that the smallest amount of formaldehyde will produce a shrink temperature so high. So I do not think the lowering of the shrink temperature is a stripping effect. It is rather a combined effect of two tannages which, we find, sometimes increases and sometimes lowers the shrinkage of the final leather.

L. M. WHITMORE (Leas & McVitty, Inc.): This is a very interesting piece of work, and I think the results on lignosulfonate indicate the usual trend. There is a distinct limit to the degree of tannage you can get with lignosulfonates. You have a hatrack, so to speak, and a lot of small molecules hanging on there, rather than the high-tannin polymers. It is a “natural” for impregnating work, where you are not interested in the high degree of tannage. You get the results of wear and whatever characteristics you want without the high degree of tannage. In the past, the high degree of tannage has been necessary, and probably in this case the blending of even more vegetable tannin with lignosulfonate would be satisfactory.

DR. SHU-TUNG TU (United Shoe Machinery Corporation): I would like to ask Dr. Seligsberger why he uses glyoxal in combination with formaldehyde. What is the advantage of introducing glyoxal, since formaldehyde is much cheaper? Is there anything that formaldehyde would not do alone?

DR. SELIGSBERGER: The main reason was that we had the impression that the glyoxal leather is fuller. Glyoxal is a slightly bigger molecule. Also, the color is not pure white, and a pure white color is not exactly what the sole leather tanner is used to.

DR. TU: Of course glyoxal is a bifunctional aldehyde, besides having a larger molecule. Does the bifunctionality have anything to do with the later treatment?

DR. SELIGSBERGER: I don't think so.