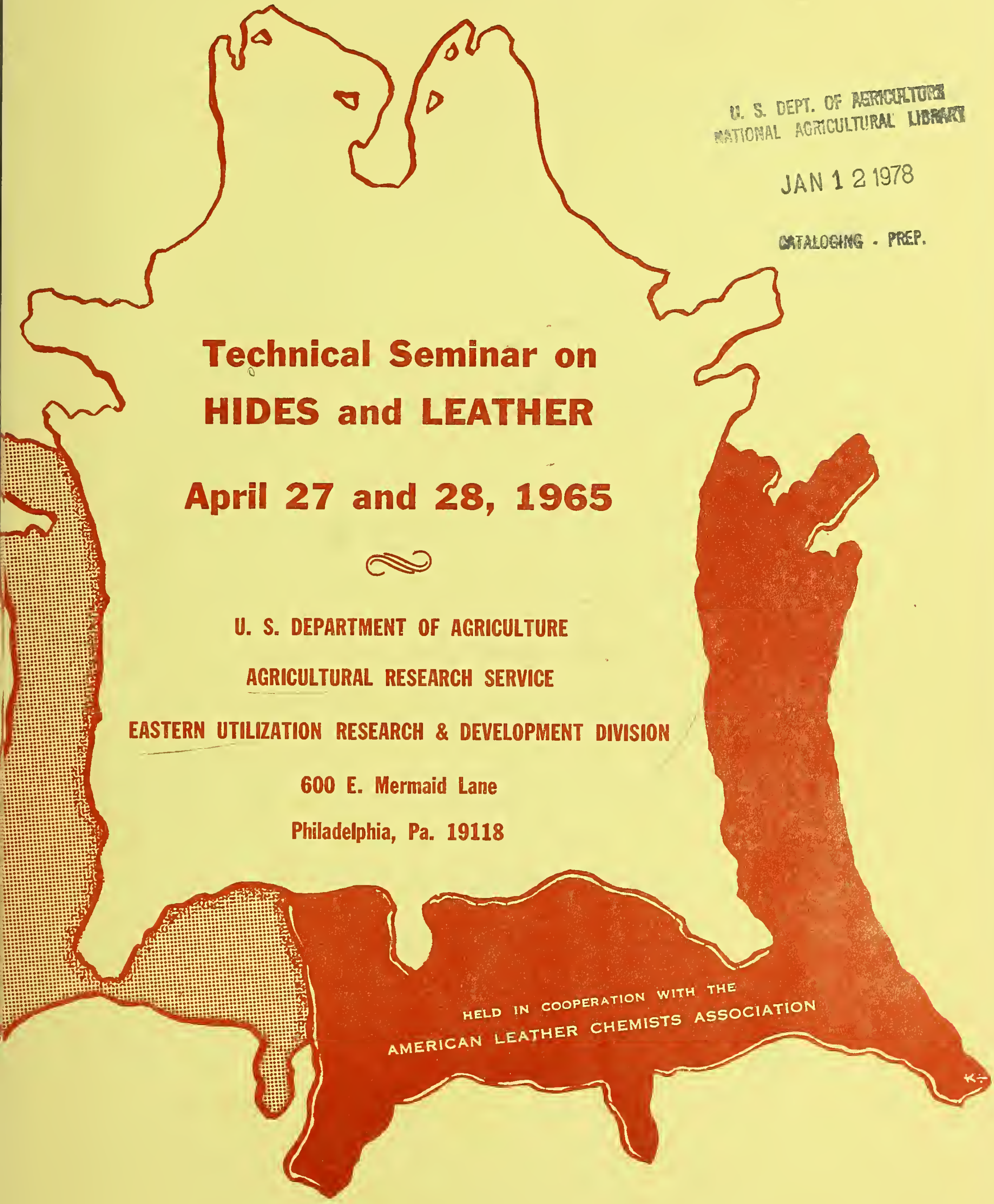

Technical Seminar on HIDES and LEATHER

April 27 and 28, 1965

U. S. DEPARTMENT OF AGRICULTURE

AGRICULTURAL RESEARCH SERVICE

EASTERN UTILIZATION RESEARCH & DEVELOPMENT DIVISION

600 E. Mermaid Lane

Philadelphia, Pa. 19118

HELD IN COOPERATION WITH THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

TECHNICAL CONFERENCE ON HIDES AND LEATHER

April 27 and 28, 1965

Program and Contents

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4. M. V. Hannigan
5. J. J. Tancous
6. J. Naghski
7. D. Meo
8. P. A. Wells
9. H. Y. Miller
10. A. M. Wisnewski
11. R. E. Lothrop
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WELCOME
by
P. A. Wells
Eastern Utilization Research and Development Division
Philadelphia, Pennsylvania

Dr. Wells welcomed the delegates to the meeting and expressed his pleasure at holding this joint seminar with representatives of the leather industry. He hoped that the results of the conference would be as valuable to the industry representatives as he felt sure they would be to the Eastern Division's staff. He expressed assurance that this meeting would in no way compete with the valuable meetings of the American Leather Chemists Association, with whom we have such close relationships; rather it would supplement the A. L. C. A. meetings. Based on our past experience with other similar conferences, there well may be sufficient interest to warrant continuing these meetings in the future. He congratulated Mr. Meo and his committee for their part in organizing this meeting for which he held out high hopes for success.

RESPONSE
by
Dominic Meo
American Leather Chemists Association
Liaison Committee on Research

Mr. Meo pointed out that the A. L. C. A. Liaison Committee was glad to sponsor this meeting. It will afford an opportunity to discuss the problems the industry is confronted with and is attempting to solve. The Wyndmoor Laboratory is the largest group interested in these problems and their solution. The seminar was set up on an invitational basis and restricted representation of the industry. When the industry people go home they should think about contributions they might make to the Laboratory's program that would be most valuable to the industry. Our industry used to depend on outside laboratories but now must depend on Wyndmoor and itself to solve its problems. It is hoped that when you go home you will give thought to setting up projects in your own laboratories.

A. L. C. A. will sponsor meetings of this kind with Wyndmoor in the future. Such meetings will be held when it is felt that they would be most fruitful to the industry.

MARKETING RESEARCH AS A TOOL FOR UTILIZATION

by
Kenneth E. Ogren
Economic Research Service
U.S. Department of Agriculture

In the early days of farming the farmer did his own marketing and received 100% of the consumer payment. His market was rather limited. Today marketing is a broad field having interrelationships with the assembling, processing, transportation, wholesaling and retailing of commodities.

One of the measures of the effect of marketing upon the distribution of agricultural products is the added value produced by marketing. In 1963 when the consumer spent 103.5 billion dollars for agricultural products, the farmer received only 23.8 billion dollars. The difference of 73.5 billion dollars is the value added by marketing.

To better understand what marketing is doing for utilization, let us first examine the trends in farming, marketing and consumption. There are fewer farmers, who are becoming more specialized and subjected to more commercialization. There is more marketing, transportation, processing, packaging, and ready-made items. There are more consumers who have higher incomes, are more urbanized and enjoy a wider choice of products.

There have been tremendous changes in processing which have brought about such innovations as the paper milk bottle, the decentralization of slaughter, preshrinking of cotton, wash and wear clothing, and the stretch weave. There is also more competition from synthetic materials in shoes, textiles, and coatings.

Let us now look at the economic factors involved in hide and leather production. The total cattle and calf population is an indication of the supply of hides. It varies with the demand for meat and milk and not with the demand for hides. In fact, since milk cows tend to remain on the farms, the supply of hides depends chiefly upon the number of beef cattle slaughtered.

Our problem today is that people (per capita) are buying more meat but using less leather shoes and other leather goods. This results in a surplus of cattlehides for export and a tremendous loss for our tanning industry. To visualize this we need only look at the market values for hide products in 1962 which indicate the tremendous value increment produced by marketing. The return to the livestock producer cannot readily be estimated, but there were $368 million worth of hides produced at the packer level. These were worth $725 million on leaving the tannery, $2.9 billion on leaving the leather goods manufacturer and and $5.3 billion when purchased by the consumer.

The Market Potentials Branch of our Division has started to investigate the economics of the hide and leather industry and has already discovered some interesting results on the economics of trimming and segmenting cattlehides. Such studies could point the way to the tanner realizing a greater proportion of the added value produced by marketing.

TECHNICAL PROBLEMS OF THE HIDE AND LEATHER INDUSTRY

by

Malcolm H. Battles
A. C. Lawrence Leather Company
Peabody, Massachusetts

The problems of the hide and leather industry are many and varied, ranging from the insects and diseases which plague the living animals all the way to considerations of disposing of sewage and by-products. It would be impossible in the short time available to do anything more than to identify and discuss a few of the major problems facing this industry.

The potential competition from leather substitutes is a very real form of economic and technological pressure on the leather industry, but it is neither new nor should it be the grounds for extreme pessimism. This simply poses one more challenge for our industry to be aggressive in reducing costs and in developing new and improved products.

Raw Stock Problems. Our greatest single cost in producing leather is the cost of raw stock, and because of the variable quality it can be the greatest variable in determining the ultimate value of the leather produced.

A. Insect Damage. Scratches and scars on the hide of the living animal downgrade the quality of leather seriously, but it is doubtful that we will substantially reduce the incidence of scratches from barbed wire or other sources. Therefore, insect damage which produces scars may be the greatest area where improvement can be effected. These include biting insects which leave a scar and those which deposit eggs and where the larva, pupa, or worms, inflict the damage. In most cases the cause is well understood, and there are effective means for control. However, there is currently a widespread damage in cowhides whose cause is unknown and requires research to identify and to find means for control.

The problem is beyond the control of the hide and leather industries, and the livestock grower has little incentive if the insect only damages the hide and does not reduce the yield of meat or affect the health of the animal.

B. Brands. A serious economic loss to the leather and hide industries results from brands. This problem has been under consideration by the Research Liaison Committee of the American Leather Chemists Association in cooperation with the Department of Agriculture. It has many ramifications, and research is necessary to determine suitable alternative means for identifying cattle. We strongly urge that such a program be undertaken by the Department of Agriculture.

C. Packing House Problems. The causes of problems resulting from packing house operations and the means for control are known, but they persist because of laxity on the part of some packers and hide brokers.

Continued pressure must be exerted by the tanners, and a program of continued education must be carried on by the organizations associated with the hide and leather industry. The following two areas need careful attention:

(1) The growth of the collector-dealer makes continued emphasis on delayed cure essential so that the hides are collected quickly and put them into cure promptly, in order to prevent tye staled hide type of damage. The Tanners' Council Laboratory has developed a test which can be used to detect the presence of proteolytic enzymes in hide resulting from delayed cure, and tanners have used this test successfully to prove incipient damage in the hide.

(2) Even with the new modified hide trim there is still a substantial amount of material received at the tannery which does not return its fair value. More emphasis should be placed upon the utilization of portions of the hide into end products of sufficient value to provide a fair return and allow more drastic trimming of hides.

D. Unhaired Raw Stock. Unhaired cattlehides will present problems to the side leather industry which have been faced and overcome by the sheepskin industry over the years. Due to the difference in beamhouse processes between suppliers, the sheepskin tanner frequently uses several tanning processes to produce the same end product. This same problem may arise in side leather. However, only the future will determine whether or not the economics are favorable and exactly what problems may arise from more widespread use of beamed cattlehides.

Tannery Problems. The tanner makes every effort to produce a more uniform high level of quality in the end product and at the same time trying to reduce operating costs. The intrinsic properties of leather are usually suitable for the end use; however, considerable effort is expended to improve the physical strengths, and such appearance factors as break, uniform temper, etc.; also considerable emphasis is placed upon the development of new appearances, new textures, etc., to enhance fashion appeal. In addition, correlary problems, such as sewage disposal, by-product utilization, etc., are becoming acute and have a direct bearing on our over-all cost of producing leather.

Within these several areas lie most of the subjects which can be discussed as problems or future possibilities.

A. Sewage Disposal. There is increasing pressure on all industry to clean up the effluents to preserve our water supply. The leather industry has a large volume of effluent of such a chemical and physical composition that it is extremely difficult to treat economically. There is also found a dearth of information specifically related to techniques for dealing with tannery effluent. This area needs scientific investigation which could be more economically done as an industry undertaking rather than by every individual tanner as the need arises.

B. Beamhouse Problems. There is need for an unhairing system which limits the quantity of lime used and which minimizes the problem due to sulfides. Both in this country and Europe work has been done on a variety of enzyme and chemical systems, but for one reason or another very few of these have met with commercial acceptance.

C. Retanning and Filling. In upper leathers bating, pickling and the basic chrome tannage do not seem to present any basic problems. In the area of retanning and the use of fillers, or resin tanning materials, there is considerable room for improvement. In a side leather tannery these operations are used to produce uniformity of temper as well as the temper desired, and they influence the break characteristics. Some of the same comments would apply to sheepskin and calfskin leathers. In the case of full grain calfskin many of the retanning techniques familiar to the side leather industry produce very undesirable characteristics from the standpoint of grain character.

Fairly recently glutaraldehyde has been evaluated as a material to be used in retanning of chrome leathers either alone or in conjunction with the conventional retanning materials. In some cases this has produced very desirable characteristics, demonstrating that there is still definitely a place for new materials and new techniques.

Retanning may complicate later processing as when treating leather to make it water resistant. The retanning system also influences ability to impregnate and finish and still come up with the desirable characteristics of the end product.

D. Coloring. The drum dyeing of leather needs definite improvement in dye fastness to reduce the tendency of the dye to bleed out onto the socks and feet of the wearer of unlined shoes. Also in the case of suede leather, glove leathers, etc., there is an increasing pressure for these dyes to be bleed resistant and in some cases dry cleanable or even washable.

E. Fat-liquoring. The industry still uses a certain few basic oils and a certain few types of emulsifying systems. The systems are economical but under special circumstances may be inconsistent with end product requirements. A change may be warranted to produce good water resistance, dry cleanability, washability and other desirable characteristics.

F. Impregnation. Impregnants on the market are either water dispersible or solvent soluble. None of the available materials has reached the ultimate in providing scuff resistance, improvement in break, or such characteristics as water resistance, etc.

G. Finishing. The finishing of leather has made great progress, but this is still the greatest single area where improvements are needed and warranted. Leather substitutes base their claims upon the durability, retention of appearance, water resistance or some other such feature of their product which is almost entirely dependent upon the finish or film used in manufacturing the product. The leather industry cannot afford to sacrifice the current esthetic qualities but could well profit from an improvement.

H. Mechanical Operations. The leather industry has been mechanizing by replacing people with machines to reduce costs. There is need for the development of straight through machines for such operations as unhairing, setting out, shaving, staking, etc. The advent of the so-called speed buffing system substantially reduced labor costs, speeded up the operation, produced a more controllable buffing job and resulted in more uniform quality.

THE CHEMISTRY OF COLLAGEN

by

Arthur Veis
Northwestern University Medical School
Chicago, Illinois

Collagen fibers can be represented as continuous cross-linked network structures. The monomer units in this polymeric network are the tropocollagen molecules, which, in turn, are composed of three peptide strands of different chemical composition. Our aim has been to establish the pattern of intermolecular cross-linking. That is, to assess the sites of origin of the cross-linkages. This has been accomplished by the controlled depolymerization of mature cross-linked bovine corium collagen and the subsequent fractionation, isolation and identification of the soluble network fragments. Carboxymethyl cellulose column chromatography, alcohol fractionation, ultracentrifugal analyses, disc electrophoresis and renaturation studies were all used for this purpose. It was found that a variety of peptide strand polymers could be obtained but that polymers of intermolecular (inter tropocollagen) origin clearly predominated over polymers of intramolecular origin (bonds between peptide strands of the same tropocollagen molecules). The hypothesis was put forward that inter and intramolecular cross-linking are competitive processes, possibly under enzymatic control, involving the same sets of functional groups. Tissue differentiation is involved in the selection of one mode of cross-linking vis a vis other modes.

THE INCIDENCE AND PREDICTABILITY OF MUSHINESS IN SIDE UPPER LEATHER

by

Jean J. Tancous
Tanners' Council Research Laboratory
Cincinnati, Ohio

The occurrence of a mushy weak textured leather used in the upper part of shoes is a serious problem that has been growing in magnitude in the past decade. Because of the economic loss caused by the condition, the Department of Agriculture has sponsored a research program at the Tanners' Council Laboratory to investigate the incidence, nature, and predictability of mushiness in various breeds of cattle hides.

Over eight hundred hides in a range of 45 to 53 pounds cured weight were selected at a tannery. The hides and their respective leathers were sampled on both sides of the backbone in the kidney area, which is the location primarily involved with mushiness. The results of a systematic analysis comparing the strength of the leather with the strength, breed type, plumpness and take-off time of the hide revealed, first of all, a difference between breeds. Defining "weakness" in leather by limits of 2000 lbs./sq. in. for tensile strength, 400 lbs./in. for slot tear and 300 lbs. for Mullen grain crack strength and "mushiness" by limits of 1350 lbs./sq. in. for tensile strength, 325 lbs./in. for slot tear and 210 lbs. for Mullen grain crack strength, it was learned that most of the weak leathers and all of the mushy leathers originated from Hereford hides rather than from Angus or Holstein hides. Eighteen per cent of the Hereford hides produced weak leather with 6 per cent being so weak they were mushy. Only 2 per cent of the Angus and Holstein hides produced weak leather; none of these were mushy. Secondly there was a difference between plump and spready hides. Hereford hides having plumpness values greater than 1.50 lbs./sq. ft. produced most of the weak leather. The Hereford hides spreadier than 1.50 lbs./sq. ft. made strong leather. There were no definite seasonal trends in the selection of hides tested.

Through comprehensive histological examinations, the weakness of the Hereford hides and the mushiness of the leathers made therefrom could be traced structurally to a poor architectural weave of the collagen fiber bundles where few fiber bundles were woven in a direction horizontal to the grain surface and many were found in a plane vertical to the grain surface. The physical strength characteristics of the hide and the leather were dependent on the orientation of the corium fiber bundles.

By comparing physical strength data of the leather samples cut from the left and right sides of the backbone, bilateral symmetry of mushiness could be investigated. There were 51 sides of mushy leather obtained from the 884 hides tested. Forty of these represented left and right sides of the hides. Out of the 11 samples remaining, 3 mushy sides had mates which were lost in the tannery and four mushy sides had mates that were weak but were not quite weak enough to be considered mushy.

By relating physical strength measurements, breed of animal and plumpness of the hide, a system for concentrating weak leather producing hides was designed. There were 1718 sides tested which were an assortment of Angus, Holstein and Hereford hides. These sides produced 169 weak sides of leather of which 51 were mushy.

The first separation removed the 828 Angus and Holstein sides. In removing these 7 per cent of the weak sides but none of the mushy sides were removed. The 890 sides of Hereford remaining produced 93 per cent of the weak sides and 100 per cent of the mushy sides.

The second separation consisted of removing the spready Hereford hides: those having plumpness values less than 50 lbs./sq. ft. This step removed 222 sides, contained 7 per cent of the weak sides and 4 per cent of the mushy sides. The 668 plump sides remaining produced 86 per cent of the weak leathers and 96 per cent of the mushy leathers.

The third separation was based on tensile strength and divided the plump Herefords into sides stronger than 2800 lbs./sq. in. and sides weaker than 2800 lbs./sq. in. This separation was not quite as definitive as the other two separations but did concentrate most of the weak leather producing hides into a group of 211 sides which was 12 per cent of the number started with. The 211 sides contained 58 per cent of the weak and 82 per cent of the mushy leather producing sides.

If the third separation was based on the puncture test, the weak leather producing hides were concentrated into a group of 203 sides which is still 12 per cent of the 1718 started with. The 203 sides contained 48 per cent of the weak and 73 per cent of the mushy leather producing hides. Puncture did not separate the hides quite as well as tensile strength but was not disregarded because it is easier to use than tensile strength.

The separation of hides producing weak and mushy leather by the three steps does have merit. It is not perfect because it is difficult to predict the strength of 4 or 5 oz. shoe upper type leather using a full thickness hide test. However, the method can eliminate a sizeable portion of the economic loss involved with the mushy condition and at the same time can remove many of the weak leather producing hides. By taking out these hides, the tanner can produce leather of more uniform qualities and assure better products for the consumer.

THE PROGRAM OF LEATHER RESEARCH AT CANADA PACKERS, LTD.

by
Ross G. Donovan
Canada Packers, Ltd.
Toronto, Ontario

Canada Packers, Ltd. with annual sales in the order of 600 million dollars, is the largest Canadian meat packer. Diversification in the period following World War II led to the construction of laboratories for Research and Development in the year 1952. These laboratories, located in Toronto, are being extended at the present time.

The activities of the Research and Development Laboratories are handled by a staff of about sixty, divided into groups whose areas encompass, respectively, Meats, Biochemistry, Organic Chemistry, Bacteriology, Oils, Statistics, Analysis, Development, and Leather.

The Leather Group is now in its second year of operation and consists of a biochemist, a chemical engineer, and a laboratory technician. The physical plant is not yet complete, but contains the standard equipment found in most tannery laboratories (i. e. balances, pH-meter, spectrophotometer, Wiley mill, and a controlled-temperature tumbling machine). In addition, equipment has been installed for enzymic work (i. e. a high-speed centrifuge and a pH-stat.). An Instron physical tester is in use, and is soon to be equipped with an environmental test chamber. A reciprocating chamber for the simulation of paddle and and drum operation is under construction for the group at the Milwaukee School of Engineering.

The Leather Group has access to the facilities of the other groups in the Research and Development Laboratories, including a sub-zero room, cold rooms, gas chromatographs, amino acid analyzers, an infrared spectrophotometer, an atomic absorption spectrometer, freeze-driers, and equipment for studies with radioactive tracers, nuclear magnetic resonance, electrophoresis, chromatography, and differential thermal analysis. An excellent library exists within the laboratories, and the services of an electronic computer are available in the Company office across the road.

The Leather Group is interested in all aspects of connective tissue from biosynthesis to by-products. This general interest, however, is being given expression in specific projects. Preservation of leather-making collagen is a prime area of interest, as it relates to curing and to wet-department operations, and to this end the Group is actively examining enzymic processes for unhairing. In addition new products of known chemical nature, requiring small-scale trials prior to in-plant testing, fall within the scope of the Group. The services of the Group are available for the investigation of long-term problems in the Company's tanneries. A final project which is in the nature of 'pure' research, is the examination of the properties of an enzyme (found in pancreatic bates) which has a high degree of specificity for peptide bonds in which valine forms the carboxyl moiety; this enzyme has been used already in some protein-structural studies, and may be of medical interest in connection with the so-called collagen diseases, as well as having a function in tanners' bates.

THERMAL STUDIES ON COLLAGEN AND LEATHER SYSTEMS

by
Antoinette Wisnewski
Eastern Utilization Research and Development Division

Differential Thermal Analysis was applied to the fundamental transitional behavior of collagen as it exists in

1) calfskin in water
2) calfskin to which citrate buffer is added
3) calfskin to which phosphate buffers is added
4) solubilized by a citrate buffer
5) calfskin conditioned at 50% relative humidity

The report is of an exploratory nature in which application of thermal analysis is used as the reference for the thermal behavior of collagen and its products.

Application of DTA to peak collagen fibers from calfskin immersed in H_2O indicated a transition peak at 72°C. It was found that after a five minute soaking of fresh collagen fibers in a citrate buffer, pH 3.4 and an ionic strength of about .3, this peak temperature was lowered to about 60°C. Several days of soaking lowered the temperature to around 50°C. On the other hand, phosphate buffer at pH 7 to almost 11 will not alter the observed 72°C transition point. It is only at a pH of almost 11.2 that an alteration, a 5°C lowering, was observed and then only after a soaking period of at least three days. At pH 12 no observable transitions were obtained indicating complete structural breakdown.

Preliminary DTA observations show the transition peak (destruction of helix) in solubilized collagen on a citrate buffer at 37°C. This peak temperature is also dependent on pH of medium becoming lower on acid medium and shifting upward as the pH increases. A fresh calfskin acetone dehydrated and conditioned at 50% relative humidity contains about 20% water. The thermodynamics associated with this water was studied quantitatively by DTA. The loss of water at atmospheric pressure results in a peak on a thermogram at approximately 120°C.

Quantitative meaning to Differential Thermal Analysis was given by application of the Clausius Clapeyron Equation. This equation relates transition temperatures and various pressures to heat of dissociation, ΔH. Transition peak temperatures on collagen fibers containing 20% water were determined as a function of pressure. Use of the Clapeyron equation to the solid-vapor equilibrium permits a calculation of ΔH, of 14.2 kcal/mole which probably should be designated "maximum heat of dissociation of collagen $(H_2O)_x$" since some water is lost at much lower temperatures than the peak of the transition on the DTA thermogram. Further application will be made with measurements as a function of water concentration at various pressures.

Exploratory results for the energy of decomposition of fresh calfskin were carried out using thermogravimetry (TGA). Determination of the slope and inflection temperature of a TGA thermogram provides precise quantitative meaning to this decomposition.

These preliminary observations indicate that with DTA, transitions in hide materials can be observed at virtually any phase in a process so that the effect of various agents can be determined after about a five minute experiment. By use of vacuum and pressure DTA or thermogravimetry quantitative data can be elucidated giving meaning to the observed transition. DTA can also be used as a control in a collagen solubilization.

STUDY OF THE MECHANICAL PROPERTIES OF LEATHER WITH A NON-DESTRUCTIVE DYNAMIC TESTER

by
William E. Palm
Eastern Utilization Research and Development Division

Measurements of the mechanical properties or quality of leather, with no destruction to the full side of leather, should be of great value to research and production. Determination of the quality of leather is made by experienced individuals who sort it for appearance and texture, using personal judgment in addition to the conventional physical test methods. These present physical test methods are destructive to the side of leather since test samples must be removed.

Recently in the field of polymer science, the measurement of mechanical properties by non-destructive methods have been undergoing extensive study. These methods are referred to as dynamic, as the specimen is subjected to a sinusoidal force or stress. From the response obtained, an elastic modulus (stiffness) and mechanical dampening (energy loss) of the material may be calculated. The advantage of dynamic mechanical testing is that rapid testing over a wide temperature range and at low strains is permitted with no destruction to the test specimen. These tests are very sensitive in detecting glass transitions, crystallinity, cross linking, and many other features related to molecular structure of materials.

A preliminary investigation of a number of leather sides has been made using a dynamic mechanical compression tester. In this investigation only the elastic component in compression was made. The frequency at resonance was measured from which the relative stiffness or apparent modulus of compression (elastic component) could be calculated. The test unit used was capable of a frequency range from 1 to 5, 000 CPS over a temperature range of -35 to 100°C. The tests reported here were made at 23°C and 50% RH at a maximum strain of . 1%.

The results obtained show a definite compression modulus pattern of variability throughout a side of leather. The results for all sides investigated show the butt-backbone areas to have the highest stiffness (most resistance to compression) whereas the belly and neck areas are the most flexible (least resistance to compression) with all other areas falling in between. This pattern although consistent is the opposite to that obtained from a dynamic flexural modulus test and static torsional modulus test. The dynamic compression method shows the highest quality or most desired area of a hide to have the highest stiffness in compression. This variation in property over the side of leather is apparently related to fiber structure and orientation. Further studies are being conducted to gain a better understanding of the meaning of these results.

APPLICATION OF MICROSCOPY TO THE STUDY OF HIDES AND LEATHER

by
Alfred L. Everett
Eastern Utilization Research and Development Division

Leather properties can be evaluated in several different ways. The subjective skill of the tannery sorter has always been highly regarded by those in the trade. Research groups have to rely on more objective measurements, and methods in this area have improved greatly in recent years. The microscope occupies an intermediate position as an investigative or measuring tool, since it shows objectively what the inside of a given piece of hide or leather looks like, yet it often requires a degree of subjective interpretation to explain the special effects created by application of stains and optical devices. To demonstrate the the versatility of microscopic techniques, a number of colored slides were shown to illustrate the characteristic structural features associated with a variety of problems encountered in processing hides and skins into leather.

Two problems associated with calfskin leathers were discussed. The first of these concerned stiff, papery leather thought to be due to improper fat liquoring. Application of fat stains and comparison with the tanner's regular production disproved this idea. Instead it was shown that poor fiber structure was the more likely explanation for the defective leather.

A larger and more elusive problem - called veininess or prominent blood vessel pattern - causes serious economic losses to producers of glazed calf. Close-up surface views of extremely veiny leather were shown, followed by cross-sections to reveal the underlying responsible vessels (which include both veins and arteries). Comparison of good and poor samples has led to the conclusion that the surface defects are reflections of relatively large void spaces around the collapsed vessels. No adequate explanation has yet been found for the cause of these voids, but the pictures suggest several directions for corrective measures: careful shaving to remove the deepest vessels; impregnation to fill the voids; retannage to plump and fill the fibers and thus lend more mechanical support to the affected areas. The last idea was illustrated by some sections taken from a matched side experiment carried out by a cooperating tanner. Regular chrome tanning left one half of a skin quite veiny, while the other half, retanned with zirconium, was appreciably better. Sections showed smaller voids in the retanned half.

To indicate the nature of some substitute materials, cross-sections of Corfam from a shoe showed a three-layered structure functionally similar to leather. The upper layer is a typical granular plastic material; then there is a single layer of woven fabric in the middle, and a thick, spongy layer of matted fibers corresponding to the corium. Polarized light showed that there were no fibers in the top layer, and helped considerably in following the fiber arrangements in the lower layers. Oil Red stain, used routinely for showing fats, was also very helpful.

An interesting short series of slides showed several layers through an insect body found deep in the grain layer of a heavy hide. Many elongated forms were visible inside the structure, and these were tentatively identified as Demodectic mites responsible for follicular mange in cattle. A few cross-sections of side leather known to be damaged by follicular mange showed the extent of destruction caused by these insects.

The problem of excessively fatty hides was then illustrated by two samples, one from a laboratory experiment and the other from Mrs. Tancous' collection. The first hide showed large fat deposits all through the corium after unhairing, and these persisted after vegetable tanning. Fat in the hide was stained with Oil Red, that in the leather with Sudan

Black, and the slides from Mrs. Tancous with Sudan IV, making an interesting comparison of fat staining in various colors. The last samples had an extremely large amount of excess fat, notably in the butt area but even carrying into the shoulder area.

Currently the most interesting problem with hide defects involves further characterization of fiber structure in pulpy or mushy hides. This first came to our attention some four years ago by means of a sample of extremely poor retan side leather. Cross-sections indicated clearly the predominantly vertical arrangement of fibers, especially after comparison with sections of regular production. Depletion of hide substance, grain crack, and extreme porosity allowing complete penetration of fat liquor and starch granules, were dominant features of this leather in addition to the abnormal fiber architecture. Polarized light was again useful for better delineation of fibers and starch.

Slides from Mrs. Tancous' contract studies were also an excellent source of material for photographic purposes. Typical samples of pulpy, weak Hereford hides were compared with normal, strong Angus hides, both as vertical and horizontal sections. The horizontals (parallel to the surface) were especially useful for demonstrating the ratio of horizontal to vertical fibers when viewed in polarized light. Then a new dimension was added to this effect by including a first-order red retardation plate (compensator) in the light path. Horizontal fibers now appeared in yellow or blue, depending on their direction, and vertical fibers were dark but translucent, permitting considerably more interpretation in all areas of the slide.

The concluding section outlined a new line of investigation which involves a combining or overlapping of the effective ranges of the light and electron microscopes to seek a more comprehensive picture of fiber organization. Resin-embedded sections, prepared for electron microscopy, were cut at thicknesses suitable for both instruments so that we could both examine the very same specimens. Slides illustrated the entirely new appearance of fiber segments utilizing phase contrast optics, as well as showing that polarized light was very helpful with thicker sections. Finally several electron micrographs, ranging in magnification from about 400 to 36, 000, demonstrated the transition from fairly large fiber bundles, through fibril bundles, to the individual fibrils with their typcial collagen fine structure.

RECENT DEVELOPMENTS WITH GLUTARALDEHYDE

1. Methods for Determination in Tanning Liquors and Leather

by
Alfred H. Korn
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New research has been applied recently in the field of aldehyde tanning leading to the discovery of the unique tanning properties of glutaraldehyde. One of the difficulties in this study was the lack of a method for determining the actual amount of glutaraldehyde bound by the hide substance. The standard procedure for estimating fixed formaldehyde in leather failed to detect the presence of aldehyde when applied to hydrolyzates of glutaraldehyde leather. An unknown substance, absorbing strongly in the ultraviolet region was, however, detected in the hydrolyzate.

Based on this observation, a spectrophotometric method has been developed for the direct determination of glutaraldehyde bound by collagen. In establishing this method, pickled stock was treated with glutaraldehyde under various conditions. At the end of tanning the spent tanning liquor was analyzed for its glutaraldehyde content. The tanned stock was then washed thoroughly to remove the unbound glutaraldehyde. The tanned skin was then hydrolyzed with 6N hydrochloric acid. The unknown compound formed on hydrolysis of glutaraldehyde-tanned collagen gave a characteristic absorption spectrum with a maximum absorption in the ultraviolet region at 265 $m\mu$. This absorbance correlated well with the uptake of glutaraldehyde as calculated by difference from that remaining in the tanning liquor.

The presence of chromium does not interfere, but vegetable tanning agents, which contain polyphenolic groups absorbing strongly in the ultraviolet region, do interfere with this method for the direct determination of bound glutaraldehyde. Other materials commonly used in finishing leather, such as syntans, leather finishes, dyes, etc. may also interfere with this method.

A new specific method was also described for the analysis of glutaraldehyde in tanning liquors. The procedure consists of treating glutaraldehyde with 2, 4-dinitrophenylhydrazine. The bis-dinitrophenylhydrazone is formed as a very insoluble precipitate which is filtered and washed to remove excess reagent. The glutaraldehyde-bis-2, 4, dinitrophenylhydrazone is dissolved in hot dichloroethane, appropriately diluted and determined spectrophotometrically at 360 $m\mu$. The glutaraldehyde content was obtained by comparing the absorption value of the unknown sample with the absorption value obtained from a standard curve. This method is rapid, specific for carbonyl compounds, and is suitable for the quantitative measurement of unreacted glutaraldehyde in the presence of amino acids, chromium salts, and vegetable tanning agents both of the condensed and hydrolyzable type.

2. Progress on Application to Shearlings

by
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Our laboratory is interested in producing shearlings with improved launderability. Previous laboratory tests indicated that leather tanned with glutaraldehyde has increased resistance to deterioration from perspiration and washing. These properties appeared to make this tannage attractive for application to shearlings. Accordingly, a research program was undertaken.

Hospital Tests - In a preliminary hospital test, a few shearlings tanned with glutaraldehyde and with a combination of glutaraldehyde and chrome were still in good condition after four to five months of continuous use and repeated laundering. To produce pads for a large-scale hospital test, two 84-skin, production-size lots of shearlings were tanned, one with 15% glutaraldehyde (25% solution) as the only tanning agent, and the other with 10% glutaraldehyde and retanned with 4% basic chromium sulfate, using essentially the same tanning procedures published in JALCA, 59, 448 (1964). These were distributed to eight hospitals and one nursing home in the Philadelphia area.

The following data indicate the present condition of a few of the pads after various periods of use by three of the hospitals.

Stability of Glutaraldehyde-Tanned Shearlings Under Hospital Use

Pad No.	Glutaraldehyde* %	Chrome† %	Times used months	Times washed	Leather April 22, 1965	Ts Processed ° C	Ts Used ° C	ΔTs ° C
1	15	-	4	6	slightly stiff	84	70	-14
2	15	-	3-1/2	4	soft, flexible	84	71	-13
3	10	4	2	3	" "	87	87	0
4	10	-	8	15	slightly stiff	78	67	-11
5	10	-	8	18	" "	79	68	-11
6	10	4	4	12	soft, flexible	95	84	-11

* 24 hr. tannage
† 24 hr. retannage

The first three pads were from the large-scale tannages while the other three were tanned in our laboratory. The above results indicate that after repeated laundering shrinkage temperature (Ts) appears to level off at between 67 to 71° C, when glutaraldehyde is the only tanning agent, and at 85 to 86° C when a combination of glutaraldehyde and chrome is used. The shearlings can be used at least four months and laundered at least twelve times if washed and dried with reasonable care.

Resistance to Urine - Cooperating hospitals found that urine voided by the incontinent patient has a deteriorating effect on shearling bed pads. T. A. Pressley, Australia, found that full chrome-tanned shearlings deteriorate rapidly in the presence of urine. *

In a preliminary test two by three-inch shearling samples were immersed in urine (pH 5.6) at room temperature for 3 hours, with stirring every 30 min. The samples were hung in sealed glass jars containing water to provide a saturated atmosphere and placed in an oven at 50° C for 48 hours, then air-dried at room temperature. The results were as follows:

* Private communication

Effect of Urine on Glutaraldehyde and Glutaraldehyde-Chrome-Tanned Shearlings

Pad No.	Glutar-aldehyde* %	Chrome† %	After 48 hr. at 50° C Area Loss %	Leather
1	10	4	2	Soft and flexible
2	-	8	10	Slightly stiff
3	15	-	23	" "
4	Commercially tanned		35	Hard

* 24 hr. tannage
† 24 hr. retannage

The above results indicate that a combination of glutaraldehyde and chrome produces the best resistance to deterioration from urine and is superior to either tanning agent used alone. The spread of the results is somewhat unexpected, and additional tests are needed to establish the full significance.

Stabilization of Wool by Glutaraldehyde - Experiments indicated that as much as 4% glutaraldehyde combines rapidly with keratin based on the dry weight of the wool. Also the glutaraldehyde-modified wool had a markedly enhanced chemical stability to alkali and sodium sulfide solubility. The 1% sodium sulfide solution dissolved only 6% of the glutaraldehyde-modified wool but dissolved 62% of the unmodified wool. The 3% sodium sulfide solution dissolved only 22% of the glutaraldehyde-modified wool but dissolved 89% of the unmodified wool.

Water Absorption - Since the absorption and dissipation of perspiration is a desirable and necessary property of a hospital bed pad, the moisture absorption of shearlings was compared with that of two synthetic materials now being used by some hospitals.

Two-inch square samples of shearlings and synthetic pads were conditioned at 50% relative humidity and 73° F then hung in separate, covered glass jars, over water, in a constant temperature room at 73 $\pm$ 1° F. The shearlings absorbed large amounts of water from the start, giving weight increases of 23 to 24% in 8 hours and 43 to 47% in 24 hours. The synthetic materials absorbed only small amounts of water. The polyurethane foam increased 3.4% in weight in 8 hours and 6.6% in 24 hours. The polyester fiber increased 2.9% in weight in 8 hours and 5.4% in 24 hours.

This test does not duplicate the weight and movement of a patient. However, the data is so much in favor of the natural fiber that it should be more comfortable than the synthetics.

3. Progress on Application to Belly Work Glove Leather

by

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This report presented preliminary work and results on belly work glove leather produced by three experimental glutaraldehyde-chrome combination tannages. These were: (1) retannage with glutaraldehyde of commercial chrome-tanned bellies (split to thickness "in the blue"); (2) simultaneous tannage of pickled bellies (full thickness) with chrome and glutaraldehyde; and (3) retannage of glutaraldehyde-tanned bellies (full thickness) with chrome.

In general the finished leathers were mellow and soft, had a good color, "feel" and stretch or "run". The glutaraldehyde-retanned and simultaneous glutaraldehyde-chrome leathers compared favorably with the control in these properties. The glutaraldehyde-tanned, chrome-retanned leather was somewhat darker in color and not quite as smooth and soft as the other leathers. Analytical data on the finished leathers are given below:

Leather	Ash	Chloroform Extract	Nitrogen	Cr_2O_3	T_s
	%	%	%	%	° F
1. Commercial	9.7	20.2	10.4	2.0	199
2. Commercially Chrome-Tanned, Glutaraldehyde Retanned	10.2	19.1	10.2	2.0	207
3. Simultaneous Glutaraldehyde Chrome	10.9	19.5	10.3	1.6	196
4. Glutaraldehyde-Tanned Chrome-Retanned	10.7	18.9	10.1	1.9	201

All results except shrinkage temperature are on the moisture-free basis.

The chrome content is low to produce a leather with good "run" or stretch and the fat content is high to impart softness, strength and improve the stretch. The shrinkage temperatures of all leathers were comparable and the high ash reflects the use of talc to produce an unctuous feel.

The average data from physical tests were as follows:

Leather*	Tensile Strength			Mullen Grain Crack	
	Thickness	Elongation	PSI	Control	After Perspiration Test
	in.	%		Lbs. to crack	Lbs. to crack
1	.055	71	2430	345	failed
2	.055	82	1840	305 (burst)	345 (burst)
3	.047	66	1395	270	285
4	.049	64	990	180	210

* For description of tannage refer to table above.

Statistically significant differences in tensile strength were observed between tannages and between bellies within a tannage except for the simultaneous tannage where the tensile strength was quite uniform.

The simultaneously-tanned leather and glutaraldehyde-tanned, chrome-retanned leather have the lowest tensile strength. It is suspected that this combination may produce a fuller or thicker leather than chrome alone and, consequently, more corium would be removed in splitting this leather as against the chrome tannage. Density determinations confirm this in that leathers with the high tensile strength had the highest densities and those with the low tensile strength had the lowest densities.

The elongation of the experimental leathers is of the right order for work glove leather.

Resistance to artificial perspiration was measured by ALCA-ASTM Method D-2322-64T. The commercial leather (control) shrank excessively, became dark, hard, brittle and failed the Mullen grain crack. The three experimental leathers containing glutaraldehyde were not deteriorated. Although there was some shrinkage and darkening, the grain could be extended again and was not weakened as measured by the Mullen grain crack.

All of these leathers show fair to good resistance to 8 cycles of alternate soaking in water for 1 hour and then drying at 104° F. However, more change occurred when the samples were alternately soaked for 1 hour in artificial perspiration solution and dried at 104° F. After 8 cycles, the commercial leather showed an area shrinkage of 24% and the Ts dropped 60° F. The glutaraldehyde-tanned leathers showed increased resistance to artificial perspiration in this test.

The data obtained from these preliminary experiments indicate that glutaraldehyde retannage of commercial chrome-tanned leather produced the best experimental work glove leather. It was similar to the commercial product. Perspiration resistance is increased and the leather had acceptable strength. This procedure is simple and practical.

SOME FACTORS AFFECTING THE WATER REPELLENCY OF LEATHER

by
William J. Hopkins
Eastern Utilization Research and Development Division

Von Fuchs found that alkenylsuccinic acid (ASA) could be used as a water repellent compound. It was also found to be an excellent leather lubricant, even when used in small amounts. This latter property indicated that ASA offered considerable promise for preparing leathers to be given water repellent treatments in general. Von Fuchs lubricated by dipping wrung wet leather in a solution of high boiling petroleum naphtha containing ASA. This procedure offers some disadvantages from a practical standpoint. It was thought that further study would contribute to developing a more suitable process for lubricating with a small amount of ASA.

The stock used in our studies was chrome-tanned, top grain cattlehide, split in the blue, and obtained from a tannery. The effect of glutaraldehyde retannage, various methods for lubrication, and amount of water repellent on the water repellency of the leather were evaluated. A dynamic flex test method (Dow Sylflex test) was used to evaluate the latter property.

It was found that tetrahydrofurfuryl alcohol (THFA) was a good solvent for ASA and permitted emulsification of ASA in water. These emulsions were readily exhausted under ordinary fat-liquoring procedures and gave leather substrates which, after air-drying and staking, proved to be suitable for treating with water-repellent compounds. This new procedure was a decidedly improved technique for effecting lubrication with ASA.

The effectiveness of this technique was tested by fat-liquoring with ASA, using both chrome stock and chrome stock retanned with glutaraldehyde, and by treating this stock with two levels of silicone (5.9% and 11.8% pickup on dry leather basis). These leathers proved to have good water resistance, as measured by the Dow Sylflex tester. The high level silicone treatments gave a higher degree of water repellency, as might be expected. Results indicate that glutaraldehyde retannage of the chrome stock has resulted in a substrate with improved effectiveness for the following water repellent treatments.

The sides lubricated by the dip method were chrome sides retanned with glutaraldehyde and wrung to approximately 63% H_2O. One of the sides was lubricated by pulling through a 2% solution of ASA in mineral spirits (Von Fuchs' process) with a pickup of 0.8% ASA on the air dry weight. Another side was pulled through a solution of 1.5% ASA in 1:1 THFA-water with a pickup of 1.0% on the air dry weight. The two sides were air-dried and staked. A comparative study of three water-repellent materials, Scotchgard FC 146, Quilon, and Silicone 1109, was made on specimens cut from each of the two sides. Selected groups of samples were dipped in the appropriate treating solutions. The silicone treatment was tested at two levels, a low level comparable to the level of Scotchgard and Quilon tested ($\cong$5.5%) and a high level ($\cong$10.5%).

On the basis of the Dow Sylflex flex values, all of the treatments imparted good water repellency regardless of whether mineral spirits or THFA:H_2O (1-1) was used as a solvent for ASA lubrication. Each of the lubricated sides ranked the treatments similarly on the basis of flex averages: high level silicone > Scotchgard > low level silicone > Quilon.

Using the drum fat-liquoring technique, a large-scale test was run using six chrome sides and six chrome sides retanned with glutaraldehyde. Using one of the sides from each group, the following treatments were applied: (1) both fat liquor and silicone applied by a tanner; (2) ASA drum fat liquor in our laboratory and silicone treatment by tanner; and (3) both ASA drum fat liquor and silicone treatment in our laboratory. Physical tests were made on samples taken from the "W" position. The chrome sides retanned with glutaraldehyde generally show higher values for tensile, grain crack as well as water resistance. A trend to higher flex values was observed for the experimental ASA drum fat-liquoring and silicone treatment when applied to either chrome stock or glutaraldehyde-retanned chrome stock.

Generally it was found that glutaraldehyde retannage of chrome sides and fat-liquoring with small amounts of ASA resulted in a leather which improved the efficiency of water-repellent treatments for the leathers.

TOUR OF LABORATORY FACILITIES

Composition of Hides (Dr. E. F. Mellon)	Room 3118
Histological Structure of Hides and Leather (Mr. A. L. Everett)	Room 1200
Processing (Dr. W. Windus)	First Floor Slab
Electron Microscope (Mr. R. J. Carroll)	Room 1121
Thermal Analysis (Miss A. Wisnewski)	Room 0120
Physical Properties (Mr. W. E. Palm)	Room 0108

LIST OF ATTENDANCE

Name	Organization	Address
Battles, M. H.	A. C. Lawrence Leather Co.	Peabody, Mass.
Benrud, N. C.	S. B. Foot Tanning Co.	Red Wing, Minn.
Berger, R. C.	Ocean Leather Corp.	Newark, N. J.
Bitcover, E. H.	East. Util. Res. & Dev. Div., ARS	Phila., Pa.
Boresen, R.	Leas & McVitty, Inc.	Salem, Va.
Braunschweig, T. D.	Loewengart & Co., Inc. (New York)	Mercersburg, Pa.
Carroll, R. J.	East. Util. Res. & Dev. Div., ARS	Phila., Pa.
Donovan, R. G.	Canada Packers Ltd.	Toronto, Canada
Dooley, W.	Geilich Tanning Co.	Taunton, Mass.
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Feairheller, S. H.	East. Util. Res. & Dev. Div., ARS	Phila., Pa.
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Greifeneder, J. G.	Beardmore & Company Ltd.	Acton, Ont., Canada
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Miller, H. R.	Pfister & Vogel Tanning Co., Inc.	Milwaukee, Wis.
Miller, H. Y.	Seton Leather Co.	Newark, N. J.
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Potts, R.	Wolverine Shoe & Tanning Corp.	Rockford, Mich.
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Roddy, W. T.	Tanners' Council Laboratory	Cincinnati, Ohio
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