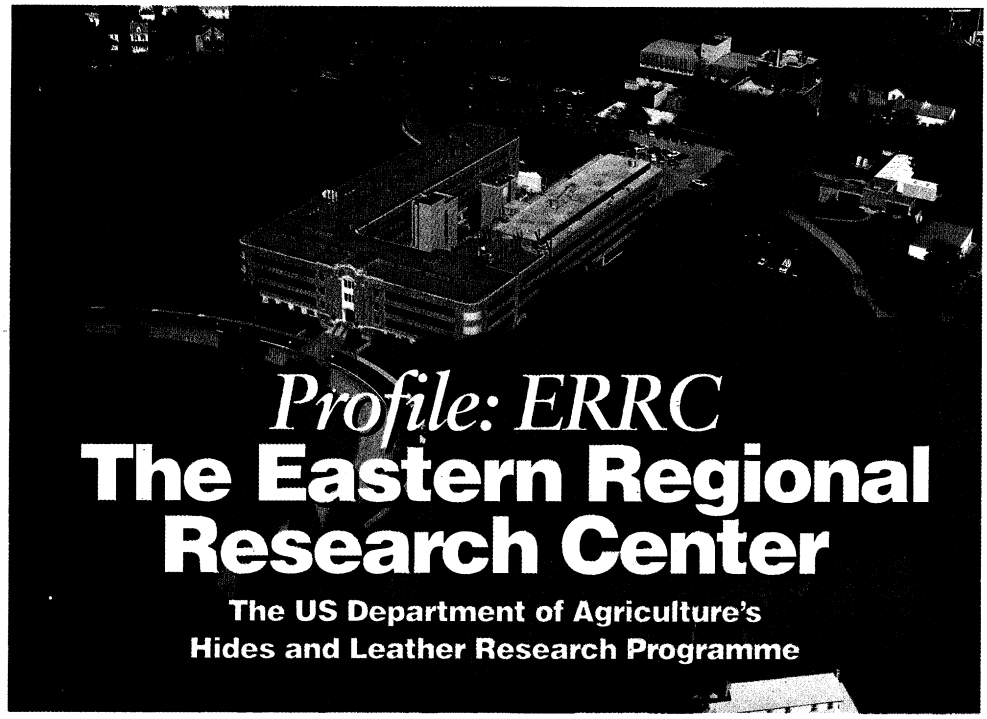


Profile: ERRC
The Eastern Regional Research Center

The US Department of Agriculture's Hides and Leather Research Programme

Hides and leather research within the United States Department of Agriculture (USDA) can be traced back to 1915 in Washington, D.C. Since 1940 it has been located at the Eastern Regional Research Center (ERRC) in Wyndmoor, Pennsylvania, just outside of Philadelphia. ERRC is a major facility of the Agricultural Research Service (ARS), USDA's $700 million inhouse research agency.

The hides and leather programme at ERRC is one of the last of the world's leather research programmes that is fully government financed. The principal objectives of the laboratory are to work on projects to improve the quality of animal hides and skins as a raw material for leather manufacture and to investigate the individual manufacturing processes of leather making to increase technical quality and to protect the environment.

The research programme has changed with the times. In the early stages, the emphasis was on development of a domestic vegetable tanning source. Along the way, ERRC's glutaraldehyde tanning became a major contribution to the tanning industry. Many of its most recent research efforts are largely directed at solving the environmental problems confronting the industry worldwide.

The research programme attempts to focus on areas that are not within the capabilities of the domestic tanning industry or their chemical suppliers. Currently there are three formal research projects in hides and leather at ERRC.

1. A 'hides' project, led by Dr. David G. Bailey,
2. a 'tanning/untanning' project led by Dr. Eleanor Brown
3. a project focusing on the physical and mechanical properties of leather and wool, led by Dr. William Marmer.

Dr. Marmer manages the hides and leather research at ERRC as the Research Leader of the Hides, Lipids and Wool Research Unit, one of seven research units at ERRC. Each research project undergoes extensive review before it is approved for a three to five year period. There is a mix of basic and applied approaches as can be seen in the summary of the overall research programme.

The laboratory maintains a close liaison with the US leather industry. Once a year the American Leather Chemists Association's Research Liaison Committee (RLC) holds a two-day meeting at the Center. The committee membership includes delegates from the US Hides Skins and Leather Association, who represent the meat packing industry, as well as tanners and leather chemists from throughout the country. At this meeting the Hides and Leather research

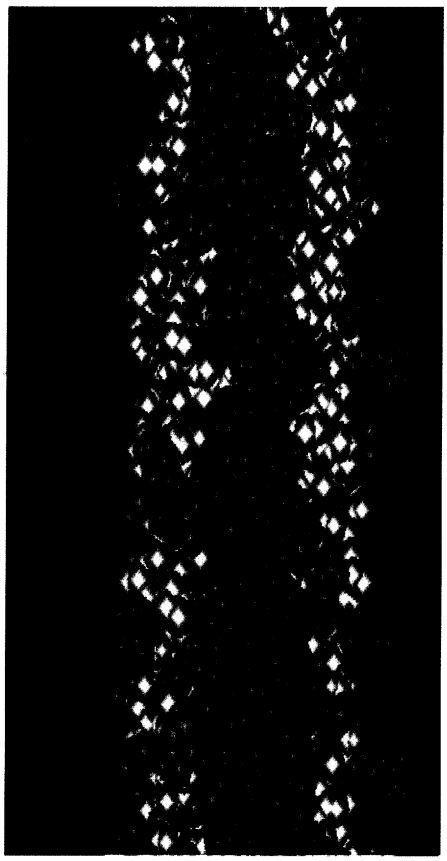


Figure 1 Example of a computer-generated three dimensional space filling stereo model of the 'Smith' microfibril structure of Type 1 collagen. The polypeptide chains are coloured red, purple and blue to show the triple helix within the packed unit. The amino side chains are also colour coded to designate chemical reactivity.

staff presents the status of all ongoing research projects. The RLC delegates, in turn, report on the state of the industry, critique the research programmes, and make suggestions for future directions.

The current staff includes eight senior research scientists, a tanner to oversee the on–site pilot plant and a technical support staff of chemists, materials engineers and biologists. This group is supplemented every year with visiting faculty from nearby universities and colleges, part–time student technicians and visiting researchers from around the world. Over the past few years researchers from Spain, the Czech Republic, Türkiye, the People's Republic of China, Australia, and Brazil have visited ERRC for periods as long as two years.

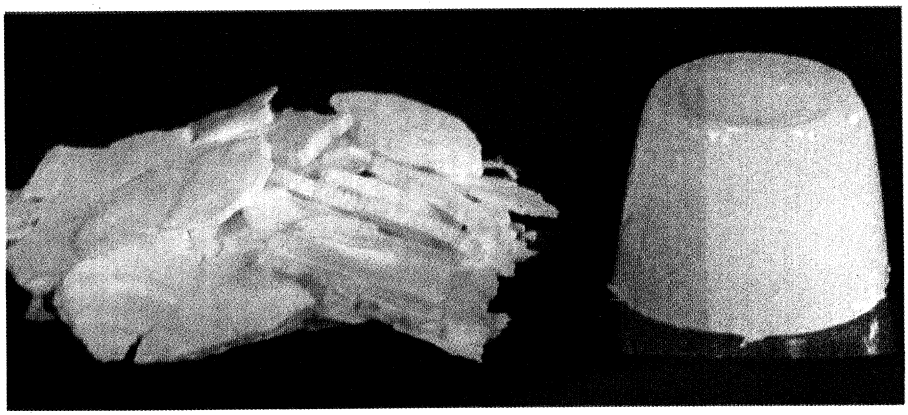
The pilot-plant tannery is a valuable resource for the research and is the only public research tannery in the USA. In addition to lending support for the various projects underway, it is also used by the Leather Industries of America for training. A two–week training programme, 'Thru–the–blue,' is held every autumn and a 'Retan/Colour/Fatliquor' course is held in the spring. These 'hands on' beamhouse and tanyard programmes are well attended by the industry and are useful for keeping ERRC staff informed of current processes in the industry.

The main 'products' of all ARS research are research publications, including patents. Since 1986 US government researchers have been encouraged to collaborate with private–sector institutions under formal agreements. These agreements promote staff exchanges, allow commercial–scale trials, and sometimes result in shared inventions. Their aim is to take government technology 'off the shelf' and move the technology into commerce and trade[1].

Molecular modelling of collagen

Drs. Eleanor Brown and Gregory King are developing a computer model of the collagen molecule as shown in figure 1.

Collagens are a ubiquitous family of extracellular proteins in the animal world. The fibril–forming collagens are the major structural proteins of the skin on the living animal. In addition to their biological functions, collagens provide the molecular frameworks which are utilised in the medical, food and leather industries. Functionality, both biological and technological, follows from protein structure.



Samples of gelable protein solution which has been lyophilised (left) and chilled gelable protein solution (right)

Computerised molecular modelling has been developed into a useful tool for visualising structure–function relationships in proteins. The first requirement for such studies is a suitable three–dimensional representation of the protein. When available, X–ray crystallographic data can be used directly to generate an acceptable computer model. In the absence of a crystal structure, any model must be continually refined to conform with experimentally obtained data.

The unique supramolecular characteristics of collagen have made it a suitable subject for model builders for more than thirty years. The bovine type 1 collagen microfibril model developed at ERRC now consists of 15 polypeptide chains of 315 amino acid residues each. This model is large enough to allow a comparison of its gross structural features with the banding patterns obtained by electron microscopy. Measurable distances pertaining to the helix, triple helix, and microfibril are within experimental error of recently reported physical data on dried collagen samples.

The model is potentially useful for studying mechanisms of both inter– and intra–microfibril crosslinking as well as for predicting the efficacy of specific modifications to the molecule or potential crosslinking agents.

The use of NMR and computer–generated models in a study of chromium binding to collagen

To augment the computer modelling studies, Dr. Brown is using nuclear magnetic resonance spectroscopy (NMR) to study the binding of chromium molecules to collagen.

Effective cross–linking of collagen in animal hides produces leather, having properties of strength and resistance to organisms that would attack and destroy the hide. For more than one hundred years, the most commonly used cross–linking agents have been complexes of chromium (III). However, tanning is more of an art form than a science and the mechanism of the chromium–collagen interaction is poorly understood. The goal at ERRC is to develop a scientific basis for improving the effectiveness and efficiency of tanning technology.

In the present study, the ERRC researchers use UV–VIS, molecular modelling, circular dichroism, and NMR spectroscopy to characterise changes in soluble collagen at the various stages of the chromium tanning process. Partial denaturation of collagen prior to chromium binding has been observed. Acidic side chains (aspartic and glutamic) disappeared from the NMR spectrum when chromium was bound to the collagen.

Spectroscopic results were correlated with segments of ERRC's previously developed molecular models of the bovine type I collagen triple helix and microfibril. This correlation serves to refine or validate the model and to visualise which properties of collagen and potential crosslinkers may be important in the design of an effective tanning agent.

The recovery of value–added products from chromium containing leather waste

Maryann Taylor has led the development of two processes to treat the chromium–containing solid waste

generated by the leather industry. The waste is treated with alkali and enzymes to extract gelable and hydrolysed protein products and recyclable chromium cake. Depending on the choice of alkali, products with varying chemical and physical properties can be obtained.

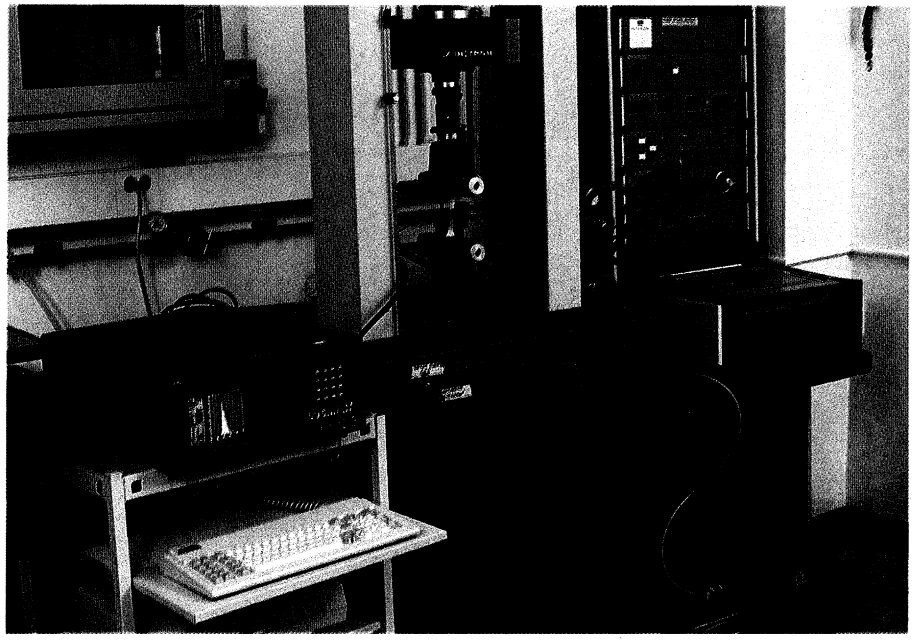
If the ash content in the products is too high, the protein solutions can be passed through mixed–bed ion–exchange columns to lower the ash content with a subsequent improvement in the physical properties. The researchers have also demonstrated, statistically, that these processes are repeatable with respect to their chemical and physical properties and that good and repeatable material balances are obtained.

The recovered protein fractions, practically devoid of chromium, have potential use in a wide range of products, including adhesives, cosmetics, films, encapsulating agents, animal feed and fertiliser. Increasing the quality of the recovered protein from chrome shavings improves the cost–effectiveness of the process as a viable alternative to widespread land filling of the shavings.

The role of minority collagens in leather processing

Dr. Paul Kronick and Susan Iandola have been investigating the role of minority collagens in leather processing. The leather making process is designed to remove nearly all the components of hide except type–1 collagen. This research demonstrates that in fact removal is only partial. By using immuno-histological techniques they have established that four types of minority collagen (III, VI, XII, and XIV) and the protein part of a proteoglycan (decorin) at least partially persist through the beamhouse. They are presently determining what effects these have on the mechanical properties of leather.

The effects of fatliquor surfactants on the stability of the collagen in leather are also being studied. The immediate binding of the sulphated portion to the cationic groups of collagen has been observed, finding the thermodynamic parameters to be similar to those for binding of a commonly used detergent, sodium lauryl sulphate. This binding has been directly localised by transmission electron microscopy. Subsequent reactions with collagen in solution have also been observed by isothermal calorimetry. This work will provide guidelines for selection from the plethora of fatliquor classes available from commercial sources.



Acoustic emission apparatus – measuring the sound emitted from breaking fibres and fibril adhesions as leather is stretched in an Instron testing apparatus

Contrary to what has been written in many textbooks about leather technology, Dr. Kronick has recently reported that the softening effect of fatliquor on chrome–tanned leather when it is dried, comes about not by 'lubrication' of the fibril, but by formation or preservation of 5-micron diameter fibres, instead of fibres ten times as thick.

A correlation has also been found between the prevalence of the larger fibres in a leather and the emission of many sonic pulses when leather is stretched even slightly. This acoustic emission almost vanishes when the leather is adequately fatliquored. Such leather can be stretched almost to failure before acoustic pulses, characteristic of breaking fibres, can be detected. A goal of this research is the development of a method for the prediction of elongation at break by a non destructive stress–strain test.

Alternatives to brine curing of hides and skins

Dr. Bailey has been studying alternatives to brine curing for most of his career. One interesting alternative that has recently been investigated is the use of potassium chloride (KC1) in place of the traditional salt, sodium chloride (NaCl). The compound was found to be almost identical to salt in terms of its ability to preserve the hide. KC1, however, has a distinct advantage over NaC1 because of its environmental compatibility due to its properties as a fertiliser. The brine produced by KC1, as a by–product of curing, can be disposed of by land application.

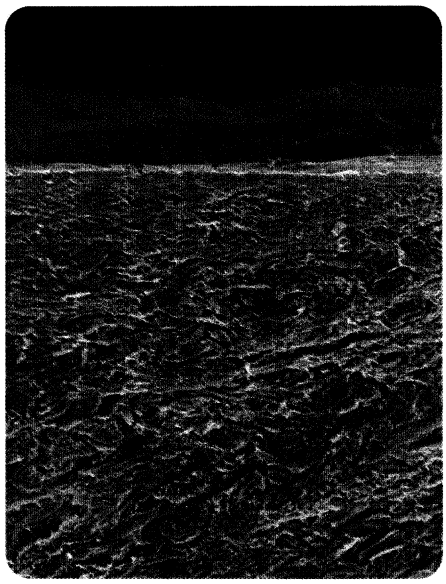
Electron beam irradiation is a widely used industrial process to sterilise medical soft goods such as bandages and surgical dressings. In this research project it was found that cattle hides could be folded up to four times and irradiated with a 10 million electron volt source of electrons preserving them for indefinite periods of time without any of the disadvantages of salt curing. The down side of the process is that the hides must be carefully maintained in a sterile condition through appropriate packaging to maintain the preservation.

Gamma irradiation of hides is also being studied for the same purpose. The physical mechanism of bacterial treatment in both these processes is substantially the same. Other aspects of handling the hides and skins, however, are quite different.

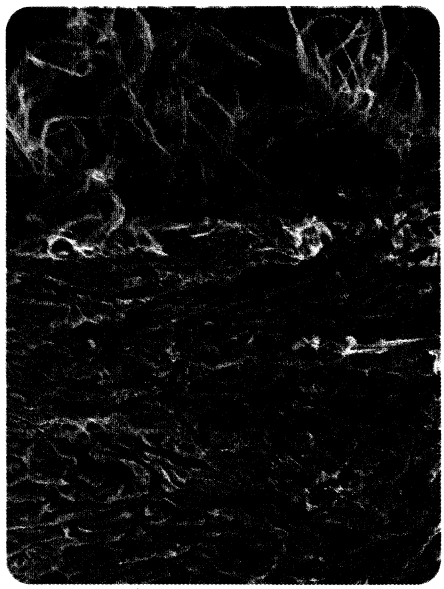
Halophilic bacteria – 'Red Heat'

Dr. Russell Vreeland, a visiting Professor from West Chester State University, had been holding a part time position with the group for several years.

High magnification electron micrograph of a halophilic bacterial colony.



Cross-sections of leather prepared from uncontaminated fresh hide



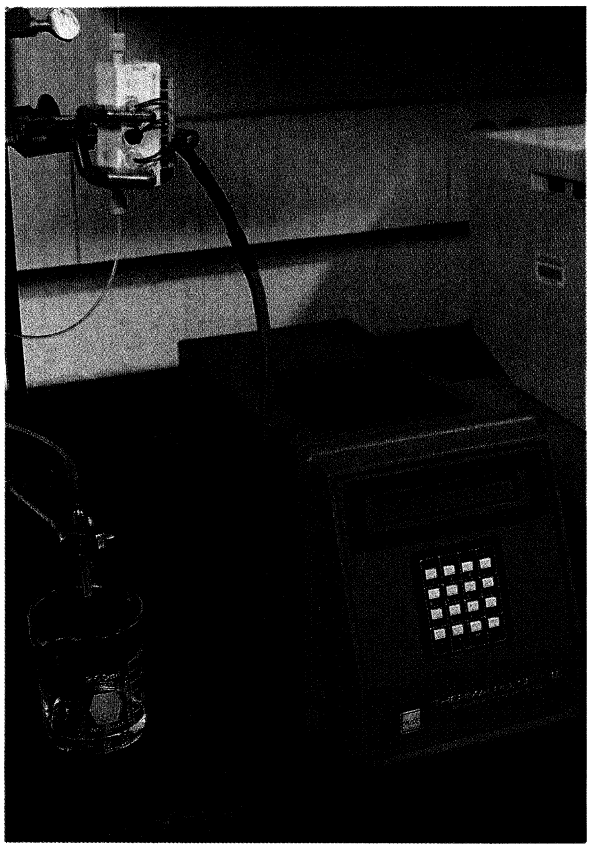
Cross-sections of leather prepared from hide incubated with halophilic bacteria.

Dr. Vreeland is an authority on halophilic bacteria and has been doing cooperative research on the effect of these bacteria on grain quality.

'Red Heat' is a condition caused by various strains of halophilic bacteria and has long been suspected of causing grain damage to brine-cured cattle hides. Cooperative research between halophilic bacteria experts from West Chester State University, Mamara University in Istanbul, and researchers at ERRC has now demonstrated the actual conditions under which this damage can occur. Studies are continuing to find effective control treatments to eliminate these bacteria from cured hides.

The measurement of collagenase activity

Dr. Samuel Mozersky has been working for several years on measuring collagenolytic halophilic bacteria on brine-cured hides. The recent work which demonstrated that halophilic bacteria are a source of damage to hides also suggests that such damage is probably mediated through the action of enzymes (collagenases) produced by the halophiles which attack the collagen of the hide. Procedures are being developed to detect and measure the extent of such contamination of the hides and of the environment to which the hide is exposed. That in turn will help determine the efficiency of modified environments and treatments that may reduce or eliminate the offending organisms and/or the collagenase which they produce. A highly soluble, commercially available, derivative of collagen has been shown to be suitable for such evaluations of collagenase activity. A procedure requiring only the simplest equipment and suitable for assay of collagenase in the tannery has been developed.



System for measurement of the viscosity of collagen solutions before, during, and after digestion by enzymes.
Upper left: flow sensing cell (white) with attached capillaries through which the solutions flow.
Lower right: electronic flow-meter, which measures the rate of liquid flow.

In all of the research the hides and leather researchers at ERRC benefit from close interactions with other scientists as well as other Center resources. These include shared facilities for electron microscopy, NMR spectroscopy, computer resources (including molecular modelling), statistical analysis services, library services, and an office for technology transfer. This office is under the direction of the former Research Leader of the leather programme, Dr. Stephen H. Feairheller.

Legend

(1) Occasionally the results of collaboration with private sector institutions may be deleted to allow for patenting. As a result a small portion of the current work at ERRC is not disclosed in this profile.