SHORT TERM PRESERVATION OF CATTLEHIDE FOR FOOD AND LEATHER USE

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SHORT TERM PRESERVATION OF CATTLEHIDE

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Scope and Method of Study: In the past 20 years, increasing interest has developed in the use of cattlehides as a source of collagen for food use. A preliminary requirement of such a process is the development of food-quality preservation methods for the freshly flayed hide. Such methods should be economically feasible and suitable for adaptation into current slaughterhouse and tannery practices. The present study involved an extensive literature search of both current and experimental methods of preservation for both cattlehide and related food products (meats and collagen).

Findings and Conclusions: Results of this study revealed that little research on food-grade preservation of hides has been done. Many food-quality preservation processes would make the resultant hide unsuitable for possible leather use, and current leather preservation techniques are unsuitable for food use. Hides which have suffered only mechanical damage, and not bacterial damage, may be used as a collagen source even though unsuitable for leather production. The key to both food- and leather-quality preservation apparently is dependent upon control of the water activity (a_w) of the hide to prevent and/or delay both microbial and enzymatic reactions.

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INTRODUCTION

It is well known and accepted that the first organized industry following medieval times was the curing and tanning of hides for clothing, shoes, and other purposes. It was noted that tanning could be carried out more easily through the cooperation of several individuals than if attempted by only one person. Even prior to this time, the Egyptians knew of salt curing, tanning, and coloring with minerals and vegetation such as leaves, bark, berries, and herbs. According to Minnoch and Minnoch (1970), excellent leather was being produced as early as 3000 to 4000 B.C. Use of hides and skins for clothing is depicted in cave paintings from the Stone Age. The actual method of curing is not known, but animal skins were used throughout Europe to protect the Stone Age man from the elements. There is no doubt that these hides were not truly tanned, but consisted of semi-permanent cures. It is believed that minerals and oils from the brains of animals were pounded into the hide in order to soften and help resist the spoilage of these skins. Smoking of the skins was another preservative technique sometimes used.

Early accounts indicate that in the lowland countries of Holland, Belgium, and Denmark, sea water was used as a preserving factor for hide. Due to essential needs during the fourteenth century, cattle became important in these lowland countries. The cheese, milk, and hide industries developed in this era, and have remained a part of

the economy of these countries ever since. It was found that, due to the salt which could be evaporated from the ocean and applied freely to the hide, a salt cure would retard decomposition and permit shipment of hide to other areas in Europe for tanning.

In Germany during the fifteenth century, extensive salt beds were found which had been deposited as a result of prehistoric ocean evaporation following the glacial periods. This discovery extended the ability to preserve hide and helped to create a leather industry in Germany and the surrounding areas.

Even today in the twenty-first century, salt is still the most commonly used preservative for raw hide. However, disposal of used salt as either a solid or a liquid results in pollution of the soil and water. Waste salt adversely affects the biofauna and bioflora of the environment, making the soil infertile, increasing the osmotic potential of water, and inducing toxicity in susceptible plant species (Krishnamurthi and Padmini, 1976; Duraiswamy et al., 1977).

Development of collagen, the fibrous component of hide and skin, as a possible protein-extender or for other food use (Eilers and Labout, 1946; Highberger, 1953; Deasy, 1959; Heidemann and Riess, 1963; Whitemore et al., 1970; Burke, 1980; Gielissen, 1980; Haberstroh, 1980; Henrickson, 1980; Lipsett, 1980; Maire and Lipsett, 1980; Pharriss, 1980; Schalk, 1980) has set new limits and demands on potential preservation methods and overall handling procedures for raw hide.

Therefore, increasing interest has been shown in alternative methods of preservation by Vivian (1969), Woods et al. (1970a, 1970b, 1970c, 1971, 1972a, 1972b), Hopkins et al. (1973), Siviparvathi and Nandy (1973), and Wada et al. (1975), among many others. This study

strives to summarize the methods developed for short term preservation of cattlehide for both food and leather use.

CHAPTER II

METHODS OF PRESERVATION

McLaughlin (1921a, 1921b, 1922), Kowalewski (1940), Kardos (1960), Muthiah et al. (1967), Benrud (1969), Thorstensen (1970), and Venkatesan et al. (1973) have reported on various structural, biochemical, and bacteriological analyses of freshly flayed hide, usually bovine. Several extensive reports are also available on the microbiology of the curing and tanning processes for hide (Woods et al., 1970a, 1970b, 1970c, 1971, 1972a, 1972b; Hendry et al., 1971). Gorin et al. (1980) have compiled many sources of published information on the science and technology of hides and leather. The available information is too voluminous to be included in this report.

Hide protein is a very perishable commodity, becoming subject to microbial decomposition as soon as the hide is removed from the animal. Therefore, immediate attention is required to prevent deterioration. If fresh hide is properly cured and stored, it retains the strength characteristics of fresh hide. However, if it is not properly cured, autolysis and bacterial action occur. Either one or both of these deteriorative forces may cause a reduction in strength of the hide and, if allowed to progress, will ruin not only the strength of the leather but mar its surface characteristics, reduce its value, and make it an unsaleable product. Curing methods (both actual and experimental) include salting (pack and brine), use of chemicals and

salt-chemical combinations, irradiation, and drying. Refrigeration and/or freezing are currently considered too cost-prohibitive for actual use, and are therefore not included in this report.

Salt Pack

For many years, the salt pack was the only method used for curing hide. The workmen took pride in spreading the salt uniformly and in building the pack properly. To build a pack properly, the floor is cleaned and covered with new rock salt. The first hide is laid out flesh side up and salt is spread evenly over the entire hide. Then the hide is folded in along the belly or hairbreak line from front to back, with a minimum of one inch of extra salt placed in the fold. Before the next hide is put down, salt is also placed on the hair side of the hide that has already been turned in. This helps to prevent hair slips. (The least amount of the hide turned in for a side edge will guarantee both a full cure and a uniform pack.) About one pound of salt is normally required for each pound of green hide. Freshly flayed calfskin requires about three-fourths pound of salt per pound of green hide. The top of the pack should be level and at an ideal height of 4 to 4-1/2 feet when completed. The pack is topped off with 2 to 3 inches of rock salt mixture to prevent the top hides from drying out (Minnoch and Minnoch, 1970).

Hides have been traditionally cured in salt pack for centuries. At some of the packing plants, the hide cellars for salt pack curing are located so that little ventilation and light are available. These conditions and uneven distribution of salt permit bacterial growth. A pound of salt per pound of hide is used to insure coverage. Because

all of the salt is not absorbed, rather than waste the salt, some processors reuse it. Using dirty salt containing blood, manure, fatty flesh tissue, and impurities from rusty metal pipes yields a cured hide that shows every color of the rainbow from the metallic stains when it is unhaired after being in the lime-sulfide liquor (used to bring about unhairing in the tannery).

While it has been a practice to leave hides in pack for a month after the pack was built, in more recent years some hides remain for as short a time as 10 days because brine run-off stops at about nine days and the hides have their maximum pack shrinkage. However, this practice attributes to inadequate cure. Maintaining a closed pack for 21 days helps in reaching a more uniform salt absorption and reduction of moisture content.

Salt has the following effects: 1) cause high osmotic pressure and hence plasmolysis of cells; 2) dehydrate hide by drawing out and tying up moisture as it dehydrates microbial cells; 3) ionize to yield the chlorine ion, which is harmful to organisms; 4) reduce the solubility of oxygen in the moisture; 5) sensitize the cell against carbon dioxide; and 6) interfere with the action of proteolytic enzymes. The effectiveness of NaCl varies directly with its concentration and the temperature (Frazier and Westhoff, 1978).

The extent and rate of salt penetration into raw hide has been studied by precipitation of the absorbed sodium chloride with silver nitrate in thin cross sections of hide (Roddy, 1965), with absorption occurring initially in the corium.

Research and experience have shown that cured hide containing more than 48 percent moisture is poorly protected, and will deteriorate much

more rapidly than cured stock with less than 48 percent moisture (Kallenberger and Lollar, 1979). In the opposite extreme, cured hide with less than 40 percent moisture often creates difficulties with limited flexibility and poor soaking qualities. By using a recommended salt content of 14% minimum (Cooper, 1973) and a maximum moisture content of 48%, hide has good storage life and may be shipped for long distances as long as it does not come into contact with water or elevated temperatures. However, hide with 12-13% salt, when stored at 95° to 113°F for six weeks, showed autolytic damage, but there is no bacteria present. At a salt content of 6-10%, autolytic and bacterial damage are noted at the end of a month. Autolytic and bacterial damage which occur at 95° to 113° are reflected in the leather, where fiber bundle splitting and a stretchy condition are observed. At 2.5-5% salt content, some bacterial damage may occur in one to three days at temperatures from 95° to 113°F. This is in the form of hair-slip and pitting of the grain surface of the hide (Minnoch and Minnoch, 1970).

However, in the initial condition of the hide, dirt and manure are often the major sources of contamination. The first innovation in modern hide curing came with the development of a heavy-duty whole hide combination fleshing-and-demanuring machine specifically designed for packinghouse use. This machine, working on both sides of the hide at once, can remove manure, grit, and as much as 18 pounds of fat and flesh per 100 pounds of hide.

The operation starts with the placing of the hide, flesh-side up, into the machine in the conventional manner. The machine is then closed, and the demanuring cylinder comes in contact with the hair

side of the hide, spreads it out and removes manure and other foreign objects imbedded in the hair. As the hide is pulled up about 7 or 8 inches, the fleshing back-up roll moves forward, pushing the flesh side of the hide in contact with revolving fleshing cylinder blades. This removes flesh and fat from the demanured hide. After the first half of the hide has been demanured and fleshed, the machine is opened hydraulically. The hide is then turned around and the remaining half is demanured and fleshed. The next improvement was the development of the hide washing machine. This device consists of a rotary screen through which the unfleshed hide is tumbled under jets of chilled water. This serves to remove much of the manure and blood from the hide and also causes the fat to harden, resulting in an improved fleshing operation.

Swift and Company was perhaps the first to flesh hides (Minnoch and Minnoch, 1970). Nevertheless, the man who did the most to bring demanuring, fleshing, and brine curing "together" and to the attention of the trade was Merle A. Delph of M. A. Delph Company, Indianapolis, Indiana. He introduced the technique to the industry at large at an open house in his company's plant in Indianapolis about 25 years ago. Everyone in the trade was invited and had the opportunity to see demanuring, fleshing, and brine curing at work and hide progress in action. Many took advantage of this opportunity, and the technique became an overnight success.

Brine Curing

Armour and Company, with the development of its "special cure" in the mid-twenties, was perhaps the first to brine cure hides.

However, Swift and Company was the real leader in making brine curing a reality. This big packer gave the agitated brine process (with paddle wheels) the momentum it needed to popularize it with the trade. Acceptance was slow at the start, but gradually brine curing caught on. Now brine curing is considered an established practice in the industry, even though there are still tanners who prefer conventionally cured hides out of pack to those produced via brine.

In the early days of brine curing, one of the outstanding authorities on the subject was Dr. F. L. DeBeukelaer, a well-known scientist and researcher. He first served Swift and Company and was later a member of the staff of the former American Meat Institute Foundation. Because of Dr. DeBeukelaer's efforts in behalf of brine curing, he is sometimes referred to as the father of that important process.

The primary purpose of brine curing was to bring about a substantial reduction in hide inventories, thereby releasing capital previously tied up in inventories for other purposes. This was done by cutting the time required for conventional curing (anywhere from 21 to 30 days in pack) to about two days. By fleshing and brining at the source instead of at the tannery, as had been the practice in the past, shipping costs were lowered considerably, since it was no longer necessary to pay freight on about 20 to 25 pounds of non-leather making material. Thus savings were substantial. Additional savings also resulted from less labor and lower handling costs. In recent years, shortages of labor have prompted many hide processors to adopt brine curing operations. In the ordinary sense, hide curing is a process in which the hides are treated with common salt to arrest bacterial and enzymatic decomposition to which they are subject within a few hours of death of the animals.

From a theoretical standpoint, most hides and skins are brine cured. Crystalline sodium chloride, or common salt, cannot be absorbed by the hide; only after the salt crystals have been dissolved in water to make a brine can the curing proceed. In the case of pack curing, the salt crystals draw moisture from the hide, which dissolves the salt. The pack is built with the intention of retaining this brine, thus completing the cure.

As the salt draws moisture from the hides, the moisture content is reduced sufficiently to produce an environment unfavorable for bacterial growth, and the near saturation of the remaining moisture with sodium chloride also has a bacteriostatic effect. These two factors, along with a reduced temperature in the curing cellar, combine to produce satisfactorily cured hides.

In the brine curing process, the hides are in contact with saturated brine at all times. This serves to reduce the time required to cure hides from 30 days in the case of pack curing to about 24 hours in agitated brine curing. Hides may be cured in brine solutions by raceway, pit, concrete mixer, or drum. The proper attention must be given to keep the brines saturated and free of filth. A hide as it is pulled from the animal may contain as much as 67% moisture; 15-20% of the original hide moisture will dilute the brine in the first two hours of cure. Sinkers (hides which sink to the bottom of the vat instead of circulating) are characteristic of low salt concentrations. The lack of buoyancy of the brine causes the hides to sink.

Raceway

The most common type of brine curing employs an oval vat with an

oval island in the center, making what has been aptly described as a "raceway vat." Two paddles at opposite sides cause the hides to move slowly around and around. The paddles usually have six blades which dip 10 to 16 inches into the brine and revolve at a rate of 12 to 16 revolutions per minutes. The raceways are usually eight feet wide and five feet deep. This system requires a minimum of four pounds of saturated brine for each pound of green uncured hide. A common volume for a raceway vat is 15,000 gallons with a capacity of about 550 hides. Some vats being used in the industry will accommodate over 800 unfleshed hides, or 1200 fleshed hides. The ideal installation consists of three vats, two of which can hold a full day's production. The third vat is used for loading the following morning while the cured hides are being removed from the first tank loaded the day before. Thus the vats are used in a constantly rotating arrangement.

As is the case with pack cured hides, moisture is drawn from the green hides in the brine tank. To prevent dilution, a portion of the brine is usually circulated through a salt dissolving chamber, commonly known as a lixator. This serves the double purpose of keeping the brine close to saturation and filtering out some of the dirt and other solids suspended in the brine. As a rule, the brine is passed through a rotary screen to remove hair and fat prior to going to the lixator. However, in some installations fine salt is slowly added to the curing tanks along with the hides and the turbulence set up by the paddles is relied on to keep the brine up to strength (Minnoch and Minnoch, 1970).

In the raceway, sufficient salt may not be absorbed because the work schedule requires removal each day of the previous day's hides

before raw hides are placed in the raceway. With the brine kept at complete saturation, over 22 hours is required for the brine to completely penetrate the hide, and some hides will often be removed from the raceway before penetration is complete. To insure that sufficient salt is in the hides, after removal from the raceway, salt may be added to the hide for storage or when bundled.

The use of disinfectants for sterilizing salt and brine solutions is recommended, but at the levels used, the chemicals will not protect an undercured brined hide from bacterial attack during storage. Salt chemicals such as sodium hypochloride have been added to the hides in the raceway. Sodium hypochloride is an excellent chemical for the control of microbial growth in the brine. However, once hides are removed from the brine, the clorine quickly evaporates and little remains to kill or eliminate organisms, so that after a few days the hides are no longer antiseptic. The astringency of the sodium hypochloride also creates a drawing of the grain in the finished leather. Therefore, additional NaCl, "safety salt," should be added to give increased protection against bacterial invasion and to improve storage life.

The reason for the popularity of raceway brine curing among the large packers and hide dealers is that this procedure lends itself to automation, thus reducing labor requirements. In modern systems, the hides are moved by conveyors to the washers, then to the fleshing machine and finally into and out of the brine tanks. Such systems are significantly more efficient than the old method of salt packs.

Paddle Vat

In another type of agitated brine cure, a tannery-type paddle vat

is used. This is a large rectangular vat with a rounded bottom. A single paddle is placed above the vat parallel to the long sides. Each vat will cure about 150 to 200 hides. This type of tank is advantageous in plants where the kill is relatively low.

Tannery Drum

In a third method of agitated cure, a tannery drum has been used. This method was a forerunner to the "cement mixer" type of drum cure which is gaining in popularity. This method uses a gigantic bass-like drum with an axle at the center so that it can turn like a wheel. The drum is constructed of wood and has an opening on the outer periphery. A solid door and a perforated door are provided for this opening.

In practice, the hides are dropped from the killing floor into the drum, and the perforated door is put in place. Then, with the drum turning, chilled water is run in through the hollow axle and is thrown out through the perforated door. This has the dual purpose of chilling and washing the hides, eliminating some of the manure and blood.

On the inner periphery of the drum are large pegs. As the drum turns, the pegs carry the hides up until they reach a height where they slip off of the pegs and fall to the bottom of the drum, utilizing the tumbling motion to increase contact with the wash water or brine (salt).

After about 20 minutes, or when the water being thrown out becomes clear, the water is shut off and the drumming is continued for 10-15 minutes to drain. Then the drum is stopped and the perforated door is removed. After addition of 33% (based on raw hide weight) of

fine salt, which brines and penetrates the hide, the drum is turned for three to four hours with the solid door in place. Disinfectants may be added to reduce microbial levels and provide a well-cured hide.

Finally, the hides are dumped into a slatted truck and the drum is ready for reloading. A drum eight feet in diameter and eight feet wide will cure up to 5,000 pounds of green hide. Since the whole operation can be performed in four hours, this provides an efficient curing method for plants with low kill rates.

Since brine curing proceeds more rapidly with an increase in agitation, drum curing takes less time than other methods. However, attention must be paid to mill action, for high temperatures due to mechanical agitation may occur. Cold water is required to prevent heat damage during washing and the hides must be chilled to below 50°F before the curing is started. Close control of the temperature during drum curing is required in order to control friction-generated heat.

Pit

The fourth method of brine curing, and one that is used rather extensively, is pit curing. The equipment consists of rectangular vats about the size and shape of an ordinary hide pack. The walls are four to five feet high and the flat bottom is pitched to one corner to permit complete drainage. The hides are placed flesh side up in this pit precisely as when building a hide pack except that no side edges or corners are necessary. As the hides are put down, they are salted using one-third to one-half pound of salt per pound of hide instead of the pound per pound used in ordinary pack cure. A fine salt is used, usually no. 1 rock salt. As the pit is being filled with hides,

saturated brine is run in so the hides are just submerged. When the pit is full, the hides are covered with burlap or topped off with curing salt. In this method of cure, the hides are usually prefleshed using the same type of washing and fleshing equipment described earlier for raceway brine curing.

Pit brined hides have, in addition to the saturated brine solution, undissolved salt crystals between each hide. Prefleshed hides are adequately cured after 48 hours, although unfleshed hides take somewhat longer. At the end of the curing period, the bottom drain is opened and the pack is drained for 24 more hours. These hides usually have a minimum salt content of 14% when they are removed from the pits after three days in cure. One at a time, the hides are hung over a wall, and then drawn from the outside onto trucks or onto a conveyer. In this way, the excess salt is recovered for reuse. If the brine is reused without being put through a lixator, future hides may show signs of bacterial attack even though the salt content is at or above the minimum normally required for preservation. After further drainage, various means are used to remove salt crystals adhering to the hair and flesh. The hides are then inspected and bundled, and held in storage.

Concrete Mixer

Commonly referred to as the "concrete mixer," the latest method for curing hides is the Brinematic Hide Processor. This method was introduced to the industry by Legallet Tanning Company of San Francisco, California. The various mixers can handle from 50 to 215 hides, according to mixer size.

While the principle of the mixer was borrowed from the concrete industry, nevertheless a number of changes were made to enable mixers to handle and cure hides, including plastic or stainless linings. The rotating drum locks and works much like a concrete mixer. One of the best features attributed to the Brinematic is the fact that it easily controls unloading of the hides via a reverse cylinder. During unloading, the hides worm their way, spiral-fashion, up through the neck or mouth of the mixer. Another advantage attributed to this system is that hot hides can be loaded into the mixer by conveyor belt or chute directly from the kill floor. The actual curing process can start when the mixer is full or at the end of the day's kill.

The process begins with a cold water washing cycle of 15 to 30 minutes to remove manure and blood from the hides. The length of the wash cycle can be varied according to the amount of manure and blood on the hides. After the wash water is drained, salt is added (15 to 20 pounds of salt per hide), along with a small amount of bacteriocide solution. The loaded mixer is operated continually for two hours and then intermittently during the rest of the night. On the following morning the hides are ready for discharge. The batch of cured hides is unloaded from the revolving drum by switching the machine into reverse. Unloading takes about 20 minutes. The final step involves palletizing the hides for storage or shipment after they are selected, rolled, and bundled.

A hide sample at the time of bundling should contain from 44-48% moisture, 12-16% ash, and a ratio of 20-26. The ratio is the combination of ash to moisture that exists at a specified moisture range (Minnoch and Minnoch, 1970). Ratio is figured as percent salt in

combination with water contained in the hide:

$$\text{Ratio} = \frac{\text{Ash}}{\text{Moisture + Ash}} \times 100.$$

Table I shows moisture, ash, and ratios of hides at various time intervals after removal from raceway (Minnoch and Minnoch, 1970).

TABLE I

CURED HIDE DRIPPING FROM RACEWAY AND SAMPLES TAKEN AT INTERVALS UP TO 100 HOURS

Samples	Moisture (%)	Ash (%)	Ratio
Dripping Hide	57.14	9.48	14.22
2 Hours Later	46.85	10.50	18.31
24 Hours Later	42.35	12.45	22.71
32 Hours Later	37.65	14.71	28.09
56 Hours Later	33.82	15.14	30.92
100 Hours Later	22.47	17.98	44.45

Source: Minnoch and Minnoch, 1970

At the present time, approximately 50% of the hides in the United States are brine cured. Of this total percentage, about 40% are demanured and fleshed to produce very good quality hide.

With continuous brining at 97° or higher (salometer reading), cortorization creating salt crusting and astringency may occur on the

grain surface. It has been further noted (Minnoch and Minnoch, 1970) that with the addition of proper chelate, salt brine can be kept more uniform throughout the entire tank, solubilizing undesirable minerals. With minimum control and maintenance of pH 6.9, very little can go wrong in brine curing. The occasional downgrading of hide from this process usually occurs from decomposition prior to brining. Caution is necessary regarding the time that the hide is in transit before brining, especially throughout the summer months and the wet season. Use of a small amount of safety salt during bundling helps to avoid adhesion of the flesh during storage, thus making it easier for tanners to open the hide bundles for soaking.

A 71 pound green hide takes up 1.33 cubic feet in space, including the salt for curing. If brine-cured hides are used in the pack, then one-third more pounds of hide can be figured per cubic foot of pack. Because of the time involved and the space required, it is understandable why the brine methods of cure have come into extensive use in the past 25 years. The hides can be handled in a shorter time, require less space, and produce hides that will make high quality leather.

Pickling

"Pickling" refers to the treatment of hide with salt and acid to bring the hide to the desired pH for either preservation or tanning. The automated processing plant of Sioux City Dressed Beef Company at Sioux City, Iowa, can produce 5,000 pickled hides on a 24-hour cycle. The plant was constructed solely for the purpose of providing a modern fleshing and pickling operation. In this process, brine curing is

eliminated completely. One of its salient features is the fact that it is continuous and does away with the need for brine curing or salt use.

The system used by the company involves all the steps that normally follow after hides leave the trimming table. The hides are washed, trimmed, and fleshed; then they are dehaired by liming. This computerized system can turn the chemical pumps on automatically at a desired time and even measure the amount of chemicals to go into each of the six large drums. This "pushbutton" operation enables the drums to be turned on automatically. Through card programming, the drums may be dumped whenever desired and the hides washed exactly the number of minutes intended. Any formula required may be put into the card programmer and the operation completed automatically.

Actually, the dehairing and pickling operations are very much the same as those performed at tanneries. Hair is removed through a hair-burning process by means of a low concentration of sulfides. After the hair has been pulped, the hides are thoroughly washed, delimed, bated (an enzymatic and catalytic purification of hide to remove degradation products and breakdown fat cells), and pickled to an end equilibrium of 2.4 to 1.6 pH. This entire operation is done in a regular tannery wooden drum. A brand name chemical (unidentified in literature) is added during the pickling process to help prevent bacteria and mold.

Pickled hides have an excellent shelf life. They have been retained under normal non-refrigerated warehouse conditions in excess of one year without adverse effects. Tests have shown no significant difference between leather made from fresh pickled hides held in storage as long as one year. From the standpoint of shipping, pickled

hides can be palletized on disposable pallets covered with polyethylene and strapped ready for shipment.

The early use of preprocessed hide by a few tanners has resulted in these findings (Minnoch and Minnoch, 1970): yields (calculating pounds of hide tanned versus leather footage produced) are greater with pickled hide. The grain from fresh hides that have been pickled is smoother and finer. It is believed that this may be due, at least in part, to the fact that the hides have not been salt cured. Also, there has been a noticeable reduction in the number of veins showing up in the finished leather. The strength of finished leather made from preprocessed hide is said to be good, and colors are reported to be clearer and brighter, perhaps because there were no salt stains. Another important feature is the elimination of hair slip that otherwise might have resulted in damage to the grain because of poor or inadequate cure.

In addition to Sioux City Dressed Beef Company, Spencer Packing Company of Spencer, Iowa, is also engaged in producing pickled hide, as is Swift and Company, which has a hide pickling plant at Grand Island, Nebraska. M. Lyon and Company has a major wet blue hide complex (Blueside Company of St. Joseph, Missouri) which processes hides through the "chrome-blue" stage before storage or shipment.

Chemicals

Preservatives added to inhibit or kill microorganisms are effective due to their physical action or chemical action or a combination of such actions (Frazier and Westhoff, 1978). Subtle changes in the environment such as pH or temperature fluctuations, which in

themselves might have only a minor influence on microbial growth, can be extremely significant factors in the control of microorganisms by virtue of their influence on the antimicrobial activity of a chemical agent. The intensity of the antimicrobial activity can often be correlated with the rate at which the antimicrobial agent gains access to the biophase or the site at which it acts (Kostenbauder, 1977).

Ferguson (1939) was one of the first to consider the relationship between toxicity of a substance and the tendency of the toxic substance to transfer from a surrounding external aqueous phase to the biophase or site of action. Antimicrobial action occurs when a physical or chemical agent interacts with a component of the organisms that is essential to its structure or metabolism. The sensitive target may be a major cell constituent or a single enzyme, and the effect on the organism varies from reversible growth inhibition to death. The principles of antimicrobial activity and the effects of various agents are discussed in depth by Gardner (1977).

The use of boric acid for temporary preservation of hides was investigated by Hughes (1974). Cuttings soaked 15 minutes in saturated boric acid were preserved for five days at 30°C, compared to two days for untreated samples. Fifty batches were preserved by consecutive soaking for 15 minutes in a boric acid bath without loss of effectiveness of the bath. In a pilot experiment, Hughes preserved 3100 kg of hides and stored the hides for up to 29 days at 14°C. The boric acid used ranged from 0.3 to 1.5 kg per hide.

Studies on the preservation of hides with antiseptics alone were made for 20 days' storage at 25°C (Cooper and Galloway, 1974). The antiseptics, which were used separately or in mixtures, were sodium

chloride, sodium silicofluoride, sodium pentachlorophenate, sodium fluoride, zinc chloride, and "Stermist" deodorant. Physical tests on garment leather produced from these antiseptic-treated skins show that these methods are capable of short term preservation of the skins, but visual assessment of leather and grain quality revealed that the antiseptic-treated skins gave leather which was of slightly inferior quality and with more grain blemishes. Sodium chlorite in the antiseptic mixture gave an inferior product.

Sodium bisulfite, sodium sulfite and acetic acid, sodium chlorite and sodium hypochlorite, alkyl dimenthyl-benzyl ammoniumchloride, biguanide polymer, and organic sulfur compounds were tested by Sipos and Vermes (1978) with temporary preservation ranging from 3 days to 30 days. In aqueous solutions, sulfur dioxide and various sulfites, including sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite, and potassium metabisulfite, form sulfurous acid, an active antimicrobial compound. Many mechanisms for the action of sulfurous acid on microbial cells have been suggested, including the reduction of disulfide linkages, formation of carbonyl compounds, reaction with ketone groups, and inhibition of respiratory mechanisms. In addition to the antimicrobial action of sulfites, they are also used to prevent enzymatic and nonenzymatic changes (Frazier and Westhoff, 1978).

Results of various combinations of acetic acid, sodium sulfite, sodium bisulfite, and sodium bisulfate have been reported by Hopkins and Bailey (1975) and Bailey and Hopkins (1975, 1977). Sulfur dioxide is the active preservative of the acid-sulfite method. Hopkins (1980) used direct application of the active ingredient as

generated by adding various concentrations of HaHSO3 to an acid solution. Treated hide samples that were stored for up to 28 days were preserved satisfactorily when judged by microbial counts and observation. Acidification with $NaHSO_3$ of the hide samples before treatment significantly lowered the amount of sulfur dioxide needed for preservation.

According to Weaver et al. (1972), hides from freshly slaughtered animals can be preserved and prevented from deteriorating by treatment with a synergistic mixture of water, acetic or propionic acid, and N,N'-bis(methoxy)methyl uron. Sodium acid sulfate can also be used in place of the acetic or propionic acid. A surfactant may be added to the mixture for wetting or emusifying purposes. However, it is not an essential element for the synergistic action. The amount of water can be varied greatly, from 10 to 100%, based on the weight of the hide, without effecting the efficacy of the treatment. Excellent results have been obtained by Weaver et al. with a mixture containing 10% water, 0.03% surfactant, 1.0% acid and 0.2% uron derivatives, all amounts based on the weight of the hide.

Haffner and Haines (1975) found that a 5% solution of sodium chlorite or a mixture of Gloquat C (15%) and Glokill 77 (10%) sprayed over the flesh surface of a hide will retard bacterial attack for a period of six days at 26°C. Hides immersed in a mixture of Vantocil IB (0.4%) and Vantoc CL (0.2%) remained in a good state of preservation for eight days at 26°C. Any biocide applied to a freshly flayed hide will be concentrated in the flesh layers.

In the late 1950s, bactericides such as phenylphates and pentachlorophenates were found to have an advantage, because they became

part of the hide once the hide had been removed from the brine. This permitted a longer storage and holding period. They resisted excess organic growth on the hide itself. However, these phenols had two disadvantages.

First, because these phenols were a tanning material in themselves, the grain of the hide, with the hair on, would become pretanned, making it difficult for the tanner to remove the hair. Phenols also cause a grain astringency which would show as drawn grain and hard spots on the finished leather. Second, after continuous use of phenols for a period of time, new strains of immune bacterial growth would start, limiting the value of such bactericides. A new bactericide had to be developed, one with low toxicity which also controlled astringency of grain and avoided immunity development of microorganisms. In the early 1960s, this was accomplished successfully in the development of a salt of chloro-napthoglucoheptonic acid (Minnoch and Minnoch, 1970).

A comparison was made by Hausam (1964) of preserving skins by the following methods: 1) standard salting with 2% soda ash and 1% naptha-lene, 2) salting with addition of 0.2% p-chloro-m-cresol (Raschit K) (equal to 0.1% on the skin), 3) using 0.1% Raschit alone or with other phenol derivatives as a powder on the skin followed in a couple of hours by normal salting. At intervals for up to 62 days, half-gram samples of skin were removed for bacterial counts on agar plates. Also, counts were made in bouillon inoculated with soak water from samples from skins cured for 62 days. The phenolic derivative and napthalene-soda were equally effective for preserving skin. After two days of good cure, bacterial count was high, then decreased rapidly to a mini-mum in about three weeks. In skin poorly treated with preservative,

the bacterial count was extremely high in two days, then decreased to a moderate level in six to seven weeks. Thus, poorly cured skins have a high bacterial count for a prolonged period. All bacteria were not killed during curing; some were only arrested in growth. When liquor from a count was added to bouillon containing 0.5% of Tween 80, which reacts with phenols, the results were 25% higher than those without Tween, showing that 25% of the bacteria were checked but not killed. Soda seemed not to be a preservative in the true sense; its action was only the result of its high alkalinity.

Bleaching powder, boric acid, zinc chloride, zinc sulfate, savlon, betrimide, merpin, paradichlorobenzene, parachlorophenol. orthochlorophenol, and parachlorometacresol were some of the chemicals used as pretreatments in a study done by George and Krishnamurthi (1966).

Pauckner and Schmidt (1980) tested 20 unidentified commercial biocides for preservation possibilities. The less effective biocides reportedly could be recognized by growing cultures using gelatin as a substrate. When tested on hide pieces, even the more potent biocides did not preserve them for more than two weeks unless three to five percent solutions were employed. Most worked better on fleshed stock. The most economical way of extending curing time was the use of one percent biocide in the presence of five or preferably ten percent NaCl. All percentages are based on green hide weight. Since tumbling the pieces in a drum containing the biocide solution was more effective than immersion or spraying, large scale experiments with the five best products which prevented hair slippage for at least three months were conducted in a drum. In these tests combining salt and biocide, four products protected about 40 days and only one over three months. Where

the hides had been folded, stains were observed first in the blue, and then later became even more pronounced after dyeing and drying, leaving no choice but the making of corrected grain leather.

Although the use of germicides as additives to salt has been investigated by numerous workers, studies on the use of preservatives to prevent delayed cure have been rather limited. Cordon et al. (1964) found that benzalkonium chloride, an antiseptic belonging to the class known as quaternary ammonium compounds, was an effective short-term preservative for hides and skins. Their studies showed that drumming calfskins in a 400% float of a 0.1% solution of benzalkonium chloride for one hour preserved the hides for at least four days when stored at about 50°F. No difficulty was experienced in processing these skins into leather, and the physical properties were equal to leather made from the control skins that were salt-cured immediately in the normal manner. Their tests also showed that skins treated with benzalkonium chloride could be salt-cured without any ill effects. Actually in some of the preliminary tests, treatment of hides and skins prior to salt-curing enhanced the effectiveness of salt under adverse storage conditions.

On the basis of his preliminary tests, Benrud (1969) reached the conclusion that one ounce of active ingredient was needed to treat each hide. He also observed that blood and serum proteins extracted into the treating solution inactivated a part of the residual benzalkonium chloride. This precluded the possibility of reusing the treatment solutions by merely restrengthening. However, Benrud suggested a simple engineering scheme for treating hides with a minimum of labor and a minimum of equipment costs. The hides were fed into a

20 foot rotating tunnel equipped with spray nozzles. The nozzles were set to deliver a predetermined amount of solution so that each hide would be uniformly treated with the required amount of antiseptic. The total amount of liquid applied was limited to what each hide could absorb (between one and two quarts) without making the hide too wet for transportation.

George and Krishnamurthi (1966) also investigated the feasibility of pretreating hides and skins at the point of collection, so as to prevent deterioration even if curing operations were delayed for several days. Of the compounds studied, they found that zinc chloride (0.75%), together with pentachlorophenate (0.1%), when applied for several hours in a 250% float, protected hides and skins from bacterial damage for at least seven days. Even after salt-curing, the effect of the preservatives persisted as evidenced by absence of red heat, which developed on the hides salted in the normal manner.

Money (1970, 1974) reported on the use of sodium chlorite, zinc chloride, and calcium hypochlorite as short term preservatives for hide. Sodium chlorite is a powerful oxidizing agent and is the basis of oxidative unhairing. Money reported that the hair and epidermis were loosened, but that there was no damage to the grain. Sodium chlorite reacts rapidly with proteins and dilute solutions are spent quickly. Thus it was found that hide soaked in dilute solutions developed slime by the sixth day. This could be prevented by the addition of 0.1% sodium pentachlorophenate, as recommended by Money.

However, the Canada Department of Agriculture (1971) has shown that fleshings grease obtained from fat trimmed from hide treated with pentachlorophenols is extremely toxic. A number of chlorodioxins have

been identified in fleshings grease, and as little as 0.5% of such material mixed with ordinary fat causes chick edema disease in broilers. The rendering of the fat probably causes the formation of chlorinated benzo-dioxin derivatives by condensation from the chlorophenols.

Benrud (1959) also reported on the practical use of quarternary ammonium compounds as a pretreatment of hides that were being transported to a central curing operation or to a tannery for immediate processing. He found that the quarternary ammonium compounds reacted rapidly with hide proteins. Maximum uptake was attained in about four minutes when hides were dipped into 150% (on hide weight basis) of a water solution containing between 0.1% and 0.2% of the active ingredient. Hides treated in this manner were found to make good leather, even after five days storage at ambient temperature, although at this time there was some odor and appreciable hair slip. Hides that were not treated, but stored under similar conditions, showed extensive deterioration.

The work of Cordon et al. (1964), Benrud (1969), and George and Krishnamurthi (1966) suggested that pretreatment of hide with an antiseptic after flaying would be beneficial in preventing the staling that occurs in localized areas during cure.

In the past, a number of effective germicides did not receive acceptance because they had a tendency to fix the hair and interfere with unhairing. Sharphouse and Kimweri (1967, 1978) suggested the use of small amounts of formalin for curing hides. Formaldehyde is an effective preservative for hides and skins and used in small quantities presents little effluent problem compared to current salting techniques,

where salt in tannery effluents constitute a major problem, as described earlier. Trials show that it is possible to preserve raw hide by drumming in as little as 0.25% formalin (40% active) with no float, and still unhair the hide in the tannery by conventional methods using sodium sulfide and produce a satisfactory upper leather.

In order to save labor, the recent trend of the tanning industry is to use unhairing processes that destroy the hair. Possibly under such circumstances, the fixation of hair by germicides such as formaldehyde would have no consequence. This means that the whole field of antiseptics in hide preservation needs to be reinvestigated in the light of this new perspective.

It should be noted that very few chemical hide preservation methods have been developed with potential food-use quality or criteria under consideration.

Irradiation

Orlita (1967) discusses antibiotic and ultrasonic hide curing, and the feasibility of using 1-6 megarads from radioisotopes for curing by beta or gamma radiation. Absorption of at least 2.5 million units produces shrink temperature and tear resistance equivalent to that of normal liming.

The possibility of disinfecting hides with gamma rays was investigated by Pastuka et al. (1964) by treating South American sheepskins (8% moisture) with 0.01, 0.05, 1, 5, 10, 50, and 100 megaroentgens (Mr) of irradiation from cobalt-60. Skin and wool were reportedly destroyed by 100 Mr. From literature data, irradiation with 1-4 Mr

will kill bacteria, and this method might, therefore, be used on hide and wool. Molds are only killed by large doses that would damage the skins.

Experiments with irradiation of fresh ox hide pieces, fresh whole skins of calf and lamb, and dry and dry salted goatskins are described in an article by Dempsey et al. (1965). All skins were sealed in bags made of polyethylene or laminated (cellophane backed by polyethylene) material before irradiation with a cobalt-60 source at dosages ranging from 0.5 to 5.5 Mrad. A dosage of about 2.5 Mrad was required for subsequent preservation in storage for up to 12 months. This dosage caused no significant abnormality in hide and leather, except some increased hair loosening during soaking. Irradiation lowered the shrinkage temperature of raw skins and limed pelts immediately, but the decrease did not continue during subsequent storage, and the finished leather had near normal shrinkage temperature, presumably because of greater chromium uptake by the irradiated skins. Irradiation dosages of four Mrad or higher caused definite hide and leather damage.

Investigations have been carried out by Strakhov and Kolarkova (1979) on the influence of ionizing irradiation (gamma-irradiation at 25 and 40 kJ/Kg) on the development of microorganisms in the preserved raw material (colonies of cocci, staphylococci, bacilli--sporiferous and non-sporiferous, anaerobic and aerobic, etc.), as well as on the influence of protective quantities of formalin added upon irradiation on the development of the above mentioned species of microorganisms. The results from the microbiological analysis and the organoleptic evaluation of the raw material testify to the effectiveness of this

microbial inactivation upon irradiating the raw material with protective additions.

However, large scale use of irradiation as a means of short term preservation is infeasible both in economics and in practice, due to stringent health and safety regulations surrounding isotope and cathode use as sources of radiation (Gorin, 1979).

Drying

Heidemann and Riess (1963) preserved hide material for experimental purposes by drying with acetone, and found that the skins could be easily rehydrated. Soaking back required 24 hours, whereas freeze-dried skin soaked back at once. Chrome leather made from acetone-dehydrated, freeze-dried, or frozen hide was more flexible than "normal" leather made from either fresh, air-dried, or wet-salted hide. Acetone, a protein-precipitating agent, cannot penetrate the fibrils of collagen but draws out the water by osmosis. In freeze-drying, the evaporation region is the surface of the individual fibers; ice crystals form between the fibers, while the fibrils within the fibers are usually cemented together.

In air-drying, the outer surface of the skin is the evaporation region, and the hide dries to a compact layer. Air-dried hide requires considerably longer periods of soaking for complete rehydration. In skins which have been dried without the benefit of salt, there may be partial gelatinization of the fibers, or adhesion of one fiber to another. Extensive damage to the hide can result if flexing of the skin breaks the stiffened fibers. Krishnamurthi et al. (1977) used a 1.0% solution of the bitter principles extracted from neem oil

as an antiseptic for air-dried hide, and to aid in the soaking back properties of such hide.

Other potential methods of drying or semi-drying hide include the addition of hydrophilic colloids such as starch-polyacrylonitrile copolymers, either alone or in combination with various bacteriostatic or fungistatic agents, including salt. In theory, such colloids have a higher affinity for the unbound water than does the hide. As a result, the colloid draws the water away from the hide and any bacteria present, causing osmotic stress and an uninhabitable environment for the microbes. Microbial growth within the colloid itself is hindered by lack of nutrients. An excess of colloid can remove too much moisture from the hide, making it unsuitable for leather production. Lower concentrations of colloid can be incorporated by addition of sodium chloride in a respective 2:1 weight ratio, and the mixture applied to hides in the same manner as the current salt pack technique, but in much smaller amounts (10% raw hide weight). Preparation of hide with a wash of 3-5% acetic acid solution, and a short drainage period prior to application of the colloid-salt mixture, has also been found to be beneficial (Sweet, 1981).

CHAPTER III

DELAYED CURE

The relation between change in bacterial flora and deterioration of the skin during storage was studied by Wada et al. (1975). Five freshly flayed calfskins were fleshed, shaved, cut into small pieces, and then stored at 30°C for up to 40 hours (some pieces were left with the hair on). Samples were extracted with 0.85% NaCl solution and the number and kind of bacteria in each extract were determined. On storage the bacterial count increased from the order of 10^6 to 10^9. The bacteria in the fresh skin were predominantly gram-positive (micrococci and bacilli), but after storage of the skins they were mainly gram-negative (enterobacteriacea and alcaligenes).

According to Rawlings et al. (1974), bacteria that attack collagen and are responsible for its degradation are present on the living animal, and contamination is not significantly increased during flaying or before cure. These results emphasize the importance of avoiding delayed cure, as the collagenolytic bacteria are already present in the hide and must be inhibited or destroyed as soon as possible after slaughter. Washing or spraying of the animals before slaughter, and washing of the hides after flaying would therefore appear to be of advantage to the hide industry.

The ability to destroy collagen is apparently much greater for bacteria isolated from the raw hide than for those isolated from the

same batch of hides after curing (Cooper et al., 1972). Pure strains of aerobic collagenolytic bacteria isolated from South African hides grow at a very fast rate; one of these bacteria can produce a few million bacteria (size of a visible colony) in five to six hours. Most of the hide bacteria during the period of active growth can double their number in less than four hours (Cooper et al., 1974). In stack salting, the time required to reach 50% saturation with salt was found to be 11 hours, while with brining the time required was 1.5 to 6 hours, according to the method used. Any factor which reduced the rate of salt penetration will extend the period of delayed curing and can cause grain decay; some of these factors are thick hides, large-sized salt crystals, dirty salt, too little salt, and the presence of blood, fat, and flesh. The effect of storage time on pieces of fresh steerhide is shown in Table II (Hopkins et al., 1973).

Sources of microorganisms from animals include the surface flora, the flora of the respiratory tract, and the flora of the gastrointestinal tract. Hides, hoofs, and hair contain not only large numbers of mircoorganisms from soil, manures, feed, and water but also important kinds of spoilage organisms. The skin of many meat animals may contain micrococci, staphylococci, and beta hemolytic streptococci (Frazier and Westhoff, 1978). Table III gives the distribution of various sources of bacterial contamination.

Delayed cure does not represent a set time from slaughter. The extent of damage and rapidity of deterioration varies widely with the temperature conditions and the type of microorganisms present, and the enzymes which are active in the hide when autolysis occurs.

TABLE II

EFFECT OF STORAGE TIME ON PIECES OF RAW STEERHIDE*

Time of Storage (Hours)	Bacteria per Gram of Hide (Millions)	Hair Tight	Odor	Visual Mold	After Liming	
					Hair Loose	Grain Damage
Fresh	5.4	Yes	Normal	No	Yes	None
24	1,900	No	Bad	No	Yes	None
48	3,500	No	Bad	No	Yes	None
72	5,600	No	Bad	No	Yes	Yes
96	6,000	No	Bad	No	Yes	Yes

Source: Hopkins et al., 1973

*The samples came from a hide that was washed, fleshed, and demanured, then stored in sealed quart jars at ambient temperatures.

TABLE III

SOURCES OF BACTERIAL CONTAMINATION

Microorganism	Animals				Water		Soil	Foods
	Skin	Intestine	Feces	Other	Salt	Fresh		
Acetobacter								+
Alcaligenes		+			+	+	+	+
Arthrobacter							+	
Bacillus			+		+	+	+	+
Brevibacterium	+				+		+	+
Clostridium		+			+	+	+	
Corynebacterium	+			+				+
Desulfotomaculum				+		+	+	+
Enterobacter			+	+		+	+	+
Escherichia		+						
Flavobacterium					+	+	+	+
Halobacterium					+			
Klebsiella		+					+	
Lactobacillus		+	+	+				+
Leuconostoc								+
Microbacterium								+
Micrococcus	+					+	+	
Pediococcus				+				+
Photobacterium				+	+			
Propionibacterium		+	+	+				+
Pseudomonas					+	+	+	
Staphylococcus	+						+	+
Streptococcus	+	+		+				+

Source: Adaptation from Frazier and Westhoff, 1978

Schmitt and Deasy (1963) developed a test method to detect delayed cure in hides. Delayed-cure hides (hides which have not been put directly into cure immediately after flaying) contain higher concentrations of enzymes (derived either from the bacteria or from the hide) than hides which are properly processed. These enzymes can be detected, even after curing and storage, by the gelatin film test. In this test an evaluation is made of the extent of removal of gelatin from a photographic film after it has been incubated with juice from a hide. Schmitt and Deasy's first tests were run on both fresh and stale pieces of hide which were placed in contact with the film in an incubator at 37°C. In as short a time as 15 minutes, enzymes in the stale hide dissolved the gelatin. The fresh hide pieces gave no such reaction. Subsequent tests were run using the "juice" pressed from large areas of a hide.

A few drops of the hide juice, adjusted to pH 7.0 to 7.6, were placed on the side of the wetted film that was covered with gelatin (the concave side), and the film (either Kodak PX-135 or Tri-X) with the layer of hide juice on it was then incubated at 98°F for 15, 30, or 60 minutes. After incubation, the film was immediately removed from the incubator and gently rinsed with water. The film was then examined for removal of the gelatin layer by holding it against the light, and rated either 0 (gelatin intact), 1 (removal of the first layer of gelatin), 2 (removal of the first layer plus parts of the second layer of gelatin), or 3 (gelatin completely dissolved). In laboratory-staled hide, a gelatin film rating above 1 within one hour was never found, except when bacteria were present within the hide prior to staling. These findings indicate that enzymes in the hide

juice are to a great extent of bacterial origin. The effect of time and temperature of staling on the gelatin film activity, histological rating, and presence of bacteria within the steer hide is given in Table IV (Schmitt and Deasy, 1963). The histological rating was determined on cross sections stained with haematoxylin and eosin on the basis of an examination of the following points: a) number of epidermal cells present, b) number of fibroblasts present, c) evidence that the epidermis has lifted from the grain, d) presence of voids in the epidermal area, and e) evidence of fiber separation.

A value of 3 was given for each of the points listed in which the hide cross section resembled that of a fresh hide. A value of 1 was given when the cross section showed marked deterioration. A value of 2 was given when the hide appeared to be intermediate in value between a fresh and a markedly deteriorated hide. A fresh or well preserved hide received the maximum histological rating of 15, while a badly deteriorated hide received the minimum rating of 5.

The presence of bacteria in the hides sampled was determined by staining a cross section with gentian violet and counterstaining with safranin. Bacteria on the surface of the section which were present only on the surface of the hide before the section was cut were disregarded, and only those bacteria that had actually invaded the interior of the hide were considered when the presence or absence of bacteria was noted.

The test for delayed cure when used systematically can give the tanner valuable information about the previous history of the hides and an indication of the quality of leather that can be made from the rawstock in question.

TABLE IV

EFFECT OF TIME AND TEMPERATURE OF STALING ON GELATIN FILM ACTIVITY, HISTOLOGICAL RATING, AND PRESENCE OF BACTERIA WITHIN THE STEERHIDE

Time of Staling	Staling Temp.	Gelatin Film Activity*	Histological Rating**	Bacteria
5 hr	60°F	0 in 1 hr	15	Absent
24 hr	59°F	0 in 1 hr‡	15	Absent
	72°F	0 in 1 hr‡	15	Absent
	81°F	0 in 1 hr	11	Absent
48 hr	59°F	0 in 1 hr	15	Absent
	72°F	0 in 1 hr	11	Few
	81°F	3 in 1 hr	7	Present
72 hr	59°F	0 in 1 hr	13	Present
	72°F	1 in 1 hr	9	Present
	81°F	3 in 30 min.	7	Present

Source: Schmitt and Deasy, 1963

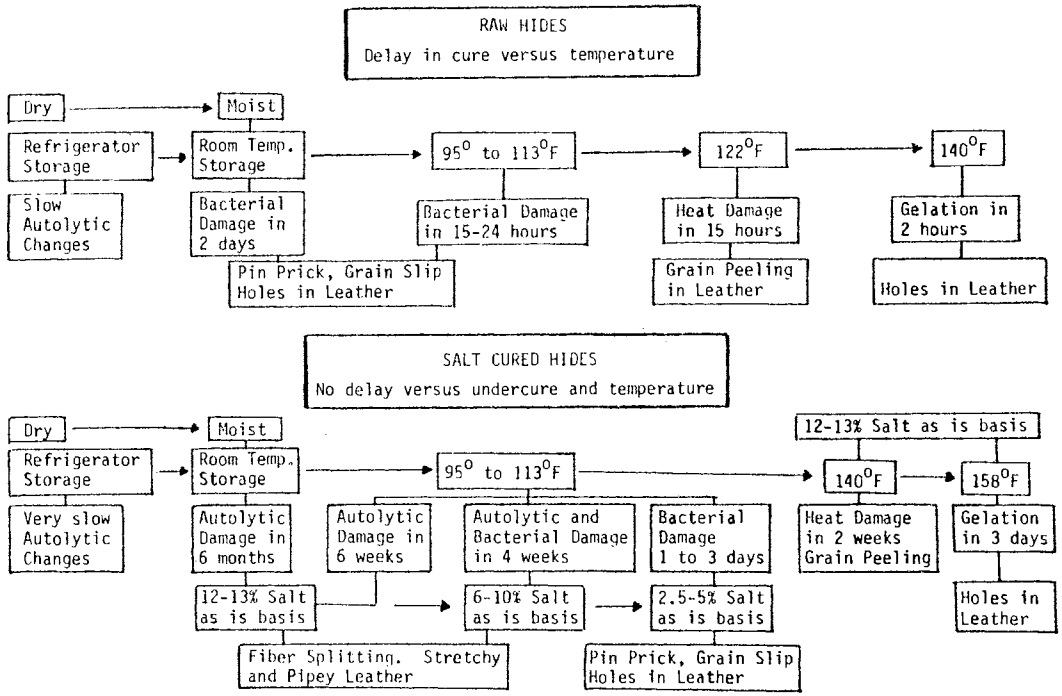
*Gelatin film activity of juice from salt-cured hide immediately after curing.

**For explanation of rating system, see text.

0 - no gelatin removed
1 - removal of first layer of gelatin
2 - removal of first plus part of second layers of gelatin
3 - complete removal of first and second layers of gelatin
‡ - gelatin film not intact, but amount removed insufficient to rate as 1

A schematic representation of raw and salt-cured hide deterioration is shown in Figure 1 (Minnoch and Minnoch, 1970). One may note that raw hide, dried by removal of the water through use of acetone or other dehydration methods or stored under referigeration, has a satisfactory storage life, so long as it is not stored in a damp place. If moisture or water is not removed from the raw hide, bacterial action occurs at room temperature within two days, as compared to the six months to one year period usual for promptly cured hides.

An in-depth report on the defects in hides and skins due directly or indirectly to curing, storage, shipping, diseases, or natural characteristics is given by Tancous et al. (1959). Updated reports are also available by Tancous (1966) and Nandy and Venkatesan (1974).



Source: Minnoch and Minnoch, 1970

Figure 1. Chart Showing the Relationship Between Hide Deterioration and Leather Defects (Arrows point in the direction of more rapid deterioration)

CHAPTER IV

DISCUSSION AND CONCLUSION

Role of Water Activity (a_w) in Hide Preservation

The skin acts as a reservoir both in receiving excess water and in making water available according to the physiological needs of the organisms. In spite of its lower water content compared to the other soft tissues of the body, a considerable mass of water is accumulated in the skin. About 75% of the total available (i.e., extracellular) water of the body is contained in the muscles and the skin, and skin contains between four and five times as much available water per unit weight of tissue as the muscles (Rothman, 1954).

The basic structural unit of connective tissue within the skin may be regarded as a fibril. Many fibrils associate laterally to form the fiber bundles, which may never branch, but may break up into smaller bundles. The fibers are interwoven into a pattern, the compactness of which varies according to both type of animal and location on the animal (Conabere et al., 1948).

The spaces between the fibers are filled by "ground substance," a semigel continuum which may be regarded basically as a transudate of plasma containing metabolic-exchange products, and containing important protein components which affect the permeability of the skin. One of the most important constituents of the ground substance is the

mucopolysaccharide, hyaluronic acid. A large portion of the water in the skin is found interstitially in the ground substance (Yates, 1971).

Calculations indicate that about 45% of the water in skin is associated with the proteins and mucopolysaccharides of the ground substance (Rothman, 1954). It is highly probable that the hyaluronic acid--protein (tropocollagen) complex is responsible for binding water in the ground substance rather than hyaluronic acid alone, because hyaluronic acid forms only a viscous solution and not a gel (Yates, 1971).

Eilers and Labout (1946) found that about 80% of the water in the skin is "free" or "unbound" water, while the remaining 20% will not dissolve even the smallest molecule of non-electrolyte. At low moisture levels, water is held to high-energy binding sites such as -OH, -COOH, or $-NH_3^+$ groups (Yates, 1971). From reports of investigation of tissues in the physiological and pathological states, it is apparent that the hyaluronic acid of the ground substance plays an important part in binding extracellular-tissue water, and that both quantity and degree of polymerization are important in determining the amount of water contained in the hide (Yates, 1971). Presence of some water is essential for maintaining the fibrillar structure of collagen (Okamura and Kawamura, 1964).

Whether or not the substrate is liquid or solid, all microorganisms grow only in aqueous solutions, with growth being impossible in the absence of water or in pure water. Growth on solid substrates of low water content or water activity (a_w) is simply a special case of growth of microorganisms in a highly concentrated solution. The

microorganisms must compete with solute molecules for the water they require for growth (Scott, 1957). The a_w of a substrate cannot be altered without changing the concentration of some or all of the constituent solutes (Christian, 1963).

A primary effect of low a_w is dehydration of the cells, including microorganisms, with the concentration of cellular solutes the immediate result. When a_w is reduced below an optimum level there is an increase in the lag of latent period, a decrease in the rate of growth, and a decrease in the amount of cell substance synthesized. These effects are very similar to those produced by reducing the temperature (Scott, 1957).

For growth, moisture must be available to the organisms and not tied up in any way, such as by solutes or by a hydrophilic colloid such as starch-polyacrylonitrile copolymers (Sweet, 1981). Solutes such as salt dissolved in the water cause an osmotic pressure that tends to draw water from the cells if the concentration of dissolved materials is greater outside the cells than inside. Osmotic stress almost invariably requires that a physiologically benign yet osmotically "active" compound accumulate intracellularly to counter the osmotic imbalance across the cell membrane when the cell is exposed to low-a_w systems. These compounds have been termed "compatible" solutes (Gould and Measures, 1977) and include potassium ions in halophilic bacteria, polyols in yeasts, proline in osmotolerant bacteria, γ-aminobutyric acid in moderately tolerant bacteria, and glutamic acid in the least osmotolerant bacteria (Troller, 1980).

Most common methods of preservation depend not on the destruction or removal of microorganisms but on delay in the initiation of growth

and hindrance of growth once it has begun (Frazier and Westhoff, 1978). An a_w of 0.75, that of saturated NaCl, is the lowest at which bacterial growth has been observed (Christian, 1963). It should be noted that preserved hide contains viable microorganisms and spores which are not able to reproduce or germinate because of the restrictive a_w. It must be remembered that drying is the most common method for preserving cultures of viable bacteria (Sulzbacher, 1973).

Conditions at the surface of the hide are rarely static. Water is continually being lost by evaporation, and this drying at the surface leads to the movement of water from the deeper tissues and a movement of solutes from the surface to the deeper tissues (Hicks, 1935). Slight fluctuations in the temperature lead to moisture migration. This results in certain areas picking up enough water to raise the a_w significantly, the a_w of the areas losing water being correspondingly lowered. Such phenomena may lead to considerable shifts in both the rate of growth and the selection of microbial types, which is further complicated by the combined influence of temperature and a_w, as already indicated. The actual situation is further complicated by the fact that once microbial growth has been triggered, this leads to the formation of water which increases a_w values locally and thus enables the growth of organisms which were previously inhibited, in addition to accelerating the proliferation of the primarily-appearing microbial spoilage association (Mossel, 1975). The fundamental purpose of dehydration is to lower the availability of water in the hide to a level at which there is no danger of growth by undesirable microorganisms. A secondary purpose is the lowering of the water content in order to minimize rates of chemical reactions (Karel, 1974). A

refreshing and stimulating review of the influence of water activity on enzyme reactivity and stability has been produced by Schwimmer (1980).

An interesting effect of a_w on chemical reactions is on the rate of lipid oxidation. As originally shown by Karel and his coworkers at M.I.T. (Maloney et al., 1966; Labuza et al., 1966; Heidelbaugh and Karel, 1970; and Quast and Karel, 1972) and reviewed by Labuza (1971, 1975), water can also influence the rate of a reaction in a fat phase. As with other reactions, as a_w decreases from high values, the rate of oxidation first decreases then increases again below the monolayer. Labuza (1980) attributed this effect to: 1) changes in hydration of trace metal catalysts which become more active as they lose water, 2) changes in availability and mobility of metal catalysts which can move to the lipid interface and increase oxidation rates, 3) hydrogen bonding of peroxide intermediates at the aqueous interface, taking them out of the reaction, and 4) increasing the rate of reaction of free radicals with other species, such as protein, in the aqueous phase.

Conclusion

Preservation of hide is dependent on control of microbial action and autolysis, both of which are, in turn, dependent upon the water activity (a_w) or amount of "unbound" water available for reactions. Addition of salt and/or chemicals and drying are two of the most feasible methods of preservation. Either of the methods serves to create an osmotically unfavorable environment for microorganisms and a catalytically unfavorable environment for autolytic reactions, thereby creating a stable product in a controlled microbiostatic state.

Increased interest in the use of hides for food supplementation as well as leather production will obliterate the possible use of some chemicals such as pentachlorophenate, arsenic, and formaldehyde, and processes such as solvent drying. While broadening the scope of the hide preservation problem, such a challenge will attract the interest and investigative powers of a widening range of professionals and organizations. Such an alliance could be beneficial to all.

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VITA

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Master of Science

Report: SHORT TERM PRESERVATION OF CATTLEHIDE FOR FOOD AND LEATHER USE

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Major Field: Natural Sciences

Scope and Method of Study: In the past 20 years, increasing interest has developed in the use of cattlehides as a source of collagen for food use. A preliminary requirement of such a process is the development of food-quality preservation methods for the freshly flayed hide. Such methods should be economically feasible and suitable for adaptation into current slaughterhouse and tannery practices. The present study involved an extensive literature search of both current and experimental methods of preservation for both cattlehide and related food products (meats and collagen).

Findings and Conclusions: Results of this study revealed that little research on food-grade preservation of hides has been done. Many food-quality preservation processes would make the resultant hide unsuitable for possible leather use, and current leather preservation techniques are unsuitable for food use. Hides which have suffered only mechanical damage, and not bacterial damage, may be used as a collagen source even though unsuitable for leather production. The key to both food- and leather-quality preservation apparently is dependent upon control of the water activity (a_w) of the hide to prevent and/or delay both microbial and enzymatic reactions.

ADVISER'S APPROVAL L. Herbert Breneau