

## OTHER TANNAGES

Very little scientific work has been done in recent years on tawing (tannage with aluminium salts), or on aldehyde and oil tannages. Moeller<sup>37</sup> has advanced some highly specula-

<sup>37</sup> *Collegium*, 1918, 25, 61, 71, 93; 1919, 61, 72; 1920, 69.

tive theories based on peptization to account for these, but his work has been severely criticized, and the German technical journals have been occupied with the resulting polemics.

## The Preparation of Skin for Tanning

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THE apparently slow development of the chemistry of leather manufacture has been due to its extreme complexity rather than to any lack of sympathy on the part of practical tanners. This branch of industrial chemistry deals with reactions between those poorly defined groups of substances, usually colloidal, whose compositions are still matters for speculation. The raw skin is composed largely of various kinds of protein matter and is complicated by a structure which varies considerably in different animals and even in different parts of the same skin. Conversion into leather involves the removal of some of these proteins by the action of alkalies, enzymes, or bacteria, and the interaction of the remainder with tanning materials, oils, soaps, emulsions, mordants, dyestuffs, gums, resins, and other complex materials. During these reactions the structure of the skin must be carefully preserved or improved, and highly developed technic is required to impart to the resulting leather certain necessary, but almost indefinable, properties, many of which it is an art even to appreciate fully. When one considers the vast amount of energy expended by organic chemists upon the materials involved in making leather and the uncertainty of our knowledge concerning the individual substances, the complexity of the whole problem becomes more apparent.

### HISTOLOGY AND CHEMICAL COMPOSITION OF SKIN

Scientific investigations in the preparation of skin for tanning have been retarded by insufficient knowledge of the histology and chemical composition of the skins of the lower animals which have structures very different from human skin. The need has been well appreciated, but very few leather chemists have had the time, facilities, or technic required to obtain the desired information.

Recently, however, the literature on the histology of skin has been greatly enhanced by a valuable series of articles published by Alfred Seymour-Jones.<sup>1</sup> In addition, studies have been in progress in the writer's laboratories during the past four years of the microscopic structure of the skins of the lower animals and the changes undergone during their conversion into leather. Part of this work has already been presented<sup>2</sup> and its scope is gradually being extended. The

<sup>1</sup> "Physiology of the Skin," *J. Soc. Leather Trades' Chem.*, 1917-21 (serially).

<sup>2</sup> "A Trip through the Tannery on the Inside of a Calfskin," presented at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 9, 1921; publication, including numerous photomicrographs, reserved for the Society's monograph on "The Chemistry of Leather Manufacture."



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importance of such studies warrants their becoming more widespread.

A review of the literature on the chemical constituents of skin has recently been made by F. L. Seymour-Jones.<sup>3</sup> The difficulty in making quantitative separations of the protein constituents of skin makes this type of study even more difficult than that of histology.

Many of our conceptions of the physical chemistry of the skin proteins have been derived from investigations on gelatin, particularly those of Procter<sup>4</sup> and his collaborators,<sup>5</sup> and of Jacques Loeb.<sup>6</sup> Loeb's work is a splendid example of the common interest which all branches of the science have in fundamental research. Although performed for its value to physiology, it has proved of great importance to leather chemistry.

### PRESERVATION AND DISINFECTION OF SKIN

Raw skins are highly putrescible, and it is necessary to preserve them in some way until the first tanning operation. This is usually done by saturating with common salt, or by drying.

The attention of chemists has frequently been drawn to the appearance of stains on salted skins, usually called salt stains because their frequency of occurrence was found to be influenced by the composition of salt used and the method of its application. The staining is apparently due to a combination of the skin proteins with iron, derived either from the skin itself or from the added salt. In their natural state the iron compounds of the skin are incapable of staining, but assume this power if rendered soluble by bacterial or purely chemical action.

J. Paessler<sup>7</sup> found that the percentage of stains could be greatly reduced by using salt containing 3 per cent of its weight of anhydrous sodium carbonate. This retarded bacterial action prevented iron from passing into solution and served as a denaturant, in place of some more harmful material, in those countries of Europe where edible salt is taxed and salt for industrial purposes must be denatured. Abt,<sup>8</sup> finding some bad cases of staining were due to calcium sulfate in the salt used, pictured the reactions as follows:

<sup>3</sup> *THIS JOURNAL*, 14 (1922), 130.

<sup>4</sup> *J. Chem. Soc.*, 105 (1914), 313; 109 (1916), 307.

<sup>5</sup> *J. Am. Chem. Soc.*, 40 (1918), 886.

<sup>6</sup> *J. General Physiol.*, 1918-22; "Proteins and the Theory of Colloidal Behavior," McGraw-Hill, 1922.

<sup>7</sup> "Salting of Hides and Skins," *Ledertechnischen Rundschau*, 1912, 137.

<sup>8</sup> "Microscopical Examination of Skin and Leather Applied to the Study of Salt Stains," *Collegium*, 1914, 130.

The calcium sulfate reacted with ammonium phosphate from the nucleic acids of the skin, precipitating calcium phosphate; the ammonium sulfate thus formed rendered soluble the ferrous carbonate naturally occurring in the skin, which in turn combined with the skin, forming a stain. Becker<sup>9</sup> showed that the stains could be produced by pure cultures of bacteria isolated from the stains. Romana and Baldracco<sup>10</sup> prevented the stains by adding sodium fluoride to the salt or by washing the lymph, containing much of the iron, out of the skins immediately after flaying, but before salting.

Dried skins often come from regions infected with certain disease germs, of which anthrax is the one most dreaded. Such skins must be disinfected and apparently the best method devised is that of Alfred Seymour-Jones,<sup>11</sup> which consists of soaking the dried skins for from 1 to 3 days in a solution of 1 per cent of formic acid and 0.02 per cent of mercuric chloride, followed by immersion in a saturated salt solution for an hour, draining and baling for shipment. Both Abt and Seymour-Jones have pointed out, however, that hides would contain no anthrax if dried in the sun immediately after flaying.

Changes begin to take place in the skin immediately after the death of the animal. McLaughlin<sup>12</sup> recently found that the degree of swelling of hide in limewater depends upon the time lapse since the death of the animal. As for the practical significance of this fact, the writer has put into process together both properly preserved skins and skins taken from animals within an hour after death and could detect no difference in the finished leathers by microscopical, chemical, and physical analysis.

#### SOAKING AND FLESHING

Among the first tannery operations are washing to remove blood and lymph, soaking in cold water for several days to swell the fibers and bring them again into equilibrium with water, and the removal of the adipose tissue or flesh. The contribution of chemists in the soaking operation has been in the direction of hastening the absorption of water, in the case of dried skins, by the addition of acids or alkalies under proper control. The reason why skins must be completely wet back before fleshing or tanning is prettily illustrated in a paper on gelatin by Sheppard and Elliott.<sup>13</sup> Cubes and cylinders of gelatin jelly always suffer a change of shape during drying because of the greater initial rate of drying and casehardening of the edges. Skins fleshed without sufficient preliminary soaking will look smooth on the flesh side upon coming from the fleshing machine, but later, when the skin has absorbed more water, the flesh side will be so ragged and uneven as to require further treatment. If dried skins are not completely soaked back before entering the tan liquors, the distortions suffered by the fibers during the original drying will be permanently fixed by the tanning action and the leather will never have the proper suppleness.

#### UNHAIRING

Recent microscopical studies have demonstrated clearly that the loosening of the hair and epidermis by the common methods of liming and sweating, as well as by the newer methods involving enzyme action, is due to the digestion of the cell walls of the Malpighian layer of the epidermis resting on the true skin, the destruction of which leaves the hair and epidermis completely separated from the rest of the skin.

<sup>9</sup> "Salt Stains," *Collegium*, **1912**, 408.

<sup>10</sup> "Salting of Hides and Avoidance of Salt Stains," *Collegium*, **1912**, 533.

<sup>11</sup> "Formic-Mercury Anthrax Sterilization Method," London, **1910**; "Anthrax Prophylaxis in the Leather Industry," *J. Am. Leather Chem. Assoc.*, **17** (1922), 55.

<sup>12</sup> *J. Am. Leather Chem. Assoc.*, **16** (1921), 435.

<sup>13</sup> *J. Am. Chem. Soc.*, **44** (1922), 373.

Since sterile limewater has little unhairing action on skins, it was long thought that bacteria were necessary for this action. But Schlichte<sup>14</sup> found that skin previously sterilized by the Seymour-Jones process could be unhaird easily after two weeks of contact with saturated limewater under sterile conditions. Wood and Law,<sup>15</sup> however, pointed out that the action may have been influenced by the previous swelling of the skin in the sterilizing solution. This action of swelling agents in making protein matter more susceptible to hydrolysis is now receiving increased attention.

Röhm<sup>16</sup> devised a process for unhairing by means of an alkaline trypsin solution. In describing Röhm's process, Hollander<sup>17</sup> pointed out that a skin can be unhaird by soaking for one day in a dilute solution of sodium hydroxide and then for one day in a solution of sodium bicarbonate to which trypsin is added after the swelling of the skin has been counteracted. In the discussion following Röhm's presentation of his paper, Eberle expressed doubt that the hair loosening was due to the enzyme. In a recent investigation, Wilson and Gallun<sup>18</sup> confirmed Hollander's findings and showed that the action proceeds slowly in the absence of the enzyme, but is greatly accelerated by its presence and by rise of temperature up to 40°; but, when the experiments were conducted under toluene to check bacterial action, there was no unhairing action at 25°, but a very marked action at 40°, indicating that pancreatin is an unhairing agent at 40° but that the action obtained at lower temperatures in practice is due to something other than pancreatin.

Ross<sup>19</sup> patented a process for unhairing with thrombase naturally occurring in skin. If proved sound, his view will be an important addition to our knowledge of the action of old lime liquors. J. T. Wood,<sup>20</sup> of Nottingham, found that formic acid will unhair a skin if sufficient time is allowed. The subject of acid unhairing has since been reviewed by Marriott.<sup>21</sup> Apparently anything that will hydrolyze the newly formed cells of the epidermis without injuring the rest of the skin is a satisfactory unhairing agent.

The extent to which the unhairing agent swells the skin has an important effect on the appearance of the finished leather, excessive swelling tending to produce a roughness of the grain surface. Atkin<sup>22</sup> was able to reason from the theories of Procter, Wilson, and Loeb<sup>23</sup> that the addition of arsenic disulfide to a lime liquor should cause less swelling than the addition of sodium sulfide and thus leave the skin with a finer grain surface. His reasoning is borne out in practice in the case of glazed kid leathers.

#### BATING

One of the greatest blessings which the industry has derived from chemistry is the replacement of the obnoxious dungs formerly used in bating by pancreatic enzymes. After liming, unhairing, and washing the skins, it was customary to put them into warm infusions of the dung of dogs or fowls until they had become very soft and flaccid. The dung appeared to be necessary to remove some undesirable constituent of the skin until Wood,<sup>24</sup> in 1898, discovered that the same action could be obtained by pancreatin under suitable

<sup>14</sup> *J. Am. Leather Chem. Assoc.*, **10** (1915), 585.

<sup>15</sup> *J. Soc. Chem. Ind.*, **35** (1916), 585.

<sup>16</sup> *Collegium*, **1913**, 374.

<sup>17</sup> *J. Am. Leather Chem. Assoc.*, **15** (1920), 477.

<sup>18</sup> "Pancreatin as an Unhairing Agent" (not yet published).

<sup>19</sup> Brit. Patent 169,730; cf. *C. A.*, **16** (1922), 853.

<sup>20</sup> Private communication to writer in 1916; *J. Am. Leather Chem. Assoc.*, **12** (1917), 114.

<sup>21</sup> *J. Soc. Leather Trades' Chem.*, **5** (1921), 2.

<sup>22</sup> *THIS JOURNAL*, **14** (1922), 412.

<sup>23</sup> *Loc. cit.*

<sup>24</sup> "Puering, Bating, and Drenching of Skins," E. and F. N. Spon, London.