THE CHEMISTRY OF LEATHER MANUFACTURE*

Applying Modern Science to an Ancient Art

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Tanning, or leather manufacture, is a very ancient art. It is an art that is known and practised by even the most primitive races; it is an art that was practised with very considerable skill by the earliest of civilized peoples. The Babylonians and Egyptians made leather very much as it is made today, and if one may judge from certain Babylonian laws that have survived, tanning has remained essentially the same for five thousand years. The Babylonian code provided that prayers, to be acceptable to God, must not be offered up within a prescribed distance from a tannery; another humane provision decreed that a tanner's wife might divorce him at any time without ceremony.

The use of skins for clothing must have begun very early in human development. Raw skin, however, is not at all desirable as a garment, as it is highly putrescible. It can be kept from rotting, among other ways, by being dried, and no doubt this was the treatment first employed by primitive men. But a dried skin is so hard and stiff as to be almost unusable. With the idea, we may suppose, of rendering the skin more pliable, men began to rub animal fats into the dried hide. The animal fat did more than lubricate the skin; oxidizable oils have a real *tanning* action—that is, they combine with the skin substance to form a stable substance that will not rot—a *leather*. Oil tannage is used today for such leathers as chamois and so-called raw-hide.

Later on, probably, leather workers discovered that a skin could also be made into leather by being soaked in a decoction of bark or wood from any one of a large number of trees. Very much more recently, it has been discovered that solutions of chromium salts accomplish the same result. Meanwhile, tanners had learned how to take off the hair without injuring the skin, how to lubricate, how to color, and how to apply lacquers to the finished product. In short, the art of making leather became highly developed, and all with little or no aid from science.

The application of science to the leather industry is a development, mostly, of the twentieth century. We still have an immense way to go before we can express every part of the process in terms of physics and chemistry, but at least we have made progress and are in possession of fairly adequate working theories as to what goes on when a skin is transformed to leather. This progress has been made by following up two lines of study: (1) the micro-structure of the skin, and (2) the physical chemistry of the proteins.

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In Figure 1 we have a highly magnified vertical section through a fresh calf skin. The main body of the skin is made up of interlacing fibers composed of the protein collagen. On the side of the skin next the body (the flesh side) is a layer of adhering fat and other tissue. Above the fibrous "true" skin, or "derma" lies a very different structure—the epidermis. The epidermis is composed of several layers of living and dead cells. The lowest tier of cells absorbs nourishment from the solutions impregnating the derma, and lives on the surface of the body almost like a parasite. These cells reproduce by division vertically. As new cells are formed, the old ones are pushed nearer the surface, are deprived of nourishment, die, dry up, and at length are rubbed off. Dandruff is nothing but these dead, dried up cells of the epidermis.

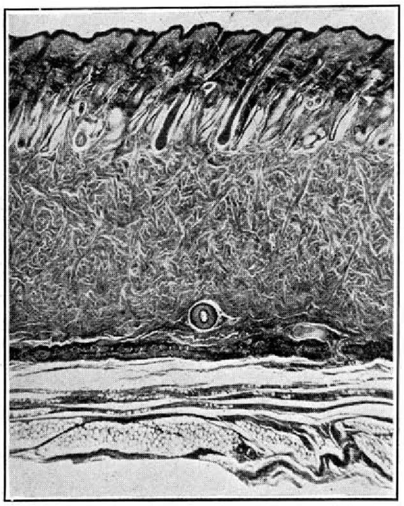

FIG. 1.—Cross section of fresh calf skin. Magnified 30 diameters.

The hairs grow in pockets in the epidermis, where the latter dips down into the true skin. Each hair is accompanied by a fat gland, a sweat gland, and a little muscle. This system helps maintain the body at a constant temperature. When the body is warm, the erector muscles are relaxed, allowing the sweat glands to pour forth their secretion onto the surface of the skin, cooling the body by evaporation. But when the skin is chilled, the tiny muscles contract, cutting off the sweat flow, erecting the hair to form a bushy covering, and squeezing out the contents of the fat glands, thus cutting off evaporation. In the human subject, this produces goose-flesh.

The skins of different animals differ considerably in details, especially in the texture of the fibrous true skin. In the calf or cow, the fibers are very numerous in a given volume, and are tightly interlaced, producing a very firm, tough, durable leather. In other species, for instance the goat, and still more so in the case of the sheep, the fibers occupy a much smaller proportion of the total volume of the skin, and this causes kid or sheep leather to be soft, spongy, and limp.

The fibrous true skin is the only portion of the hide that is suitable for leather. It is the tanner's first task to remove both the flesh layer and the entire epidermal system, including the hair.

Skins as received in the tannery are usually dried or salted. It is necessary first of all to restore the skin as nearly as possible to the condition in which it existed on the animal's back. This is accomplished by soaking the skin in water for several days. It is highly important, during this stage, to retard bacterial growth as much as possible, which end is accomplished by keeping down the temperature and changing the water frequently. After the soaking operation is complete, the skin is in the condition of a jelly, containing about eighty per cent of water, and easily penetrable by the various solutions to whose action it is to be subjected.

FIG. 2.—Cross section of calf skin after liming, before unhairing. Magnified 35 diameters.

Next comes the removal of the hair. The skin is treated with a saturated solution of lime, to which is often added a little sodium sulfide. An excess of lime is used to maintain a constant hydroxyl-ion concentration. At the alkalinity of saturated lime water, $p_H = 12.5$, the cells of the lower layer of the epidermis are attacked before any appreciable hydrolysis of the true skin occurs. During liming the lower layers of the epidermis are dissolved away (Figure 2), leaving the hairs loose in their follicles, and by means of a blunt knife or a suitable machine the hair and other remnants of the epidermis are easily scraped away.

Either before or after liming, the flesh layer is cut away by another machine.

The skin as it comes out of the lime liquor is swollen and rubbery. Before being tanned, it must be reduced to a soft and flaccid state, and delimed, since tanning can occur only in slightly acid solution. This is brought about by a very curious process known as "bating." Originally this process consisted in digesting the skins in an infusion of dog dung or pigeon manure. This repulsive material has now given place to artificial bates. The old dung bates owed their efficacy to two constituents—ammonium salts, which remove lime and bring the skin to a p_H value of about 8, and digestive enzymes, which remove certain minor constituents of the skin whose presence in the finished leather is objectionable. Artificial bates consist essentially of ammonium salts and pancreatic enzymes from the packing houses.

Two distinct methods of tanning are in general use for all kinds of leather.

These employ, respectively, natural tanning materials—oak, chestnut, hemlock, and many other barks, quebracho wood from South America, and other exotic plant materials, and chromium salts. In the natural tanning process, the skins are suspended, first, in a very weak solution of wood or bark extract, and are shifted daily into successively stronger liquors, until the tannin has "struck through." The hydrogen-ion concentration of the liquors must be carefully regulated, since if the liquor gets too acid the skins become swollen and distorted,[1] while if the liquor is not acid enough the fixation of tannin is reduced, and the resulting leather will be flat and "empty." This natural tanning process requires from a week up to several months, depending on the thickness of the skins. In mineral tanning, the skins are treated with a slightly acid solution of chromium sulfate. After the liquor has penetrated the skins, bicarbonate of soda is added to bring the acidity down to the point just above that at which precipitation of chromium hydroxide would take place. The chromium then combines with the fibers, as does also considerable sulfuric acid.

The theory of vegetable tannage is in a fairly satisfactory state. We know that collagen, like other proteins, is built up of amino acids. These amino acids are amphoteric, and the property of combining with either acid or base is also possessed by the protein. On the acid side of its isoelectric point, collagen behaves like a weak base. The tannins, on the other hand, are weak acids. Thus, when a skin is placed in a weakly acid solution of a tannin, the basic protein and the acid tannin combine chemically to form a new compound—collagen tannate. The mechanism of chrome tanning is not quite so clear. We believe that the final product is chromium collagenate, in which the chromium acts as the base and the collagen as the acid, but there is some reason to think that at first the combination is between collagen and some of the complex ions that chromium forms so very readily.

Chrome tannage has largely displaced natural tannage for light leathers, such as are used for the uppers of shoes. This has come about because chrome tannage is much quicker, cheaper, and less difficult to regulate properly than the older method. This change has not been altogether a blessing to the consumer. Chrome leather (Figure 4) has a much looser texture than natural-tanned leather (Figure 3), because chromium has a much lower combining weight than the complex tannin molecule, and consequently a given weight of skin substance combines with very much less chrome than tannin. Chrome leather is, therefore, spongier and stretches

[1] The effect of acids, bases, and salts upon the swelling of skin—a problem which occurs in the leather manufacturing process at almost every stage—is a beautiful example of the application of pure scientific research to an industrial problem. See "The Chemistry of Leather Manufacture" (A. C. S. Monograph) by John Arthur Wilson; and Jacques Loeb, "Proteins and the Theory of Colloidal Behavior," 2nd edition, New York, 1924.

more easily than natural leather. Chrome leather also contains several per cent of sulfuric acid in combination with the collagen, it is true; still, a portion of this acid may at times be liberated by hydrolysis and cause chrome leather shoes to impart a slight burning sensation to the feet after a long walk. Perhaps due to its acid content, chrome leather takes on and gives up moisture to a much greater extent than does natural-tanned leather with changes in atmospheric humidity. With the change in water content goes a great change in area, and consequently a considerable change in the size of chrome leather shoes every time the weather changes. This may be

FIG. 3.—Natural tanned calf skin. Magnified 75 diameters.

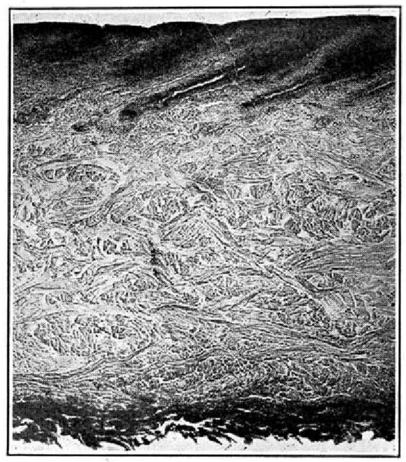

FIG. 4.—Chrome tanned calf skin. Magnified 75 diameters.

an advantage to amateur weather prophets, who are wont to foretell changes by the deportment of their corns, but scarcely to the general run of shoe wearers.

When the skin comes out of the last tan vat, or the chrome tanning drum, its conversion into leather is complete. Leather at this stage, however, is far from being a merchantable product. The operations performed on the skin subsequent to tanning include: (1) *fat-liquoring*, whereby oil (in some cases as much as 15–20% of the weight of the skin) is incorporated by drumming the skin in an emulsion; (2) *coloring*, now done chiefly with coal-tar dyes; and (3) *finishing*, which consists in the application of a thin, lustrous coating to the grain surface. Besides these main operations, each skin is subjected to a great variety of purely mechanical treatments, too numerous to enumerate.

The application of this brief survey of the chemistry of leather manufacture to chemical education is to be found, probably, in the instruction of those students who pursue chemistry as a cultural rather than as a professional subject. It is of little use to try to instruct a prospective chemist in the practical details of making leather. If he is to be of use, as a chemist, in the tannery, it can only be through his ability to apply the fundamental principles of science to the problems that he will be called upon to solve. The best service that educational institutions can give to future industrial chemists is to give them all the pure chemistry they can absorb—the more the better.

It is, however, very regrettable that the public in general knows so little about the chemistry of so universally used a product as leather, and especially about the differences in skins and methods of tanning that produce such marked differences in the shoes we wear. It is not too much to say that most shoes are purchased because of fine points of superficial appearance that cease to exist before the shoes have been worn a week. This ignorance it may be the function of the chemistry teacher to dispel.

And, finally, it may be that the beginning student will be interested to learn that

$$\text{Skin substance} + \text{tannin} = \text{leather}$$

is just as good an example of a chemical equation as

$$2H_2 + O_2 = 2H_2O.$$

The former equation has the additional merit of being easy to balance.

Fish Valuable Food Says Scientist. Mineral elements necessary for human nutrition lacking in most foods are supplied by fish. According to Dr. Donald K. Tressler, of the Mellon Institute of Industrial Research, we should all eat more sea food to supply the calcium, phosphorus, and iodine constituents lacking in most ordinary diets.

Canned fish, he said, is particularly desirable because the bones as well as the flesh are eaten. The value of fish bones lies in the fact that they consist almost entirely of calcium phosphate, necessary for growth and repair of human bones and teeth.

The generally recognized fact that small quantities of iodine in the diet will prevent or help goiter and other disturbances of the thyroid gland is a strong argument, declared Dr. Tressler, for an increased consumption of fish and the edible seaweeds. Both sea foods and plants are known to contain more of this necessary element than anything that grows on land.

Scientists have found that the fats and proteins of fish are as easily digested as those of meat. By careful analysis it has been found, according to Dr. Tressler, that "upon digestion fish proteins furnish all of the amino acids needed for the building up of the complex protoplasmic structure we call our body. All of the amino acids needed for the construction and repair of our bodies occur in ample proportions. Curiously, the composition of fish proteins resembles that of the proteins of chicken muscles. This fact is especially important when we consider the high nutritive value ordinarily assigned to chicken meat."—*Science Service*