THE CHEMISTRY OF LEATHER MANUFACTURE

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THIS BOOK

IS

DEDICATED TO THE MEMORY

OF

JOHN ARTHUR WILSON

(1890–1942)

GENERAL INTRODUCTION

American Chemical Society Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A.C.S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this introduction) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first monograph of the series appeared in 1921. After twenty-three years of experience certain modifications of general policy are indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. This differentiation is fast becoming nebulous. Research in private enterprise has grown apace and not a little of it is pursued on the frontiers of knowledge. Furthermore, most workers in the sciences are coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and now frankly recognize that their objectives are common, namely the search for new knowledge for the service of man. The officers of the Society therefore have combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the series, it seemed expedient to construe rather broadly the definition of a monograph. Needs of workers had to be recognized. Consequently among the first one hundred monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the monograph character which means more complete and critical treatment of relatively restricted areas, and where a broader field needs coverage, to subdivide it into logical sub-areas. The prodigious expansion of new knowledge makes such a change desirable.

These monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

Preface

The purpose of this monograph is two-fold. It is designed primarily to summarize and to appraise our present scientific knowledge of the conversion of animal skin into leather. Its other purpose is to serve as a memorial to the life and work of a gifted pioneer leather scientist, John Arthur Wilson, the author of its first two editions, published in 1923 and 1929 respectively.

The chemistry of leather manufacture is actually the chemistry of connective tissue, of the organic tanning materials, of various inorganic tanning agents, and finally of the reactions that occur between skin proteins and tanning agents whereby leather is formed. This being true, progress in the so-called pure chemistry of these various fields has contributed directly to the progress of tanning technology. In turn, the advances within recent years in the chemistry of tanning have happily and significantly contributed to the sum of general scientific knowledge. It is for this reason that we confidently hope this book may prove of interest outside of its more restricted field.

The present need for this monograph has been accentuated by the war effort. Leather is an indispensable article in times of peace, and becomes a critical material during war. Coincident with the expanded war need, there has occurred a sharp diminution of the normally large importations of hides and skins and tanning materials. This difficult situation can be met only by a better utilization of domestic materials. The technical men of the industry—whose problem this is—realize that better utilization is possible only through scientific knowledge. And they further realize that when peace is restored the leather industry will face grave competition from substitute materials.

A scientific field so complex and so far-flung as that of tanning lends itself to many, and often seemingly conflicting, viewpoints. Recognizing this, we have been primarily concerned with the presentation of experimental evidence and pertinent data, believing that while interpretations may change, the data remain vital. At the same time, we have sought to present adequately current and significant theoretical interpretations.

In order to expand certain subjects and yet remain within the limits of one volume, we have had to omit some of the subjects considered in the two volumes of the second edition. These omissions relate more particularly to descriptions of dyes and finishes, patent leather, furs and microscopic and histologic methods. We have also greatly reduced the number of illustrations dealing with the histology of skin. All these omitted subjects are of interest and value and they may be found, as noted, in the second edition.

Each chapter of this volume was submitted to various colleagues especially qualified to criticize it. In this way we received many valuable suggestions from the following friends; R. S. Adams, D. H. Cameron, F. L. DeBeukelaer, J. H. Highberger, F. O'Flaherty, A. Schubert, G. W. Schultz, H. G. Turley and H. R. Wilson. Our special thanks are due Doctor Max Bergmann who read and criticized the entire manuscript. Nor would the senior author fail to express his appreciation of the time and facilities provided him by the B. D. Eisendrath Tanning Company of Racine, Wisconsin.

The chapter on the chemical composition of skin was written by John H. Highberger; that dealing with syntans by Karl F. Ruppenthal; the chapter on fatliquoring by Ralph E. Porter; and that on the physical testing of leather by Warren E. Emley.

For the loan of cuts and plates we are indebted to the *Journal of the American Leather Chemists' Association.*

G. D. McL.
E. R. T.

New York, N. Y.
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Chapter 1

Introduction

If we list those materials necessary for human activity, leather is found to occupy an important place. It is therefore not surprising to find that tanning was probably the first manufacturing process in which man engaged, since both the clothing and protective armor of primitive man were of leather. Thus leather has been an indispensable item throughout history and is necessary to modern civilization in the form of shoes, clothing, harness, belting, and endless other useful articles.

All leather is made by treating animal skin with a tanning agent whereby the resulting product possesses qualities that are quite different from those of the original skin. The moist skin which has been removed from the animal's carcass is quickly decomposed by bacterial enzymes; it is rapidly dissolved by warm water; and if it is dried out, it becomes hard and largely useless. But when properly tanned, the skin is practically impervious to digestion by enzymes; it is insoluble in water and may be given whatever degree of softness is desired. It is the purpose of the following chapters to describe and to explain what is known of the principles which underlie that interesting and exceedingly complex reaction known as tanning.

A marked change has occurred in the leather industry during the past generation. Thirty years ago there were approximately 740 tanneries in the United States compared with 440 today, although the present volume of leather produced is considerably greater. This centralization of production went hand in hand with the growth and application of tanning science, and the unscientific tanner was unable to survive. The present tanning generation faces an even greater test, because many leather-substitute materials have appeared and others are being studied by competent scientific minds. It is a hopeful sign, however, that the leather industry is becoming increasingly aware that empirical methods must be replaced by scientifically sound procedures. This is evidenced by the fact that many research institutions devoted to the study of tanning have been founded throughout the world. But many tanning concerns are still unaware of their need for scientifically trained staffs; without such personnel they cannot hope to maintain their position in the competitive struggle which lies ahead. The most "practical" and successful tanner is he who not only respects the scientific approach but who is impatient with any other.

While each phase of the tanning process will be discussed in its relation to the end product, leather, it will be helpful at this point to summarize briefly the general steps involved.

Skins are, of course, produced all over the world and under a great variety of conditions. In any case the skin must be cured; that is, it must be so treated as to reduce or prevent its digestion by the many proteolytic bacteria which are present when the skin is flayed. This curing may be accomplished in certain cases by merely drying the skin, in other cases by partially dehydrating it with common salt, and in still other cases, by a combination of drying and salting. Light-weight skins, like those from small animals such as goats or sheep, or from immature animals such as calves, are referred to in the leather industry as "skins." Heavy-weight skins coming from large, mature animals such as steers, cows, or buffalo are termed "hides." When the term *skin* is used in this summary, it is employed in its inclusive sense and refers to both light and heavy skins.

When the cured skin reaches the tannery, it is "soaked." That is, it is treated with water to rehydrate it and to remove surface dirt, undesirable proteins, and the curing salt, in the case of salted skins.

After soaking, the skin receives the "unhairing" treatment. That is, it is placed in a solution of a chemical that will decompose the epidermal tissues and thus permit mechanical removal of the hair, while it partially saponifies the skin fat and produces desirable chemical and physical changes in the actual skin substance as well. The unhairing agent employed is usually a saturated solution of calcium hydroxide, to which various other chemicals known as accelerators are generally added. The time required for the unhairing process varies with the kind of skin and its condition, together with the nature of the unhairing solution and process and may range from one to ten days. Unhairing may also be accomplished by treating the soaked skin with certain enzymes or by "sweating," in which case the soaked skin is hung in a warm, humid room until the proteolytic bacteria it contains have digested its epidermis. But the great bulk of all skins are unhaired by the "liming" process, noted above. The only leathers not passing through the unhairing process are those included under furs; these are not considered in this book.

After the unhairing process, the skin is mechanically treated to remove the loosened hair, the disintegrated epidermis, much of the saponified animal fat, and also, the flesh, muscle, and adipose tissues adhering to the skin surface that was next to the animal's body. This side of the skin is termed its "flesh" side, while the outside surface which contained the hair is referred to as the "grain" side.

The skin is now delimed by soaking it in a solution of a chemical that will combine with the lime present in the skin to form a soluble lime salt, which is then washed out with water. After deliming, the skin is "bated"—that is, it is usually treated with an aqueous infusion of an enzyme. This treatment brings about certain necessary chemical and physical changes in the skin. The skin is then ready for the tanning process.

In the case of heavy hides that are to be vegetable tanned, the bating treatment referred to above may be greatly curtailed in comparison to that given light skins, or it may be omitted entirely. In either event the heavy hide is placed in a very weak tannin infusion which is mellow in nature and in action; that is, it lacks astringency. This tan liquor is gradually increased in strength and astringency, until after a period of days, weeks, or months the hide is said to be tanned. Light skins that are to be tanned with either organic agents (such as the vegetable tannins) or with inorganic agents (such as the salts of chromium) are bated much more extensively than in the case of heavy skins or hides. This is because of the very different leather qualities desired in light leathers, such as shoe uppers, compared with heavy leather, such as sole.

When light skins are to be chrome tanned, they are first "pickled"; this means they are treated with a solution containing sulfuric or hydrochloric acid and sodium chloride. The acid rapidly combines with the skin protein and would cause it to swell were it not for the restraining action of the salt. The object of pickling is to bring the entire skin to a uniform chemical and physical condition and, also, to prevent the too rapid combination between skin substance and astringent chromium compound. The pickled skin is now agitated with a solution of a basic chromium compound, usually chromium sulfate, until it is considered to be tanned; this condition is coincident with a marked heat stability of the chrome tanned leather, which may be unaffected even by boiling water. The chrome tanning process is very much more rapid than vegetable tanning.

The chrome tanned skin is next treated with a mild alkaline solution to remove any unbound or free acid it may contain; this process is termed "neutralizing." After neutralizing the skin is dyed.

At the completion of heavy-leather vegetable tannage, and after neutralization and dyeing in the case of chrome tannage, the leathers are treated with the proper amount and kind of fatty materials; this process is termed "oiling" or "stuffing" in the case of heavy leathers and "fatliquoring" in the case of light leathers. The purpose of the process is to restore to the hide or skin the equivalent of the natural fatty materials that were saponified and removed by the liming process, since the finished leather would otherwise lack tensile strength and the proper elasticity.

After oiling or fatliquoring, the leather is dried and is ready for numerous "finishing" operations. These include various mechanical treatments, as well as the application of additional coats of coloring materials in the case of dyed leathers.

All the foregoing processes are further described and discussed in books dealing with the practical procedures of tanning, to which we refer the interested reader. The purpose of this volume is to discuss the more theoretical phases of tanning, since the future progress of leather manufacture is directly related to the extent to which scientific procedure replaces empirical practice.

Chapter 2

Histology of Skin

Our understanding of all of the processes involved in tanning has been enhanced by histological studies; and it may be said, in fact, that without a minimum of such knowledge we cannot hope to study or control tanning processes intelligently. But it must be pointed out that leather histology is a distinct science, requiring special technique and long experience in preparing and in interpreting skin sections, and that the lack of such knowledge has often led to disappointing and unfortunate results. Elaborate histological studies of human skin have been made, and these have greatly aided the leather histologist. But modern experience has shown that while there are many similarities between human skin and that of the animal skins used in tanning, there are also many differences. It is these differences, as well as the changes induced by the processes of tanning, which make necessary a distinct histology of tanning.

The whole subject of leather histology has been dealt with at great length by Wilson in the second edition of this monograph, to which the interested reader is referred, since lack of space prevents our giving more than a brief outline of the subject.

The first adequate histological studies of animal skin and leather were probably those of Boulanger[1] in 1908, but these were unfortunately published in journals not generally accessible to leather scientists. In 1917-21 Alfred Seymour-Jones[5] published a series of important articles which were valuable in themselves and which furnished stimulus to other investigators as well. Among the more recent general histological studies, and in addition to those of Wilson[8] already mentioned, are those of Turley,[7] Küntzel,[2] O'Flaherty and McLaughlin,[4] Theis and Serfass,[6] and D. J. Lloyd[3] and her collaborators.

Animal skin is made up of a number of distinct tissues and contains a number of distinct organs, as would be expected when the several physiologic functions of skin are considered. The tissues may be divided into the following classes: epithelial, connective, muscular, nervous, glandular, fatty, and the blood tissues. The organs include: voluntary and involuntary muscles, fat glands, sweat glands, nerves and blood vessels. These organs are illustrated and designated in Plate 1.[4]

The physiologic functions of the skin are of very great importance. One of the main functions of the skin is to keep constant the temperature of the body it covers; this it does by permitting loss of heat by means of the sweat glands, or retaining body heat, when necessary, by means of the fat glands which can automatically cover the surface of the skin with oil and thus reduce surface evaporation. The skin is one of the principal excretory organs of

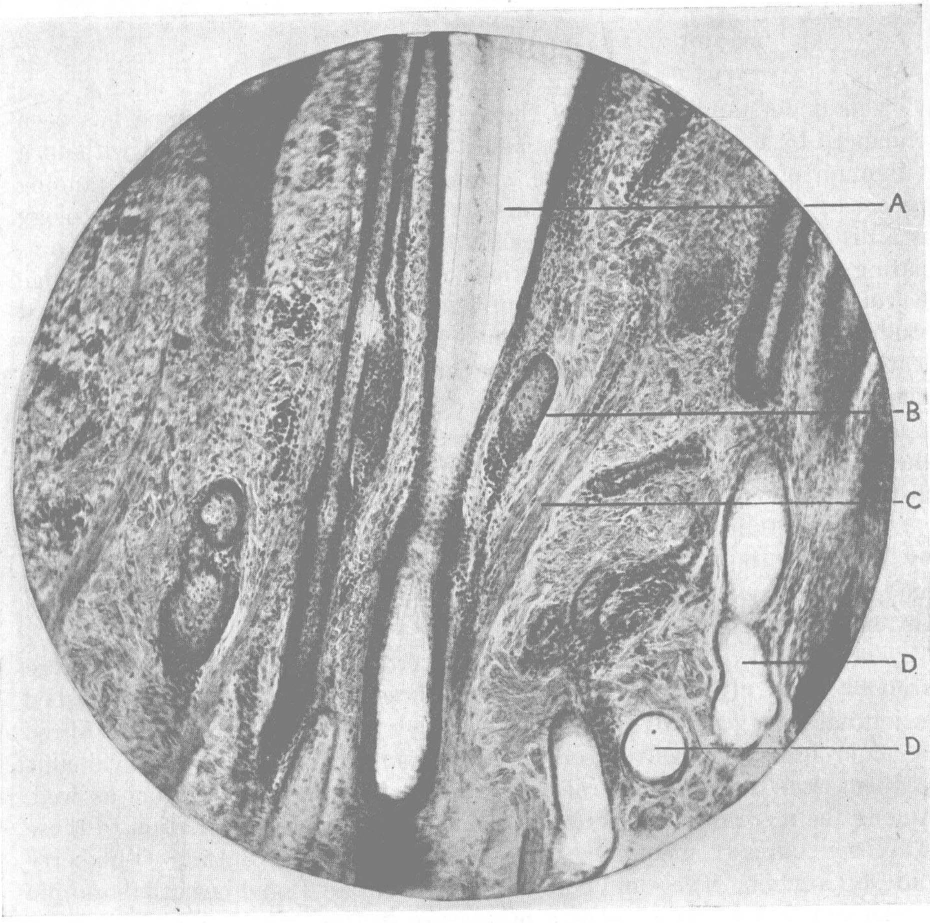

Plate 1. Frozen Section Steer Hide—Hematoxylin and Eosin Stain Showing:

A. Hair Follicle and Hair. C. Erector Muscle.
B. Oil Gland of Hair. D. Sweat Glands.

the body and protects it against bacterial invasion or mechanical damage as well. Another function of the skin is the development of what may be termed color filters to protect underlying tissues from the harmful action of the ultraviolet rays of the sun.

When the animal skin as received by the tanner is considered anatomically, it may first be divided into three distinct and superimposed layers: flesh, derma or corium, and epidermis. These three general layers are subject to further division, as described below.

Flesh. Strictly speaking, this tissue is not a part of the skin proper. Skin is attached to the underlying body by means of areolar connective tissue. When the skin is removed or flayed from the carcass, part of this areolar tissue remains attached to the skin, together with varying quantities of adipose tissue, yellow connective tissue, blood vessels, nerves, and voluntary muscle. All these tissues combined compose the "flesh," as it is expressed in tanning terminology. The flesh must be mechanically removed from the skin during its preparation for tanning, and this process is termed "fleshing." If the flesh were not removed, the diffusion of tanning materials or other chemicals into the skin from its flesh side would be impeded.

Derma. The derma, corium, or true skin, as it is variously designated, constitutes the leather-making material of skin, since both flesh and epidermis will have been removed prior to the tanning of the skin. The derma may be divided into an upper portion and a lower portion. The upper contains glands, muscles, and hair follicles, and has been aptly designated the "thermostat layer" by Wilson,[8] since it contains those organs concerned with the regulation of body temperature. The lower portion of the derma is usually termed the "reticular" layer, since the interlacing collagen fibers of which it is composed present a net-like appearance. The proportion which the thermostat layer bears to the total derma thickness varies greatly with the age of the animal. We have found that, as a general rule, the thermostat layer of a young calf, for example, represents a very much greater proportion of its derma thickness than in the case of the skin of a matured steer or cow. And we have noted that these proportionate differences seem to be a function of increased thickness of the reticular layer in the older animals, the actual thickness of the thermostat layer tending to remain approximately constant regardless of the animal's age.

The chemical constituents of skin are discussed in Chapter 3. But it will be well at this point to note that the main protein constituent of both dermal layers is collagen, which is arranged in interlacing bundles of fibers or fibrils. Seymour-Jones[5] suggested that the fiber bundles were enclosed in very thin sheaths of a substance he termed "fiber sarcolemma." These sheaths were later demonstrated by Turley.[7] Kaye and Lloyd[3] have shown photomicrographically that when collagen fibers of fresh skin are swollen in acidic or alkaline solutions, they show constrictions which seem to be due to tiny encircling threads of reticulin. The derma also contains a smaller amount of yellow connective tissue fibers composed of elastin. These fibers are located mainly at the lower and at the upper surfaces of the skin. Their