NATURE *and* CONTROL *of* TANNERY PROCESSES

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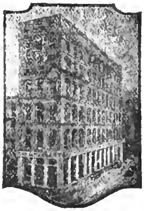

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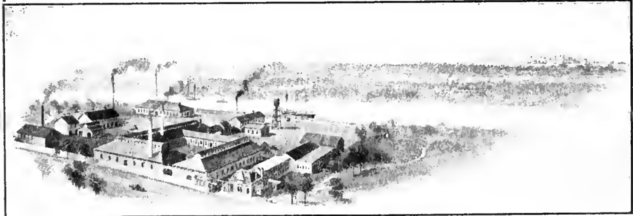

Nature and Control of Tannery Processes

A Practical Exposition of the Purposes and Functions of the
Beamhouse, Chrome Tanning, and Fat Liquoring
Processes, as Revealed by the Latest Researches, and of the Means for the
Economic Control of these
Processes Within the
Tannery

By JOSEPH R. LORENZ

PRINTED AND PUBLISHED BY THE
SHOE AND LEATHER REPORTER
Price $2.00

Author's Preface

The rapid strides made within the past five years by all branches of the tanning industry, especially by that of chrome tanning, is a matter of knowledge to all leather-chemists who follow the work of such of their colleagues as Wilson and Thomas in America, and Stiasny, Fahrion, and Alfred Seymour-Jones in Europe; these names have, in fact, become as well-known to most tannery-chemists of today, as were those of Procter and Wood associated in the minds of leather-chemists of a generation ago with the pioneering work in the chemistry of tanning with which Procter and Wood are universally credited.

To the investigations of our modern workers may be said to belong the distinction of having disclosed to the tanner the real nature of most of the important processes employed today in the manufacture of leather. The effect of thirty years or more of effort on the part of the leather-chemists, as directed toward the solution of the "mysteries" of tanning, has thus been to elevate the art of leather-making from the position of obscurity in which it remained throughout the ages, to that of an exact chemical industry, in which it may safely be said to find itself today.

This little book is addressed to the practical tanner and manufacturer of chrome-tanned upper-leather, as well as to the tannery-chemist. As its title indicates, it is an exposition of the purposes and functions of the beamhouse, chrome tanning and fat-liquoring processes, as revealed by the latest authoritative researches, and of the means for the chemical control of these processes within the tannery. It is so written that anyone having a high-school education, or its equivalent, can understand the principles set forth in it. In the subject-matter will be found a digest of the principal journal-articles bearing on leather-chemistry, as related to chrome-tanning, which have appeared to notice in the last fifteen years; at the close of each of the descriptive chapters on the processes of tanning will be found, in addition, a guide to the analytical control of the process described, this having been prepared, to a great extent, from data gathered by the author during the term of his own experience of eight years as tannery-chemist; finally, in the chapter on "The Fat-Liquoring Process" will be found the principles of J. R. Blockey's recent book on the "Application of Oils and Greases to Leather."

The author is indebted to Mr. Irving W. Skilton, president of the North-eastern Leather Company, for valuable counsel given in the preparation of this treatise.

J. R. L.

Retanning of Chrome Leather

During the war the United States Government, as well as the Governments of the Allies, placed orders for large quantities of retanned Chrome upper leather. This leather was found essential for soldiers' trench shoes, being practically waterproof with excellent wearing qualities.

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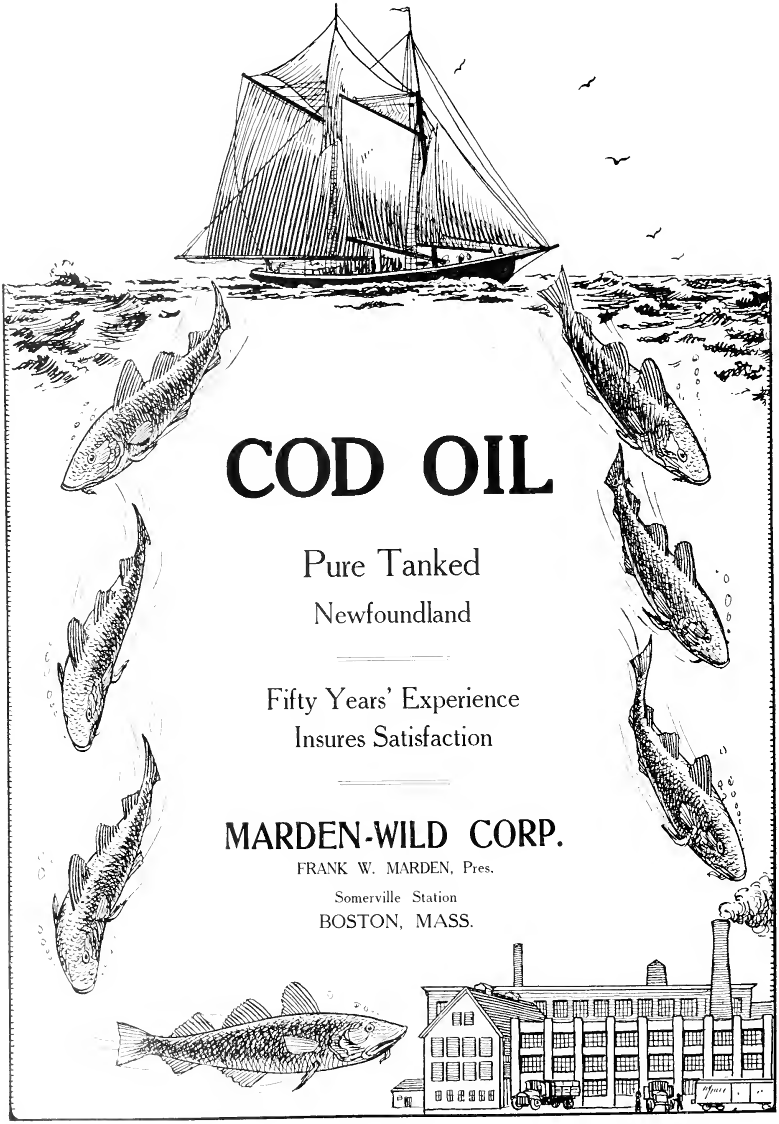

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A Practical Exposition of the Purposes and Functions of the Beamhouse, Chrome-Tanning and Fat-Liquoring Processes, as Revealed by the Latest Researches, and of the Means for the Economic Control of These Processes Within the Tannery

By Joseph R. Lorenz

Soaking of Hides

The purpose of the first tannery process, namely, the soaking in water of the green salted or dry hides, is twofold; it may be stated as follows:

(1) By causing the hides to absorb water, to permit the semi-dry condition of the raw stock to return to the original moist (and therefore workable) condition of the hide in which it was removed from the animal.

(2) To remove by mechanical action the blood, dirt, and dung adhering to the hides, and to dissolve the salt and any other soluble curing—or preservative-substances used in the preparation of the hides at the slaughter-houses.

The softening action of the soak is hastened in the case of dry hides by the addition to the soak-water of caustic soda or sodium sulfide (in the amount of one-tenth per cent of either material on weight of stock in the soak); these materials, by giving rise to alkaline swelling accelerate the absorption of the liquor by the hides.

Adhering blood, dung and salt removed from the hides remain in the soak-pit; the blood and dung are partly dissolved, while the salt is completely dissolved by the soak-water. Those portions of blood and dung dissolved by the water (collectively termed "dissolved organic matter") furnish a medium (i. e., a vehicle) for the propagation of the micro-organisms (namely, bacteria, bacilli, etc.,) that are carried into the soak-liquor by the hides. The majority of the micro-organisms originally in contact with the hides belong to species which—while possibly including some of pathogenic (i. e., disease-producing) origin,—are harmless in character insofar as their action on the hides is concerned. Accompanying the various harmless types, however, are other micro-organisms known as "liquefying bacteria" which, through the action of enzyme-substances[1] which they secrete, indirectly have the power of dissolving protein-bodies (such as albumin, hide-substance, etc.), especially in weakly alkaline media. In a freshly-used soak-liquor the number of liquefying bacteria present is generally small; the nutrient-substances in the form of the blood and the dung introduced by the hides, however, cause a rapid multiplication of the original few; at the same time, the enzymes secreted by these bacteria are actively at work digesting the said nutrient-substances, and further, in splitting up the complex chemical structure of these into products of a simpler chemical construction. In the course of a few days, where repeated use is made of the same soak-liquor, the family of liquefying bacteria will have grown to such dimensions that the supply of blood and dung furnished them becomes inadequate; at this point, therefore, the enzyme-bodies produced will attack the hides in the pit, and, in the process of supplying their mother-bacteria with additional nutrient-material, they will cause a loss of hide-substance, and, ultimately, the total destruction of the hides. It follows from this that the more or less commou practise of using the same soak-liquor for successively treating a number of packs of goods is, by nature, a wasteful process; for, as the "mellow" property of an old soak-liquor is seen to depend on the activity of the bacterial enzyme-bodies which it contains so will the extra softening-effect be gained only at the expense of much hide-substance lost in the process.

Except common salt, many of the curing—and preservative substances dissolved from the hides during soaking are known to have a solvent action on hide-substance, especially in medium dilutions[2]; if allowed to accumulate (as in the case of an old or "mellow" soak-liquor), their presence, including that of common salt, will interfere with the proper swelling of, and absorption of liquor by the hides. (See the role of salts in the Pickling and Chrome-Tanning Processes.)

Analytical Control. The analytical control of the soaking process is ordinarily confined to those cases which, for any reason, require the use of the same soak-liquor over and over again. The determination of the quantity of dissolved organic-matter accumulating in such liquors should be made from time to time, as indicating the extent to which the liquefying organisms present are being encouraged to thrive. (It might be suggested here that by the judicious use of germicidal materials which are also capable of acting as anti-ferments, all the micro-organisms present in the liquor might be rendered innocuous, and further destructive action by the enzyme-bodies stopped. The possible hardening or "tanning" effect upon hide-substance of any germicidal substance employed should, of course, be taken into consideration.) The nature of the salts, and the quantities of these and of common salt dissolved by the soak-liquor may also be determined, if desired. Whenever the concentration of the salts is found to interfere with the proper swelling of the goods, it may be reduced by the addition of fresh water to the liquor in the pit.

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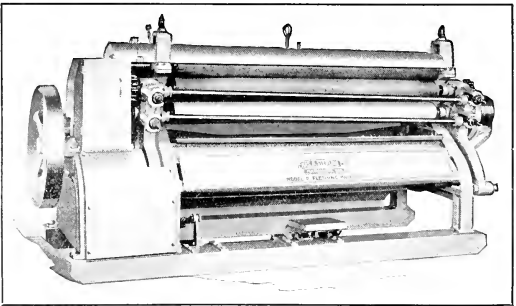
[1] Enzyme: The active principle of digestive fluids secreted by living body cells; examples of enzyme substances are pepsin and rennin (found in gastric juice), and ptyalin (amylase)—the digestive principle of saliva.

[2] H R Procter—"Leather Industries Laboratory Book."



First Fleshing

Hides having much surplus flesh and tallow attached require a thorough fleshing before being placed into the lime liquors. The importance of ridding the hides at this stage of every trace of tallow, especially, is evident from two considerations; namely, (1) that the action of lime upon the fats is to produce insoluble soaps, and that lime cannot, therefore, be depended upon to remove the fats; and (2), that the form of blemish known as "fat-spue" appearing on the surface of the finished leather has been observed by W. Fahrion[3] to arise most frequently in the presence of the "crystalline" fats (stearin and palmitin), of which tallow is composed, rather than from the constituents of the fish oils normally used in the fat-liquoring of the leather.

Chemical Behavior of Acids, Alkalies, and Salts Employed in Tanning

For the purpose of enabling the non-technical reader to form a true mental picture of the course of action of the liming, deliming, pickling and chrome-tanning processes, an explanation will be attempted, first of all, of those fundamental chemical principles upon which the mechanism of these processes rests.

The reader (assuming he is not already familiar with the subject) is therefore asked to consider, briefly, the chemical structure or "make-up" of the simpler acids, alkalies (or "bases"), and salts. It would be found, first, that every acid, alkali, and salt is chemically constructed of **two principal components,** consisting of groups of certain chemical elements examples of which are hydrogen, oxygen, sulfur, chlorine, calcium, sodium and potassium, these groups being known as "radicals;" secondly, that these groups exist within every acid, alkali, and salt, **irrespective of the number or variety of individual elements which the substance may contain.**

Now, when any acid, alkali, or salt is decomposed (i. e., caused to be "broken-up" into its constituent parts), it will be evident that the immediate products of the decomposition will consist,—not of the individual elements of which the substance was composed,—but, instead, of the two groups or radicals, in which these elements may still be found residing. In other words, the first step of the "breaking-up" process, in general, will do no more than separate the groups in the compound, the groups themselves remaining intact. For the purpose of this discussion, the foregoing principle, upon which the course of chemical reactions, in general, may be said to depend, may be stated as follows: **The behavior of the chemical groups or radicals composing any chemical compound is, in general, that of primary, or elementary bodies.**

Taking for consideration the principal acids, alkalies and salts employed in the tannery, it is possible to establish a connection between the physical properties (e. g., taste) of these and their chemical structure. Thus, acids are familiarly associated with a sour taste, alkalies with a "caustic" or "soapy" taste, and salts with a saline or bitter taste; again, the chemical formula of sulfuric acid, for example, is H_2SO_4 (meaning the combination of two parts of hydrogen with one of sulfur and four of oxygen), while that of hydrochloric (or "muriatic") acid is HCl (or, one part of hydrogen combined with one part of chlorine). In each of the formulae of the two acids named it will be noted that the element hydrogen is written first; if the whole list of acids were surveyed it would be found that hydrogen is a common constituent of all. Hydrogen is, therefore, a "group-element" with respect to the acids. To the "hydrogen-radical"[4], as this group is called, then, is due the "acidity" or sour states of the acids. In the case of the family of alkalies, of which ordinary slaked lime (or calcium hydroxide), caustic soda (or sodium hydroxide), and aqua ammonia (or ammonium hydroxide) are some of the best known members, that particular chemical radical which determines the "causticity" (or "alkalinity") of these substances may, on inspection of their chemical formulae, be readily identified; the formula of lime is $Ca(OH)_2$ (meaning the combination of two parts of the oxygen-hydrogen group with one part of the metal calcium); that of caustic soda is $NaOH$ (wherein one part of the oxygen-hydrogen group is united to one part of the metal sodium, whose symbol is Na); while that of aqua ammonia is NH_4OH (wherein the oxygen-hydrogen group is attached to the ammonium-radical, the latter being constructed, as the formula shows, of one part of nitrogen, and four parts of hydrogen). Clearly, then, the common radical of the alkalies, and the one to which these bodies owe their caustic property and "soapy" taste, is the oxygen-hydrogen group, or better known as the "hydroxyl-radical." To consider, finally, the remaining class of substances, namely the "salts." A salt is produced whenever an acid combines with an alkali, or vice versa, the process being the familiar one of "neutralization." The following equation, which is typical of all neutralization reactions, shows how a salt is produced.

$$\begin{array}{l} H_2SO_4+2(NaOH)=Na_2SO_4+2(H_2O) \\ \text{Acid}+\text{Alkali}\quad\text{Salt}+\text{Water} \end{array}$$

In this equation it will be noted that the SO_4-radical of the acid has united itself to the Na_2-radical of the alkali, these together forming the "neutral" salt Na_2So_4 (sodium sulfate, or "Glauber's Salt"); simultaneously, the hydrogen-radical (H_2) of the acid has attached itself to the hydroxyl-radical ($2OH$) of the alkali, the two thus combining to form water. (The fact that might be pointed out as of interest here is that the two last-named groups, to which the power of all acids and alkalies respectively, is due, are merely the constituent parts of that well-known substance—water.) Compared with either the acids or the alkalies, the salts are much the more stable (i. e., chemically inactive) substances, a firmer union existing between the groups that compose a salt; again, the saline or bitter taste of a salt is not due to any one of its two significant groups, but resides in the combination of these as a whole.

It now remains to be explained why some acids are chemically more powerful or "stronger" than others, or why the alkali lime, for instance, is so much weaker in action than the alkali caustic soda. As any one who has ever experimented with chemicals knows, a perfectly dry substance is entirely without action upon another perfectly dry substance; on dissolving the first substance in water, however, and adding to it the second substance also dissolved in water, chemical combination between the two

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[3] "On the Retention of Fat in Leather." Chemischen Rundschau, through Gerber, 43, 123 (1917).

[4] Also known as the "metal-radical," as, in combining with the alkalies, this group of the acids is replaced by the metallic group of the alkalies.

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substances may be at once effected. That water must be present in order to cause two chemicals to combine is, therefore, evident[4]. Now, the part that water plays when any acid, alkali or salt is dissolved in it is simply this: Water causes the two chemical groups or radicals composing the compound to disunite and become separated[5]. **Only when thus separated, or "released for duty," as it were, are the radicals of one chemical compound able to combine with the radicals similarly released from another chemical compound.** Plainly, then, once a chemical compound is dissolved in water, it must exist in that first stage of decomposition to which reference was made at the beginning. For illustration, taking the composition of sulfuric acid as H_2SO_4, that of a solution of this acid in water would read:

$$(H_2)+(SO_4)+(\text{Water})+(\text{Unchanged } H_2SO_4)$$ [6a].

Thus, while a portion of the total quantity of acid dissolved becomes dissociated, yielding its H_2— and SO_4— groups to the water, the remainder escapes dissociation; that is, its H_2— and SO_4 groups remain united in the presence of the water. Disregarding this latter portion, there are found in the dissociated portion the "active" groups; that is, those groups capable of entering into chemical union with other substances. Now, the number of groups that water is capable of releasing **varies with every chemical substance;** in other words, irrespective of how concentrated or "strong" the solution of an acid, alkali or salt might be made, for every such substance there is a fixed limit to the number of "active" groups present in the solution, and this limit is, therefore, a measure of the chemical power or "strength" of that substance. Thus, for instance, the number of hydrogen-radicals (or acid-groups) that become released when the different acids are dissolved in water (and, hence, the relative "strengths" of these acids) has been determined for each of the acids named in the appended table, as follows:

Acid	Relative Strength
Hydrochloric	200 (approx.)
Sulfuric	200 (approx.)
Oxalic	0.1
Formic	0.0214
Lactic	0.0138
Acetic	0.0018
Butyric	0.00115
Boracic	0.0000001

The acids listed are thus arranged in the order of their "strengths." It will be noted that the two mineral acids, namely, hydrochloric and sulfuric, are each approximately two thousand times "stronger" than the "strongest" organic acid, namely, oxalic; formic acid comes next, then lactic, acetic, and butyric acids, while boracic acid, although a "mineral acid," is seen to be the "weakest" acid of all; compared with oxalic acid, boracic acid possesses but one-millionth the "strength" of oxalic acid!

In like manner can the difference in the "strengths" of the various alkalies be explained. In the absence of actual figures[7], it may be stated that, of the common alkalies, caustic potash (potassium hydroxide) is the "strongest"; caustic soda is next in order, then slaked lime, and, finally, aqua ammonia.

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[4] With certain exceptions, this holds true for all classes of chemical reactions occurring at ordinary temperatures.

[5] This separation, or "release" by water of the chemical groups in a dissolved substance, is technically known as "dissociation."

[6a] Sulfuric acid actually dissociates into H+H.SO4. For practical purposes, however, the dissociation products of this acid may be regarded as consisting of H_2—and SO_4— groups.

[7] See, however, "Tabulation of Hydrogen and Hydroxyl-ion concentration of Some Acids and Bases"—Arthur W. Thomas, Jour. A. L. C. A., 15, 133 (1920).

The Liming Process

The primary purpose of the liming process is, of course, familiarly known; it is to effect the removal of the hair on the hides. That the liming process, in addition to loosening or destroying the hair, causes at the same time a change in the character of the hides, is a fact also known to all tanners. The various phenomena observed in the treatment of hides with a "straight" lime-liquor (i. e., a saturated solution in water of slaked lime only), for instance, are the following:

(1) Swelling, or increase in weight and volume of the hides caused by the absorption of the lime-liquor.
(2) Plumping effect, or change from the soft and yielding state to a more elastic or "rubbery" state.
(3) Loosening of the hair at the roots.

Aside from these visible phenomena there occur in liming a number of reactions which can be tested chemically; of these, some may be said to be well defined, while their connection with the phenomena of swelling, plumping and unhairing has been, of late, established by a number of investigators.

To begin with the lime-liquor itself, it is known that the solubility of lime in plain water is very slight; at 32° Fahrenheit, for instance, 100 parts of water dissolve but 17/100 of one part of slaked lime; moreover, and contrary to the general tendency, the solubility diminishes with increase in temperature; thus at 212° Fahrenheit it becomes 8/100 per cent, or less than one-half the solubility it possesses in water at freezing temperature[8]. By reason of its slight solubility, therefore, of the relatively large quantities of lime employed in practise, by far the greater portion remains undissolved (or suspended) in the lime-liquor; as the dissolved portion is removed from solution by the hides, however, more of the solid lime passes into solution, the latter being thus kept in a saturated condition (i. e., at maximum concentration) at all times throughout the process[9].

When lime is dissolved in water, the two chemical groups composing it, viz., Ca and $(OH)_2$, become separated (or dissociated) in the manner already described; thus existing "freed" within the lime-liquor these groups are prepared for action—each in the direction peculiar to itself.

The first action, namely, swelling, which ensues when the softened hides are placed into the lime-liquor, is produced by the hydroxyl, or OH-groups released from the lime[10]. In other words, swelling is purely a function of the "alkalinity" of the liquor. The swelling power of lime (and of alkalies in general) diminishes with rise in temperature of the liquors; the explanation of this lies in the fact that, as the temperature increases, the hide also becomes less elastic or "cohesive." In reference to the phenomena of plumping and unhairing it may be stated that these do not arise in any simple manner comparable to that in which the swelling of the hide is effected. Broadly considered, plumping and unhairing find their origin in the joint action upon the hide of the two lime groups, plus—in the case of unhairing—that of the bacterial enzyme-products formed in the lime-liquor soon after the hides are introduced. Again taking the case of the alkalies in general, plumping may be said to be more distinctly influenced by the nature of the metal-group of the alkali; thus—while the plumping and swelling produced by "pure" solutions of the alkalies are known to occur simultaneously, both in diminishing ratio, from the "strongest" alkali down—plumping is not a necessary accompaniment of swelling nor is swelling always accompanied by plumping. The unhairing power of the alkalies, on the other hand, increases as the alkali becomes "weaker"; in other words, caustic potash and caustic soda — although exhibiting the strongest swelling action—cause least unhairing, while ammonia—possessing minimum swelling power—is most rapid in unhairing action. It must not be supposed, however, that this increase in depilatory power is gained as a result of the lesser hydroxyl-group concentration of the "weaker" alkali; on the contrary, the hydroxyl groups, as will be seen, play a very important role in the unhairing process; moreover, the unhairing power of any alkali will increase in proportion to the concentration of its solution (e. g., the unhairing effect of caustic soda may be made to equal that of ammonia simply by employing a relatively "stronger" solution of the soda). The explanation of this paradoxical behavior of the alkalies with respect to unhairing rests—as it does in the case of plumping—upon the difference in the nature of the metal-group by which one alkali is distinguished from another.

In the case of liming, the mechanism of unhairing may be described as follows[11]: The hydroxyl-groups in the lime-liquor first soften the epidermis (or "outer skin") of the hide, and then dissolve it, together with the coriin (or cementing substance of the hair roots); the dissolved epidermis and coriin, in turn, furnish a nutrient-medium for the bacteria present, enabling these bodies to secrete enzyme-substances, by whose solvent action the hair is still further loosened. The process is thus seen to consist of a cycle of operations, and it will be apparent that the longer it continues, the richer must the lime-liquor become in enzyme-content, and, hence, the more powerful in unhairing effect[12].

Now, as the lime-liquor grows "mellow," the solvent action which it normally exerts upon the hide itself becomes greater and greater. A "mellow" lime-liquor thus compares with a "mellow" soaking-liquor both causing losses of hide-substance. By reason of its alkali-content, however, the lime-liquor will be the more destructive of the two; in other words, a certain loss of hide-substance occurring in the liming process may result from the purely chemical action of the alkaline liquor. Thus, in general, the greater the concentration of hydroxyl-groups (i. e., the more "alkaline" the liquor), the greater will be the loss of hide-substance. The one exception to this rule, however, is ammonia; far from exhibiting the minimum solvent action, ammonia causes instead the greatest loss of hide-substance[13].

Besides giving rise to the foregoing phenomena, a further function of the liming process is to remove the seba-

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[8] Van Nostrand's Chemical Annual—Olsen.

[9] This will, however, not be the case unless some means are employed of agitating the lime-liquor during use.

[10] All alkalies, therefore, are capable of swelling hide. Since, however, up to the "limiting point" the degree of swelling produced is in distinct proportion to the number of hydroxyl-groups released, all alkalies have not the same power to swell hide; thus, caustic potash, which in solution yields the greatest number of these groups, possesses the maximum swelling power of the alkalies, while ammonia—giving rise to the least—is weakest in swelling action.

[11] Donald Burton ("The Analysis of Lime Liquors")—Jour. A. L. C. A., 15, 308 (1920).

[12] The unhairing enzymes are secreted freely in media otherwise unfavorable to the rapid growth of the bacteria, such as, for instance, lime-liquors.

[13] "The Nature of The Liming Process"—Edmund Stiasny—Jour. S. L. T. C. (120), 1919.

ceous (or fat) glands situated at the roots of the hair on the hide; the removal of these glands is effected by the mild saponifying action which lime exerts upon the fats. The removal of these glands should be complete, else "spueing" of the finished leather may result.

Thus far, the action of a "straight" lime-liquor has been considered. In modern practise, however, the period in which the hides remain in contact with the lime-liquor is shortened as much as possible by the employment of liquors containing in addition to lime, certain materials designed to accelerate the unhairing process. Such so-called "sharpening" materials may be divided into two groups[14]:

(1) Those serving to increase the "alkalinity" of the lime-liquor.

(2) Those which form hydrosulfide (SH)-groups.

The first group of sharpening materials may be further divided into two classes, viz.:

(a) Substances which in solution yield a greater number of hydroxyl-groups than lime alone can produce; e. g., caustic potash, caustic soda, ammonia, etc. Of ammonia a word may be said here; ammonia enters into a loose combination with lime, forming a calcium-ammonium compound similar to the corresponding barium and zinc compounds; in so doing, the "alkalinity" of the liquor becomes actually lowered, in consequence of which the swelling and unhairing power of the liquor will be inhibited. In the presence of lime, therefore, ammonia is quite without value as a "sharpening" agent, and the belief long held that the ammonia-content is a measure of the unhairing power of a lime-liquor is, therefore, unfounded.

(b) "Neutral" salts of bases "stronger" than lime. The manner in which these render the lime-liquor more "alkaline" may be illustrated by taking the case of sodium sulfate (or Glauber's Salt), Na_2So_4; in contact with lime, sodium sulfate reacts with it, becoming itself converted to caustic soda, and changing the lime to calcium sulfate, or,

$$Ca(OH)_2+Na_2SO_4 = 2NaOH+CaSO_4;$$

thus, in place of the lime will remain the "stronger" alkali, caustic soda.

Of the second group of sharpening materials, sodium sulfide (Na_2S) is the most prominent member. Notwithstanding the loss of the hair which it ordinarily causes (for sodium sulfide attacks keratin—the substance of which hair is composed), this material finds favor in the tannery on account of the rapidity of its action in loosening the hair when employed either alone or in combination with lime.

Dissolved in water, sodium sulfide releases its two chemical groups, Na_2 and S, which, however, immediately combine with the two water-groups, H and OH, to form the substances NaOH (caustic soda) and NaSH (sodium hydrosulfide), in accordance with the following equation:

$$Na_2S+H_2O=NaOH+NaSH.$$

The caustic soda and sodium hydrosulfide, in turn, become dissociated into metal groups (Na_2), hydroxyl-groups (OH), and hydrosulfide-groups (SH). In the presence of lime a second metal-group, namely Ca, is further introduced as a dissociation-product of the calcium hydrosulfide ($Ca(SH)_2$) that is formed when lime reacts with sodium sulfide[15].

The most prominent characteristics of the various chemical groups present in a sulfide, or sulfide-lime liquor, as enumerated above, have been brought to light by Stiasny[16], and may be summarized as follows:

(1) The hydrosulfide-group alone possesses neither swelling, plumping nor unhairing properties.

(2) Only by the combined action of the hydrosulfide- and hydroxyl-groups is the powerful unhairing effect exhibited by a sulfide-liquor produced.

(3) The extent to which the swelling, plumping and unhairing effects manifested by a sulfide-liquor occur depends on the proportion of hydrosulfide-groups to hydroxyl-groups present, the most favorable ratio being 1 : 1[17].

(4) An excess of hydroxyl-groups (i. e., an increase in alkalinity) has little effect on the action of the liquor. A preponderance of hydrosulfide-groups, on the other hand, adversely affects the action of the liquor.

In presence of an excess of hydrosulfide-groups, swelling, plumping and unhairing are all markedly inhibited. In practise, a sulfide-liquor may suffer loss of alkalinity through the use of "hard" water in preparing the liquor. "Hard" water uses up the hydroxyl-groups, leaving the hydrosulfide-groups in excess. The deficiency in alkalinity thus produced can, however, be restored by the use of a small quantity of lime in admixture with the sulfide.

It will be noted that the active alkali of both sulfide-liquors and sulfide-lime liquors is caustic soda. By reason of the ready solubility and powerful action of this alkali compared with lime, greater care is necessarily required in the use of sulfide-liquors, in general, than would be demanded of a "straight" lime-liquor. Thus, in the repeated use of the same sulfide-liquor, the excess caustic soda which accumulates in the liquor must be removed. For this purpose, probably the best means is calcium chloride ($CaCl_2$)[18]. Added to a sulfide-liquor, calcium chloride destroys the caustic soda by converting it into common salt (NaCl), at the same time regenerating caustic lime in accordance with the following equation:

$$CaCl_2+2NaOH = 2NaCl+Ca(OH)_2.$$

The action upon hide of a sulfide-liquor has been observed to differ from that of a lime-liquor in one important respect, to wit, that sodium sulfide attacks the keratin of the hair, upon which, on the other hand, lime exerts little or no solvent action. From this it may be inferred that the sweat ducts of the hide, being keratinous in structure, would also be dissolved by treatment with sulfide-liquor; a "straight" liming treatment, on the other hand, would leave the sweat ducts intact in the hide.

Analytical Control. The following considerations

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[14] Edmund Stiasny—Loc. Cit.

[15] The reaction is as follows:

$$Ca(OH)_2+2NaOH+2NaSH = Ca(SH)_2+4NaOH$$

The conversion of the lime into the strong alkali, caustic soda, explains the increased swelling and plumping action exhibited by a lime sulfide mixture.

[16] Loc Cit.

[17] Or, the ratio in which these groups are found to exist in the material, sodium sulfide.

[18] Payne Pullman Process. In practise, one part of calcium chloride to three parts of crystallized sodium sulfide are employed.

"Colors for Leather"

should govern the procedure employed for the analytical control of any particular form of the liming process[17]:

(1) That the "alkalinity" of a pure lime-liquor in contact with solid lime remains at a practically constant point throughout the liming treatment[18]; thus, the alkali-content of fifty cubic centimeters of a saturated lime-solution, measured at 60 Fahrenheit, will be found to correspond to 23.6 cubic centimeters of a tenth-normal acid solution. A higher figure will indicate the presence of one or more of the "stronger" bases, viz., caustic potash or soda; a lower figure, on the other hand, may mean

  (a) that the liquor holds in solution "neutral" salts, or decomposition-products of hide-substance and lime, or both, or

  (b) that the liquor contains ammonia in combination with lime, or

  (c) that the liquor has been insufficiently agitated.

(2) That the influence of ammonia, formed by the action of lime and bacteria upon the dissolved organic-matter, is positively detrimental. Where the conservation of hide-substance is of any importance, a lime-liquor that has become strongly ammoniacal through repeated use had best be drained into the sewer.

(3) That dissolved organic-matter accumulating in the liquors consists of both epidermal matter (which it is the function of lime to remove from the hides), and portions of the hide itself. In the absence of analytical means permitting the differentiation of the products of the normal action of the lime, on the one hand, from the dissolved hide-fibres, on the other, it will be evident that the estimation of dissolved organic-matter in lime-liquors is of limited usefulness only. For control purposes, however, the quantity of organic matter normally dissolved by the liquors under any given set of conditions during the liming treatment may be determined, and losses of hide-substance made possible of detection, by any increase which the value thus established may show in subsequent runs.

(4) That the unhairing power of a lime-liquor increases with the age of the liquor, the age of the liquor, in turn, being measured by the amount of ammonia and dissolved organic-matter which it contains.

(5) That the unhairing power of a sulfide-liquor, or a sulfide-lime liquor, depends principally on two factors, viz.:

  (a) the strength of the liquor in terms of sulfide (SH); and

  (b) the proportion of sulfide to alkali (SH : OH) present.

In the analysis of sulfide-liquors, therefore, the important determinations to be carried out are (1) Sulfide as Na_2S[19] and (2) Alkali in combination with the sulfide[20]

WASHING OF LIMED HIDES

The first step in the removal of lime from the hides consists in washing the limed goods, after unhairing and fleshing, for a period of one-half hour or longer, in a revolving wheel supplied with a stream of water.

The maximum washing effect is gained (1) when the water used is quite free from "temporary hardness," and (2) when the temperature of the water is kept at the proper (or "optimum") point.

The effect of "temporary hardness" (consisting of calcium and magnesium bicarbonates dissolved in the water) is exceedingly detrimental. In the presence of "temporary hardness," the caustic lime, with which the hides are impregnated, is immediately converted into insoluble calcium carbonate (chalk); once formed in the hides, calcium carbonate cannot be removed by further washing, but will require an acid treatment for its removal.

The question of what is the most effective temperature of the wash-water cannot, in the absence of specific data, be answered definitely. While it is true that cold water will dissolve more lime than warm water, it must be remembered that cold water will also produce the greater swelling of the hide, and by thus allowing the hide to retain more lime-liquor, the action of cold water is to actually decrease the effectiveness of the washing. The choice of temperature, hence, would appear to be one of compromise, and luke-warm water, it would seem, should remove in a given space of time the greatest quantity of lime from the hides.

The passage of the limed hides through the unhairing and fleshing machines serves to rid the goods of about thirty-five per cent of the lime; another thirty per cent. is dissolved out during the one-half hour period of washing, the lime-content of the washed hides being thus reduced to about thirty-five per cent of the original amount.

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[19] See "The Determination of Alkaline Sulfides in Lime Liquors."—Fini G. A Enna.—Jour. S. L. T. C., 5, 131 (1921)

[20] See "The Analysis of Lime Liquors."—Donald Burton—Loc Cit.


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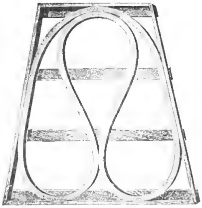

Deliming and Bating

The final beamhouse operation, by which the last of the non-essential portions of the hide are removed, and the hides are made ready for tanning, is that of bating.

Bating has for its object [21], [22]:

(1) The reduction of the swelling of the limed hides.

(2) The digestion (a) of the elastin fibres present in the outer layers of the hides, and (b) of the cementing substance surrounding the fibres of the main body of the hide.

In the present-day production of chrome-tanned upper leather, deliming and bating are generally carried out in one operation by the use of some proprietary preparation of the type of "Oropon," of which the active ingredients are (1) ammonium chloride ("Sal Ammoniac"), and (2) the digestive principle (tryptic enzymes) extracted from the pancreas of hogs and cattle.

The reduction, in the first place, of the swelling of the hides is of prime importance, for hard leather would otherwise result were the hides tanned in a swollen state [23]. The first essential of bating, therefore, is the removal of the caustic lime producing the swelling, and this is brought about by the chemical action of the ammonium chloride present in the bating material. Ammonium chloride finds preference over a host of other deliming materials because

(1) it forms with caustic lime one of the few lime-salts that are readily soluble in water, namely, calcium chloride;

(2) its base, namely ammonia, which is set free by the action of the lime, is known to produce less swelling of hide than any other alkali, and ammonia can, moreover, be readily washed out of hide;

(3) ammonium chloride is comparatively low in cost.

The fact should be stated, however, that ammonium chloride will not attack any calcium carbonate that may have been formed in the hide by the action of "hard" water, if the latter was employed in the washing of the limed goods. Calcium carbonate, however, being a "neutral" substance, has no swelling power, and may be conveniently left in the goods until these are placed into the pickle, when, by the solvent action of the acid liquor, the hide will be freed of the carbonate.

So far, the purely chemical action of the bate in removing the lime from the hides has received mention. True "bating," however, commences when the digestive principles in the form of the pancreatic enzymes contained in the bate-liquor begin to act upon, and to dissolve the elastin fibres present in the outer layers of the hide. The elastin fibres form the chief support of th grain structure of the hide, and their slow removal causes the grain-membrane to gradually collapse, producing what is known as the "bated-effect." The hide thus becomes flaccid—a desirable condition, from the standpoint of the tanner, as productive of "silky-grained" leather. A further function of bating, however, has been described by Robert H. Marriott [24] to consist in dissolving the cementing substance surrounding the fibres of the main body of the hide. A portion of this cementing substance is removed during liming, and the effect of its complete removal by the subsequent action of the bate would be to cause the hide-structure to fall together a little,—thus contributing to the "bated-effect" as a whole. The last-described action would explain the characteristic effect which bating has upon the appearance of the grain-side of the hide, the grain showing up prominently once the hair-holes and sweat-ducts thereon have been opened up and cleared of gummy matter.

In the modern short-time method of bating with artificial materials, destructive tendencies—well-known as a feature of the earlier drug bates—may be said to scarcely enter. Indeed, it is to be questioned whether any true "bated-effect" at all is gained during the extremely short period in which the hides are left, for instance, in an "Oropon"-liquor. Wilson [25] has thus shown that in order to deprive a calf-skin of its elastin fibres it must be digested for a period of twenty-four hours in a liquor containing trypsin. That the action of the modern bate-liquor is practically confined to that of the ammonium chloride present in removing lime from, and in reducing the swelling of the hide, seems, therefore, most likely.

Analytical Control. The actual measurement of the "bating-power" of a bate-liquor cannot be performed by any simple means. For this reason, the analytical control of the bating process is but seldom practised; the deliming power of a fresh or used bate-liquor, however, may be readily ascertained by chemical analysis. In the beamhouse, the test for the presence of caustic lime remaining in the bated hides may be conveniently made by moistening a freshly-cut edge of the hide with phenol-phthalein solution, which will turn red in the presence of the free alkali.

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[21] "The Mechanism of Bating."—John Arthur Wilson—Jour. Ind. Eng. Chem., 12, 1087 (1920).

[22] "The Removal of Elastin During Bating."—Robert H. Marriott—Jour, S. L. T. C., 5, 280 (1921).

[23] Cf. Sole Leather, which receives no bating.

[24] Loc. Cit.

[25] Loc. Cit.

Method of Ascertaining Weight of Dry Leather-Forming Substance in Wet Hides[26]

At the conclusion of one or another of the various beamhouse processes, it is often desirable to know the actual weight of dry leather-forming substance in the raw material, and consequently, the maximum weight of leather which the material may be expected to yield. Calculation of the dry weight from the weights of the soaked or limed hides leads to variable figures by reason of the variability of the swelling of the hides in practise, while actual drying and weighing of portions of the hide-material itself is impracticable on account of the impossibility of getting really average samples.

The method to be described is an old one, but is given here for the benefit of those who may not know of its existence. The method consists in weighing the wet hide while it is totally immersed in water. The hide is suspended from the arm of a delicate balance (of ten to fifteen pounds capacity) by means of a thin copper wire into the water contained in a pit deep enough to allow the hide to hang free from contact with the sides or bottom, and its weight in this position is then noted. The weight in water of the hide multiplied by 3.38 will be found to equal the average weight of the hide when perfectly dry. By subtracting the dry weight thus obtained from the original wet weight, a true measure is obtained of the amount of swelling which the hide has undergone.

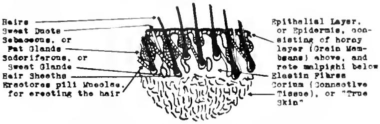

Figure A. Vertical Section of Calf-Skin (Magnified). (Procter's "Leather Industries Laboratory Book").

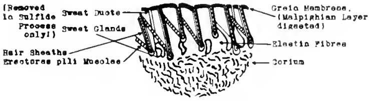

Figure B. Showing Parts of Skin Remaining after Liming and Unhairing Hide.

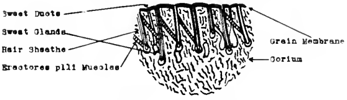

Figure C. Showing Parts of Skin Remaining after Bating Treatment.

Diagram of Sections of Raw Hides Before and After Liming and Bating Treatments Respectively.

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[26] Procter's "Leather Industries Laboratory Book"—p. 98

The Pickling Process

Next in order after bating comes the pickling of the hides. Pickling serves a two-fold purpose; viz.,

(1) it removes from the hide any lime remaining in the form of calcium carbonate.

(2) it imparts to the hide just out of the alkaline bate-liquor an acid charge, making the hide receptive to the subsequent entrance of the acid chrome-tanning liquor by thus preventing the precipitation of basic chrome on the surface of the hide.

Pickling is, in a strict sense, a part of the chrome-tanning process, or, at least, a prerequisite of it. Pickling consists in paddling or drumming the bated goods for an average period of twelve hours in a one-half to one per cent. solution of some moderately strong acid, the solution containing, besides the acid, a large proportion (e. g., ten per cent.) of common salt. Almost any acid will do, but sulfuric acid is preferred on account of its low cost. Using sulfuric acid, then, in the presence of an excess of common salt, the composition of the finished pickle-liquor will include the following substances: viz.,

(a) Common salt, as NaCl;
(b) Glauber's Salt, as Na_2SO_4; and
(c) hydrochloric acid as HCl,

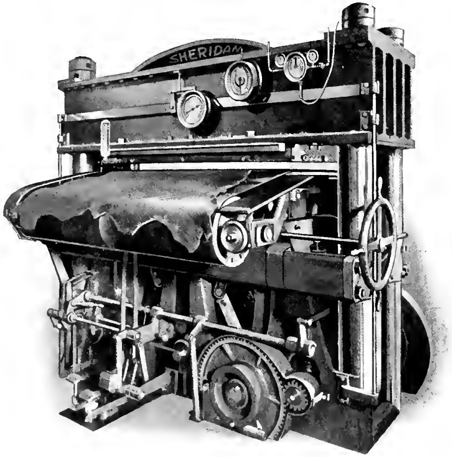
the sulfuric acid originally used disappearing from the liquor after combining with the common salt present to form Glauber's Salt, and releasing its equivalent of hydrochloric acid, according to the following equation:

$$H_2SO_4+2NaCl=Na_2SO_4+2HCl.$$

The action of the pickle-liquor in removing from the hides any lime remaining in the form of calcium carbonate depends on that of the hydrochloric acid present, by which the insoluble calcium carbonate is converted into soluble calcium chloride.

Apropos of the second and principal function of the pickling process, namely, that of imparting to the hide an acid charge, it should be stated, first of all, that hide-substance is amphoteric by nature; i. e., hide-substance is capable of acting either as a weak base, or as a weak acid. Hide-substance, therefore, will combine with either acids or alkalies to the accompaniment of swelling. Now, just as the swelling produced by alkalies is known to be due to the "active" hydroxyl, or OH-groups released by them, so is the swelling produced by acids due to the "active" hydrogen, or H-groups, common to all acids. The swelling of hide produced by alkalies, on the one hand, and by acids, on the other, is similar in all respects save one; namely, that while alkaline-swelling is accompanied by more or less plumping (or, increase in elasticity) of the hide, acid-swelling is attended by little or no plumping.

In the pickling process, however, the object is not to swell the hide, but merely to impart to it an acid charge. Now, it is known that the degree of swelling is proportional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to the number of "active" hydrogen, or acid-groups present in the liquor; i. e., the more "active" groups in solution, the greater will be the swelling of the hide. Were hide placed, for example, in a pure solution—however "weak" it may be—of one of the strongest mineral acids, such as sulfuric or hydrochloric, it would swell so enormously as to be in great danger of bursting. The problem, then, is that of reducing the number of "active" groups released in solution by the acid, and so keep the swelling of the hide down to a minimum. To this end there fortunately exists a simple means, and that consists in putting common salt into the pickle-liquor along with the acid. The salt is itself dissociated in solution—i. e., its chemical groups, namely Na and Cl, become released (neither of these groups, however, having any swelling action upon hide); in the presence of these salt-groups, however, a **lesser number of acid, or hydrogen-groups are split from the acid in the liquor,** the number of "active" acid-groups thus becoming reduced [27]. An exact analogy of the foregoing phenomenon may be drawn by taking the case of two water-soluble substances. Of the one substance, water will dissolve a certain definite percentage, of the other, also a definite percentage, which may or may not be the same as the first. Now, suppose that the second substance was to be dissolved in water already containing in solution some of the first substance; in this case, of course, less of it could be brought into solution than if the water were entirely free from the first substance. So it is with regard to the effect of the salt present in the pickle-liquor, only here it is not the question of the solubilities of the salt and acid in water, but that of the dissociation of these substances which is of importance.

The function of the salt in pickling, then, is to inhibit the swelling action of the acid upon the hide. Notwithstanding, however, the large quantity of salt normally employed in pickling, considerable swelling does occur in practise. Thus, the amount of liquor which the hides ordinarily absorb along with the acid during pickling has been found to average sixty-five per cent. of their drained pickle-weight.

The uniform penetration of the pickle-liquor into the goods is of great importance. If, owing to the presence of grease in the hide, or to some other cause, certain areas do not receive so much acid as the remainder of the hide, uneven coloring will result in tanning, the color of the chrome-substance deposited in the hide varying in shade according to the amount of acid with which it is able to combine.

Analytical Control. In practise, a pickle-liquor is seldom discarded after being used in the treatment of a single pack of goods; instead, for the sake of economy, it is replenished with more acid and salt, after which it receives the second pack of goods; this process may be repeated until as many as thirty packs of goods have passed in succession through the liquor. In the replenishment of a pickle-liquor, careful chemical control is a necessary feature. The quantity of acid absorbed by the goods during pickling will amount to about 93 per cent of the total weight of acid in the liquor; this figure, however, is by no means constant, and unless the amount of acid left in the liquor is accurately known, too little or too much may be added when the liquor is replenished. For practical purposes, however, it is quite sufficient to check the acid-content of a pickle-liquor after the passage of every four or five packs of goods through it. The quantity of salt removed along with the acid by the goods from the pickle-liquor is approximately 25 per cent of the amount dissolved in the liquor. The actual quantities of both common salt and Glauber's salt removed depend upon the concentration in which these salts existed in the liquor, and are proportional to the quantity of liquor simultaneously absorbed by the hides. Below are given some typical figures obtained in practise (by chemical analysis of the used liquors), showing the amounts of common salt and of Glauber's salt removed by the different packs of goods (all being of practically uniform weight) as these were passed in succession through a pickle-liquor—originally containing 1,800 pounds of common salt—which was replenished, as each pack was removed, with acid and additional salt in the amounts shown in the last column:

Order of Packs	Pounds Removed from Liquor by Each Pack		Pounds per Pack of Common Salt with which Liquor was Replenished
	of Common Salt as NaCl	of Glauber's Salt as Na_2SO_4	
1st	425	10	...
2nd to 4th	390	47	300
5th to 9th	365	72	330
10th to 14th	366	81	390
15th to 21st	375	88	400

In restoring the salt-content of a used pickle-liquor to its original value, it is usually most convenient to employ the hydrometer, the specific gravity reading of a fresh liquor at 60° Fahrenheit being normally about 1.07, or 9.5° Baume. If, however, the total volume of the liquor is known, it is more accurate to determine the salt-concentration by chemical analysis of the liquor.

The percentage of acid and total salts present, as found by analysis, when taken together, will give some idea of the rate of action and swelling power of a pickle-liquor. The direct measurement of the swelling power, however, is best performed by means of the electro-metric method, and this is the most accurate for the purpose, measuring, as it does, the actual number present of free hydrogen-groups, to which the swelling property of the liquor is due.

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[27] Law of Mass—Action

The Chrome-Tanning Process

The function of the chrome-tanning process, like that of the vegetable, or any other form of tanning process, is that of converting the raw hide into leather; i. e., without altering the essential form and structure of the hide, of changing its easily decomposable substance to another of an imputrescible nature

The chemistry of chrome-tanning is linked with that of alum and iron-tanning, the three elements, namely, aluminium, chromium, and iron having similar properties, and being therefore placed into one chemical family. Essential differences, however, exist between the action upon hide of the three substances named; alum, for instance, remains combined with hide only so long as the leather is kept out of water; in other words, alum may be readily washed out of hide; iron-tannage is more stable than alum-tannage, yet not so permanent as chrome-tannage. Chrome-tannage, it may be safely assumed, is the most enduring of all forms of tannage hitherto discovered, including that of the older vegetable or bark processes.

The chemical compounds of chromium are numerous and varied in character. All chromium compounds are highly-colored; this fact giving rise to the name of the element from the Greek word "chroma," meaning color. Among the important salts of chromium are (1) the chromates—of the type of sodium chromate, Na_2CrO_4, which is yellow in color; (2) the dichromates—formed by treating chromates with acid—of which sodium dichromate, $Na_2Cr_2O_7$, is an example, and which are usually orange in color; and (3) the chromic compounds, e. g., chromic sulfate, $Cr_2(SO_4)_3$—formed by reducing (i. e., depriving of oxygen) the dichromates in the presence of acid—which are green or violet in color. Chrome-salts dissolved in water are, as a rule, acid in character. In the case of the dichromates this may be explained by the fact that the chromic-acid group (CrO_4) which is released in solution is a relatively much "stronger" substance than the accompanying basic-group, namely Na, which also is set free; in the case of the chromic-compounds, chromium (Cr) forms the base, while the acid is generally sulfuric, or hydrochloric; the acid groups (in this case SO_4 or Cl) which are here released in solution, being again in excess of the relatively "weaker" chrome-groups, cause the solution again to have acidic properties.

Relative to the tanning effect of chromium compounds, it is a well-known fact that only the chromic-salts possess the property of converting raw hide into leather; i. e., only when in its "reduced" state will chrome combine with hide in such a manner as to remain fixed and be resistant to the action of water.

Practical chrome-tanning is divided into two general processes, namely, the "two-bath" process, and the "one-bath" process. Either of these processes yields a leather readily distinguishable from that produced by the other; that produced by the "two-bath" process being soft and light-colored, that tanned by the "one-bath" process being firm and darker in color. The nature of "one-bath" tanning is, moreover, slow and progressive, while that of "two-bath" tanning is sudden and complex.

"Two-bath" tanning, as the name implies, is carried out in two liquors. The hides are first drummed in a solution of sodium dichromate and sulfuric acid until "struck through," i. e., until the dichromate-acid mixture has uniformly penetrated the goods. The action of the acid upon the dichromate is to form chromic acid (H_2CrO_4), in accordance with the following equation:

$$Na_2Cr_2O_7+H_2SO_4+H_2O=2H_2CrO_4+Na_2SO_4.$$

The chromed hides are now drummed in a second liquor containing sodium thiosulfate, or "hypo," ($Na_2S_2O_3$), and sulfuric acid, which serves to "reduce" the yellow chromic acid in the hide to green chromic sulfate, $Cr(OH)SO_4$, by which the hides are converted into leather. The action which takes place may be represented thus[28]:

$$2H_2CrO_4+3Na_2S_2O_3+2H_2SO_4$$
$$=2Cr(OH)SO_4+3Na_2SO_4+3H_2O+3S.$$

The free sulfur (S) that is liberated in the foregoing reaction—being the product of a side-reaction between the sulfuric acid and sodium thiosulfate (viz., $H_2SO_4+Na_2S_2O_3=S+SO_2+H_2O+Na_2SO_4$)—is deposited within the interior of the hide, and, acting as a lubricant, gives to the leather the soft feel, and also the light color characteristic of "two bath"-tanned leather. Certain precautions are necessary in the tanning of hides by the "two-bath" method. In the first place, chromic acid is a powerful oxidizing substance, having potential destructive tendencies in the presence of all organic matter, including hide-substance. The yellow chromed hides should not be exposed to light for any longer period than is necessary, for the destructive action of the chromic acid is said to commence in the presence of strong sunlight[29]. "Two-bath" tannage finds application in the production of inner-sole splits and linings, glove-leathers, etc.—in general, whenever a soft leather is required.

In the "one-bath" process of chrome-tanning, the chrome is not reduced within the hide, but is present in already-reduced form in the liquor in which the hide is tanned. A "one-bath" chrome-liquor is, therefore, green or violet in color. The principle of "one-bath" tanning depends upon the impregnation of the pickled hides by a solution of chromic sulfate (or, rarely, chromic chloride), which is acid at first, but later in the process is made "basic" (i. e., reduced in acidity) in order to "fix," or render insoluble, the chrome compound absorbed by the hides.

"One-bath" chrome-liquors are prepared, either (1) by dissolving in water some proprietary preparation in dry form of the type of "Tanolin," (the latter consisting of basic chromic sulfate in admixture with sodium sulfate and other substances), or (2) by "reducing" a dichromate-sulfuric-acid solution prepared in the tannery with

(a) sodium thiosulphate; or with
(b) sodium bisulfite ($NaHSO_3$); or with
(c) gaseous sulfur dioxide (SO_2); or with
(d) cane sugar, or glucose; or with
(e) glycerine; or with
(f) a mixture of two or more of the aforenamed substances.

When the reduction of the dichromate-acid solution is effected by means of the first substance, namely sodium thiosulfate, free sulfur is formed, and will remain suspended in the finished liquor; sodium bisulfite and gaseous sulfur dioxide, on the other hand, yield chrome-liquors that are free from sulfur, such liquors being used whenever an especially firm, and "tight" leather (e. g., "patent" leather) is desired. Cane sugar, glucose, and glycerin, being organic materials, behave in a different manner in contact with the chromic-acid mixture than do the inorganic materials referred to above (as a, b, and c): the chrome, it

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[28] According to Eitner

[29] There exists, however, no experimental evidence confirming this commonly accepted view.


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is true, becomes reduced as before, but much less heat is evolved in the reaction[30], while less than half the quantity of the sugar or glycerin employed is "used-up" (i. e., becomes oxidized) by the chromic acid, the finished chrome-liquor being usually violet in color. On account of the presence of the excess reducing agent and the aldehydic-oxidation-products formed by the action of the chromic-acid upon the sugar or glycerin, and also because the chrome in such a liquor is present in modified form, a sugar or glycerin chrome-liquor is "milder" (i. e., less astringent) in action (also less uniform in composition) than a "hypo" or bisulfite-reduced liquor, and is used principally in the production of the finer leathers, namely, calf and kip.

The color of the reduced chrome-liquor has been described as being either green or violet. Violet chrome-liquor, for instance, may be formed by dissolving any reduced chrome-salt (e. g., chromic sulfate) in **cold** water. Green chrome-liquor, on the other hand, may be made, either by dissolving the chrome-salt in **hot** water, or by heating to boiling the violet solution. Now, in chemical composition, both the green and violet chrome solutions are identical. The green chrome-liquor, however, is found to produce greater swelling of hide, and to tan more rapidly than the violet liquor. The explanation of this dissimilarity in action between the two chrome substances is found in the difference between the dissociation-coefficients of (i. e., in the number of chrome and acid-groups released in solution by) the two substances; thus, the dissociation-coefficient of the green solution has been found to be more than ten times that of the violet solution; i. e., more than ten times the number of chrome and acid-groups are released within the green chrome-liquor, than are split from the violet salt in solution. This, therefore, explains the greater activity or "astringency" of "hypo" or bisulfite chrome-liquors which, being formed at boiling temperature, are green in color, than that of sugar or glycerin liquors which having been produced at lower temperatures, are therefore, violet in color.

The tanning constituent of "one-bath" chrome-liquors, namely chromic sulfate, has been referred to as being present in the liquor in dissociated form; i. e., it exists in the form of its two separated chemical groups. The composition of these groups, however, is not constant for every kind of chrome-liquor, but varies with the "basicity"[31] of the liquor. Thus, if the "basicity," as determined by chemical analysis, reads, for instance, 0.63, the liquor contains pure chromic sulfate ($Cr_2(SO_4)3$) only; if the "basicity" is 0.95, the dissolved chrome compound has the composition $Cr_2(SO_4)_2(OH)_2$—known as the "first-basic-chromic-sulfate"—this being formed by the addition to the liquor of just the right amount of some alkaline substance (such as caustic soda), of which the effect is to replace one of the SO_4, or "acid"-groups in the chromic sulfate with two hydroxyl, or OH-groups derived from the alkali; finally, if the "basicity" of the chrome compound is found to be 1.89, its chemical formula would read $Cr_2(SO_4)(OH)_4$—this being known as the "second-basic-chromic-sulfate"—and in this it will be seen that two of the three SO_4-groups originally present have been replaced by four O.H groups from the alkali. Chrome-liquors having intermediate basicity-values consist of a mixture of two, or, possibly, of oven three of the compounds described. **Now, as the "basicity" of the chrome substance increases, its solubility in water diminishes;** i. e., the more OH or hydroxyl-groups there are added to the chromic sulfate, the less soluble does the latter become. On this extremely valuable property of the chromic compounds does the principle of "one-bath" tanning depend. The final chrome-product which would be obtained were all three of the SO_4-groups in chromic sulfate replaced by OH-groups—in other words, were the chromic sulfate completely "neutralized"—is chromic hydroxide, $Cr_2(OH)_6$—a quite insoluble substance, but one also devoid of tanning properties.

Whichever method of preparing a "one-bath" stock-liquor is employed, the tanning liquor made therefrom should contain an amount of chrome equivalent to approximately two per cent of chromic-oxide (Cr_2O_3), or four per cent of sodium bichromate on the drained weight of the pickled hides. Approximately one-third of this amount of chrome is dissolved in the liquor into which the hides are entered, the remaining two-thirds being added in two or four doses at intervals of every hour or half-hour. (All of the chrome is not added to the liquor at one time, for that would produce too rapid surface-tanning, and so hinder the penetration of the chrome into the interior of the hide.) The "acidity" of the tanning-liquor at the start should be so adjusted that the proportion of chromic-oxide to acid (Cr_2O_3 : SO_3) is approximately 1 : 1; in other words, the "basicity" should average 1.00. The concentration (i. e., the "strength") of the liquor, in terms of chromic-oxide, may vary,—in the case of paddle-tanning, from one-half to three-fourths per cent; in that of drum-tanning, from one to one and one-half per cent. In addition to the chrome, the tanning-liquor should contain about one-third pound of common salt, or Glauber's salt, or a mixture of both, to one gallon of the liquor. The specific gravity reading of chrome paddle-liquors may vary from 5° to 9° Baume.

From the foregoing it will be noted that the percentage of "neutral" salts (viz., common salt and Glauber's salt) dissolved in the tanning-liquor is only about one-half of that required by the pickle-liquor previously described. The immediate effect upon the pickled hides of this reduced salt-concentration of the chrome-liquor is to cause the hides to swell still further; thus, in practise, where the pickled hides have absorbed sixty-five per cent of pickle-liquor, they will absorb, in addition, during the tanning process ten or twelve per cent of the chrome-liquor. It is of no advantage to have more salt present in the chrome-liquor with the object of retarding this further swelling, for the effect of more salt would be to decrease the rate of tanning, after the manner about to be described. The presence of the chrome, moreover, will prevent too great swelling, for the hides receive a surface-tanning almost as soon as they are placed into the liquor.

During the first hour or two in which the hides are in contact with the chrome-liquor, a greater number of acid-groups are removed from solution than chrome-groups. The basicity-value of the liquor is thus caused to rise at first. After this, however, and during the remainder of the tanning period, the relative absorption of the acid and chrome groups becomes reversed, i. e., more chrome than acid-groups are taken out of the liquor, the excess acid-groups then causing the "basicity" of the liquor to fall in value. Now, inasmuch as the rate of tanning is greater the more "basic" the chrome liquor, and vice versa, the effect of the increased acidity of the liquor as the tanning proceeds is to slow up the tannage, and, finally, to stop it altogether. In order to allow tanning to proceed once more, then, the excess acid groups must be removed from solution by neutralizing them with alkali. In the first stage

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[30] The reaction, indeed, being often aided by the application of heat.

[31] The term "basicity" as herein used applies to the ratio of Cr_2O_3 : SO_3.

of tanning, i. e., until the hides are "struck through" by the chrome liquor, no alkali must be added to the liquor, else the insoluble chrome tanning compound thereby formed is deposited in the surface-layer of the hide, and this would prevent the entrance of the chrome-liquor into the interior of the hide. The addition of alkali to chrome tanning-liquors is, therefore, made about midway in the process, i. e., after the lapse of, say, the first twenty hours of paddle-tanning, or that of the first four hours of drum-tanning.

In practise, the amount of alkali (which may be in the form of caustic soda, sodium carbonate, or sodium bicarbonate,—preferably the latter) that is added to chrome tanning-liquors averages one per cent of the drained weight of the pickled goods. This quantity of alkali is dissolved in water, and one of four or six equal portions of the solution is added to the tanning-liquor (which must be kept agitated) at an interval of every two hours, or of every hour. For rendering chrome tanning-liquors "basic," the ideal quantity of alkali is one which, when dissolved in the chrome-liquor exactly neutralizes the excess acid-groups released in tanning, and then brings the liquor almost, but not quite, to the "precipitating-point," i. e., to the point at which the chromic sulfate in solution has combined with so many OH-groups as to have become nearly insoluble; **for, tanning will proceed at the greatest rate (i. e., the fixation of chrome will be a maximum) when the liquor is almost, but not quite at the "precipitating-point."**

Now, the "precipitating-point" of a chrome-liquor is quite independent of the basicity-value of the liquor; in fact, it bears but little relation to the "basicity" in the ordinary sense of this term. The "precipitating-point"—and, hence, the amount of alkali that must be used in order to approach this point—is controlled by at least five variables; these may be summed up as follows:

(1) The concentration of the tanning-liquor.
(2) The "basicity" of the liquor at the start of operations.
(3) The "basicity" of the liquor at the point the alkali is to be added.
(4) The percentage of dissolved "neutral" salts in the liquor.
(5) The temperature of the tanning-liquor.

The concentration of the chrome-liquor affects the "precipitating-point" by causing the chrome to precipitate out sooner the further the liquor is diluted. This is especially true of very "basic" liquors. The nature of this phenomenon is not perfectly understood, but may find explanation of a kind similar to that which accounts for the effect of "neutral" salts upon the action of chrome-liquors (see below). The difference between the initial and final basicity-values of the tanning-liquor—showing the extent to which the tannage has progressed—is a measure of the number of excess acid-groups released in solution; the greater this difference (i. e., the more excess acid-groups in solution), therefore, the more alkali will the liquor require. The presence of "neutral" salts in the chrome-liquor affects the "precipitating-point" in a very marked manner. Without increasing the total acidity—in other words, without lowering the measurable basicity-value of the liquor, yet in the presence of "neutral" salts, and in proportion thereto, more alkali will be required to bring the liquor to its "precipitating-point" than if no such salts were present. Wilson and Kern[8] account for the effect of dissolved "neutral" salts upon chrome tanning, by stating that such salts become "hydrated" in solution (i. e., the salts attach to themselves, or combine with, a certain amount of water); by thus lessening the volume of water in which the acid-groups are dissolved, the effect of the salts is to increase the acid-concentration of the solution; the effect of more acid, then, is to make the use of a greater quantity of alkali necessary. The different "neutral" salts are, however, not all "hydrated" to the same extent; sodium sulfate, for example, has been found to combine with nearly twice the quantity of water that unites itself to sodium chloride, or common salt. To sum up, then, the effect of dissolved salts is to retard the tanning action of the chrome-liquors, and to make the use of comparatively "basic" chrome-liquors possible. Lastly, the influence of temperature upon the alkali-requirement of a chrome-liquor is simply a sequel to the "neutral"-salts-effect; i. e., the higher the temperature of the tanning-liquor, the less the "hydration" of the salts, and the lower, therefore, the concentration of the acid-groups in the liquor. A warm chrome-liquor, being, in effect, more "basic" than a cold liquor, will, therefore, require less alkali to bring it to the "precipitating-point" than would the cold liquor.

To the five variables referred to, another should be added, namely, that of the weight of the pickled goods entering the tanning-liquor. According to the weight of the pack, a greater or less amount of alkali will be required by the chrome-liquor, as more or less acid is introduced by the pickled hides.

From what has been written, the fact will be apparent that chrome-tanning liquors can be completely exhausted, or deprived of their chrome-content,—in other words, all the dissolved chrome can be deposited in the hides,—if a sufficient quantity of alkali, added in small doses, and at the proper intervals during tanning be employed. Leather produced in this manner will, however, be of a soft and flexible (i. e., "stretchy") nature, resembling "two-bath"-tanned leather. Such a leather is not well-adapted for use in making shoe-uppers, for which a firm and "tight" leather is more to be preferred. Very "basic" liquors are also known to tan irregularly. Moreover, inasmuch as the swelling of hide, which—other things being equal—is known to take place, not only through the transverse dimensions, but also throughout the length and breadth of the hide, the more "basic" the chrome-liquor is kept during tanning, the lower will be the yield of leather as measured by the surface area obtained. The foregoing considerations must, hence, be allowed to govern the amount of alkali that is to be used in tanning, and this, in practise, is kept very carefully regulated.

Analytical Control. The procedure to be followed in the analytical control of the chrome-tanning process will depend on whether the "two-bath" process, or the "one-bath" process is being used.

In "two-bath" tanning, an important requirement is the complete reduction of the chromic-acid absorbed by the goods from the first liquor. To test whether or not the chrome has been completely reduced, the spent liquor, or washings from the wet leather may be treated with dilute acid, potassium iodide, and starch, when a blue color will develop in the presence of unreduced chrome. The quantities of chrome absorbed by the goods, or conversely, those remaining in the spent-liquor, may also be determined by any of the well-known methods.

In "one-bath" tanning, each batch of stock chrome-liquor is, first of all, tested for

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[8] "The Action of Neutral Salts Upon Chrome Liquors."—Jour. A. L. C. A. 12, 445 (1917)

(1) The percentage of chrome, as Cr_2O_3;

(2) The percentage of acid, as SO_3;

(3) The basicity-value (found by dividing the percentage of Cr_2O_3 by that of the SO_3);

(4) Unreduced chrome (if the liquor was prepared in the tannery by the reduction of a dichromate-acid solution);

(5) The percentage of "free" sulfur (if the liquor was reduced with sodium thiosulfate, or "hypo.")

From the percentage of chrome found by analysis may be calculated the number of pounds of chromic-oxide, or of sodium dichromate, present in every gallon of the liquor; on the basis of this value, then, the number of gallons of the liquor required in the tanning of a given weight of the pickled goods is measured out. Chrome stock-liquors containing unreduced chrome should not be used until such liquors have been treated with a further quantity of reducing-agent.

The routine control of a "one-bath" chrome tanning-liquor in process should include the following determinations: viz.,

(1) That of the quantity of alkali required near the end of the tanning period to bring the liquor to its "precipitating-point";

(2) That of the basicity-value of the spent-liquor, and of the percentages of chrome and acid remaining in the liquor at the end of the tanning period.

The quantity of alkali that must be added to the liquor to bring the latter to its "precipitating-point" is most readily determined by titrating a measured volume of the filtered liquor with an alkali-solution, until the "precipitating-point" is caused to appear[33]. A sample of the liquor is withdrawn from the paddle-vat or drum, treated with kaolin, and filtered through paper until perfectly clear; of the filtered liquor, an aliquot is measured out into a flat-bottomed glass dish, the latter placed upon a water-bath and heated until the liquor is of the same temperature as that of the liquor in the paddle-vat or drum; the dish is now supported upon a ring-stand placed over a white surface in such a position as to allow the entrance of light from a window through the sides and bottom of the dish; the standard alkali-solution, contained in a burette, is now slowly run into the liquor— which must be kept stirred —until the first appearance of a turbidity that remains permanent is noted. The number of cubic centimeters of alkali-solution used is read off, and the number of pounds of alkali required by the liquor-contents of the paddle-vat or drum is then calculated on the basis of the known strength of the standard solution, and upon that of the gross volume of the tanning-liquor. The titration of the liquor should preferably be carried out with a pure caustic-soda or borax-solution, and not with a sodium-carbonate or bicarbonate-solution, even where the carbonate or bicarbonate will be subsequently used for rendering the tanning-liquor "basic"; the reason caustic-soda or borax should be used for this purpose is that neither of these substances liberates carbon dioxide (CO_2) during the titration, the effect of carbon dioxide—acting in solution as an acid—being to delay the "precipitating-point" of the chrome-liquor beyond the point at which it should occur. The use of sodium carbonate, or bicarbonate, in the tanning-liquor, on the other hand, is to be preferred to that of caustic soda, for in this case, the presence of the carbon dioxide will act as a factor of safety in preventing the possible precipitation of a portion of the chrome in the vat-liquor to which the alkali is being added.

The determination of the basicity-value of the spent chrome-liquor, and that of the percentages of chrome and acid remaining in the liquor at the end of the tanning period, are made to show the extent to which the tannage has progressed, as well as to furnish an indication of the quantity of chrome that is run to waste as each paddle-vat or drum is drained of its liquor.

In addition to the foregoing determination, the measurement of the swelling power of a chrome-liquor may be made—as in the case of pickle-liquors—by means of the electro-metric method, and this will also show the rate of tanning of which the liquor is capable.

The percentage of chrome absorbed and fixed by the hides during the usual process of "one-bath" paddle—or drum-tanning is about two-thirds of that initially present in the tanning-liquor. The remaining one-third is, more often than not, run to waste in the "spent" liquor, and as chrome is not an inexpensive substance, the money-loss resulting from this practice will amount to a considerable figure in the course of, say a year's operation. As in the case of a pickle-liquor, however, it is quite practicable to restore a used chrome tanning-liquor to its original strength—merely by the addition of more stock-liquor,—and to use the same liquor repeatedly for, perhaps, ten or more packs of goods. Practical experiments in chrome paddle-tanning[34] conducted some time ago by the author of this paper have shown that the only variable difficult of control in the replenishment of chrome liquors is the "neutral" salts-content of the liquors. Thus, during tanning, the percentage of common salt, and of Glauber's Salt in the liquor gradually rises, a greater quantity of these salts being always found in the spent-liquor than had been initially used in preparing the fresh liquor. Of course, on entering the pack of pickled goods into the chrome-liquor, the original salt-content of the latter becomes at once increased by several hundred pounds; inasmuch, however, as the hides undergo further swelling during tanning, in other words, since the amount of liquor absorbed by the goods is greater after tanning than it was before, it actually happens that a portion of the salts used in preparing the tanning-liquor is removed therefrom by the pack of goods. The increase in the salt-content of the liquor after tanning is, therefore, not due to the salts transferred to it by the hides from the pickle-liquor, but is produced, in fact, (1) by the Glauber's Salt present in the stock chrome-liquor from which the tanning-liquor was made, and (2) by the alkali that is subsequently added for the purpose of rendering the liquor "basic"; in the latter case, the action of the acid in the tanning-liquor is to neutralize the alkali added thereto, and so produce a further quantity of Glauber's Salt. The Glauber's Salt thus added to a paddle-vat liquor during tanning will amount to, in practise, 75 or 100 pounds. By means of the above-described alkali-titration, however, it is possible, to a great extent, to counteract the effect of the increased salt-concentration of the replenished chrome-liquor, and merely by employing the amount of alkali indicated in the titration, to cause the replenished liquor to tan just as rapidly, and quite as uniformly, as a freshly-prepared chrome-liquor.

The replenishment of a "one-bath" chrome tanning-liquor may be practised with entire success if the following means of control are adopted as a routine measure; viz.,

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[33] "The Analysis of One-Bath Chrome Liquors."—Douglas McCandlish—Jour. A. L. C. A., 12. 140 (1917)

[34] Unpublished work

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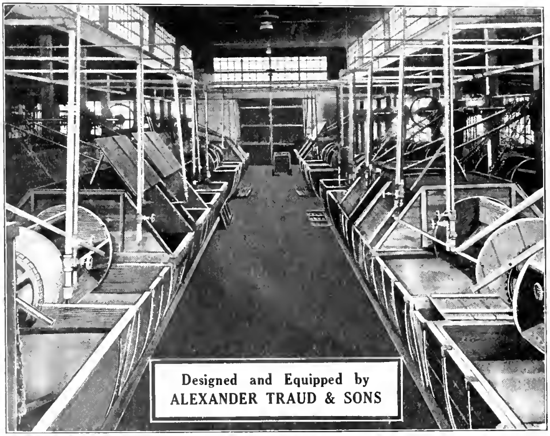

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(1) Before replenishing the spent-liquor, determine, by analysis, its chrome-content and basicity-value.

(2) On the basis of the chrome-content, add enough stock-liquor to restore the strength of the tanning-liquor to its original value; then, to the resulting liquor, add enough alkali to bring the basicity-value of the liquor up to its former point also.

(3) Perform the alkali-titration of the tanning-liquor in the usual manner, and at the proper time, and add to the liquor the amount of alkali indicated in the titration.

(4) After the passage of three or four packs of goods through the liquor, determine the specific gravity of the latter by means of an hydrometer. If the specific gravity is found to exceed 9° Baume, add enough water to the spent-liquor to reduce the reading to below 9°, determine the chrome-content and basicity-value of the diluted liquor, and proceed as in (2).

Method for Finding the Capacity of Tannery Paddle-Vats Tanks and Pits without Resorting to Measurements

In routine control-work involving the analysis of tannery-liquors, results are usually expressed in percentage by volume (e. g., in grams per one-hundred cubic centimeters), or, less frequently, in percentage by weight (e. g., in grams per one-hundred grams, or pounds per one-hundred pounds). When the object is to compare the one liquor with another, this manner of expressing analytical results is the only one that allows of comparisons to be made. When, however, it is desired to replenish a given liquor in order that it may be used over again, or where the inventory-value of such a liquor is to be determined, it then becomes necessary to calculate from the analysis the total number of pounds that the liquor contains of lime, or salt, or acid, or chrome,—as the case may be. In order to arrive at these values, then, the gross volume of liquor that is being dealt with must be known,—in other words, the capacity in gallons or in pounds of the vat or drum holding the liquor must first be determined. In the case of square pits, or cylindrical drums or tanks having plane ends, it is, of course, a simple matter to find the volume or capacity of these, merely by obtaining certain dimensions of the vessel, and then multiplying these together. On account of the irregular shape of paddle-vats, however, the finding of their capacity by geometric means is a complex problem, involving the use of calculus.

The following simple method has been devised by the author, and used by him with considerable success for the calibration—by analytical means, instead of by measurement—the liquor-contents of tannery paddle-vats. The first requirement is that the position of the water-line within the vat that is to be calibrated be fixed with respect to the height at which the vat, when placed into use, will be filled with liquor. Wooden strips marking the water-line are therefore nailed around the inside walls of the vat, and in all subsequent operations the volume of the liquor is kept constant by always bringing the latter to a level with the upper end of the wooden marking-strips referred to. The calibration of the vat is then performed in the following manner: The vat is filled with water to the level of the water-line, and a quantity (in the proportion of approximately ten pounds to 2,000 gallons) of sulfuric acid (or any soluble acid, salt, or alkali, of known percentage purity, and whose recovery from solution may be quantitatively effected) is added, allowed to dissolve, and the solution thoroughly mixed by plunging it (say, for five minutes, by hand), or by other effective means. A sample (1) of the acid-liquor thus prepared is withdrawn and set aside. To the contents of the vat is now added a second portion of two or three times the quantity of acid originally given, **this portion being, however, accurately weighed to within two per cent,** the acid allowed to dissolve, and the liquor again thoroughly mixed; of the acid-solution in the vat, a second sample (2) is withdrawn and set aside. The second addition of acid is followed by a third of the same, or a larger quantity, the same degree of accuracy being observed in weighing, and a third sample (3) is taken of the acid-liquor in the vat. Fifty-cubic-centimeter aliquots of the different samples are now titrated with a tenth-normal alkali-solution, and the acid values thus found are expressed in grams—100 cubic-centimeters of sulfuric acid (H_2SO_4) present in each sample. The volume of the liquor in the vat is calculated in the following manner:

Letting A, B and C equal the g/100cc of H_2SO_4 found in samples (1), (2) and (3), respectively;

and L′, and L″ the weight in pounds of sulfuric acid added to the liquor the **second** and **third times,** respectively;

and P the percentage strength (correct to the first decimal) of the acid used;

and G the volume in U. S., gallons of liquor in the vat;

then, inasmuch as 11.983 g/100cc are equivalent to one-pound/gallon,

$$G \text{ will equal } \frac{L' \times P \times 11.983}{B - A} \quad \text{I:}$$

or (check),

$$G \text{ will equal } \frac{L'' \times P \times 11.983}{C - B} \quad \text{II.}$$

If the capacity of the vat thus obtained is found to be in the vicinity of 2,000 gallons, the results of equations I and II should check to within fifteen gallons, the accuracy of the foregoing method having been found to be 99.2 per cent.

Retanning of Chrome Leather

The object of retanning chrome-leather is to complete the tanning of the goods. In the production of combination-tanned leather (i. e., of leather tanned with both chrome and vegetable materials), the purpose of retanning is two-fold; viz.,

(1) To complete the tannage, and
(2) To impart to the resulting leather the appearance and character of vegetable-tanned leather.

By reason of the peculiar nature of "one-bath" chrome-tannage, it is practically impossible to produce fully-tanned leather by this process without leaving the goods in contact with the liquor for an excessive length of time, or without the use of an excessive amount of alkali, the effect of which is to render the leather soft. Because of this tendency of a "one-bath" chrome-liquor to produce soft leather when caused to yield all of its chrome to the hide, such a liquor is never allowed to become completely exhausted during tanning. Instead, at the conclusion of the allotted period in which the goods are in contact with the liquor, the goods are moved into a fresh chrome-liquor, and allowed to absorb a further amount of chrome, the latter being subsequently "fixed" by the use of alkali in the manner already described under "The Chrome Tanning Process."

Chrome-retanning is unusually carried out in a drum by the use of a "one-bath" liquor, of which the percentage-strength is about one-half of that employed for the initial tanning-liquor. The quantity of alkali used is proportionately less, and the period of retanning is usually about one hour.

After retanning, the wet leather is piled for a period of several days on the floor, the piles being covered with burlap for the purpose of preventing the goods from becoming dry. During the time in which the leather is left thus, the greater portion of the dissolved chrome in the liquor held by the goods will unite with the leather (i.e., the chrome will become "fixed"), the additional tannage thus produced (amounting, in practise, to about 70 per cent of the available chrome present) causing the absorbed liquor to become quite acid in reaction.

"Neutralizing" of Chrome Tanned Leather

The final step of the "one-bath" chrome-tanning process consists in neutralising the excess acid released in tanning. The object of "neutralising" chrome-tanned leather, then, is

(1) To render the chrome-substance deposited in the hide still more "basic", thus making the tannage quite stable and permanent; and
(2) To prepare the leather for the subsequent fat-liquoring process by removing the excess acid referred to, together with the soluble chrome-salts remaining in the leather.

The name "neutralisation," as applied to this final step of chrome-tanning, is a misnomer. The object in treating the chromed hides with alkaline solutions is not to neutralise the leather itself, but merely to reduce the "acidity" of the leather. "Neutralisation" is, therefore, a somewhat delicate operation; if carried too far, it would result in a portion of the chrome-substance in the hide being converted into chromic hydroxide,—a substance known to possess no tanning power. The foregoing circumstance obviously excludes the use of any of the "stronger" alkalies, such as caustic soda, or even soda ash, in the neutralisation-treatment, for, even in very dilute solution, any strong alkali would carry the neutralisation of the surface of the leather too far before the interior was thoroughly penetrated.

In practise, "neutralisation" of chrome-leather is effected by the use of borax, or some equally mild alkali. The chromed hides are first washed in a drum with water, which serves to remove the greater portion of the acid and uncombined chrome-salts. The leather is then drummed in a one-half percent solution of the alkali (of which, in the case of borax, up to three per cent on the weight of the chromed stock may be given) until the desired degree of "neutralisation" is obtained.

Probably the safest method of "neutralising" chrome-leather is that of Stiasny, of which method brief mention may here be made. In the method of Stiasny, the leather is paddled or drummed in a solution of ammonium sulfate ($(NH_4)_2SO_4$) and soda crystals ($NaOH+Na_2CO_3$). This is equivalent to, but cheaper than using a mixture of ammonium sulfate and ammonia, the soda in the former case reacting immediately with the ammonium salt and liberating ammonia in accordance with the following equation:

$$(NH_4)_2SO_4 + 2NaOH = 2NH_3 + Na_2SO_4 + 2H_2O.$$

The ammonia thus set free combines with the excess acid in the leather, while the presence of the "neutral" salt Na_2SO_4, simultaneously formed, so reduces the already feeble dissociation of the ammonia, that by varying the concentration and proportion of these materials, the "neutralisation" may be exactly regulated to the required extent[5].

Analytical Control. The percentage of "free" acid remaining in the leather after "neutralising" may be determined by digesting in water a weighed portion of the finely-divided leather, and titrating the resulting extract with a standard alkali-solution. Absolute results cannot, however, be obtained by any such method, for it must be remembered that the chrome-substance in the hide will continue to yield a portion of its combined acid so long as the leather is in contact with water. For control purposes, however, the results will be relative if the proportion of leather to water, the temperature of the latter, and the time of digestion be kept constant.

A more accurate idea of the extent of the neutralisation is obtained from the "basicity" of the chrome-substance in the leather, found by determining the percentages of both chrome (as Cr_2O_3) and total acid (as SO_3) by the fusion method, and then dividing the one result by the other.

In most cases it will be found sufficient to test for the

[5] H. R. Procter. Loc. Cit.

"degree" of acidity in the "neutralised" leather by determining the reaction of the wash-liquor in which the "neutralisation" was effected. The spent liquor should in all cases show a neutral, or an acid reaction to methyl-orange indicator, showing that the neutralisation-treatment has not been carried too far.

After the leather has been "neutralised," cuttings from the neck and butt portions are immersed in boiling water for a period of five minutes. If fully tanned, the leather will show no loss of pliability at the conclusion of the boiling period; if, on the other hand, the leather has been insufficiently tanned, the action of the boiling water will cause the cuttings to shrink and curl up, and to become "horny" when dry.

Chrome-leather should not be undertanned. The best chrome leathers contain from four to five per cent of chromic-oxide (Cr_2O_3). Well-filled leather is obtained by keeping the chrome tanning-liquor as nearly neutral (i. e., as "basic") as possible. The more a leather is tanned, the more fat-liquor will it require, and the better will be the penetration. The heavier the leather is tanned, the less "stretch" will it give, and the more resistant to friction will it be [46].

[46] "Chrome Leather Defects" A Seymour Jones Leather Trades Review, April 28, 1915.

The Fat Liquoring Process

The purpose of fat-liquoring chrome-tanned leather is three-fold; namely,

(1) To restore to the leather the oils or fats removed from the hide in the beamhouse processes, and thus to prevent the leather from becoming hard and "cracky" when dry;
(2) To increase the tensile strength of the leather;
(3) To render the leather wholly, or partially water-resistant.

In the case of chrome-leather, the fact is well-known that before it has received a small quantity of oil, chrome-leather cannot be "wetted-back" again (i. e., the leather becomes water repellent) once it has been allowed to dry out.

Fat-liquoring is merely a special form of applying oil to leather, the oil being given in the form of a water-emulsion to the wet leather. The advantage of employing a water-emulsion of the oil, instead of applying the oil in its natural form to the dry leather, is that, in the former case, a small quantity of oil suffices to render the leather soft and flexible, while to produce the same effect with dry leather, a much greater quantity of oil would have to be applied. The reason that this is the case will be stated below.

Fat-liquoring renders leather soft, and increases its tensile strength by lubricating and separating the fibres of the leather. The principal effect of the oil is, in fact, the separation of the fibres composing the leather, for it has been shown that the tensile strength of degreased leather, —while less than that of the leather with its fat-liquor left in,—is always greater than that of the leather before it has received any fat-liquor [47]. Fat-liquoring, therefore, alters the fibrous structure of leather. The more oil in the form of fat-liquor that is incorporated with the leather, the more water-resistant, and the greater will be the tensile strength of the leather.

All natural oils may be caused to emulsify (i. e., may be caused to mix with water) by several means. The first requirement is that the oil be broken up into small particles (or, globules), which, in practise, is effected mechanically by vigorous shaking or agitating. The "breakingup" of the oil must be effected in the presence of an "emulsifying-agent," which may consist of any water-soluble colloid, such as

(1) Gum acacia, gum tragacanth, "Tragasol," "Irish Moss," etc.;
(2) Albumin, casein, or gelatin;
(3) Sulfonated oil;
(4) Soft, or hard soap;
(5) Wool fat, or degras,

of which the effect is to form a film around the oil-globules, and so prevent these from "running together" (or, coalescing). Milk may be cited as a typical emulsion. In milk, butter-fat is held in water-suspension by the action of the dissolved casein, the casein preventing the fat-globules from rising to the surface.

The readiness with which an oil may be "broken-up," or emulsified, depends principally upon its surface tension (i.e., upon the natural force which keeps the molecules composing liquids from repelling each other); the lower the surface tension of the oil, the more readily is it emulsified, and the more permanent is the emulsion. Neatsfoot, linseed and olive oils are more easily emulsified, and form more stable emulsions than either castor oil or mineral oil, because, of the oils in the first-named group, the surface tension is only about one-half of that of castor oil or mineral oil. True emulsions are characterised as being more viscous (i. e., less "fluid") than the oils from which they are made. Emulsified oils penetrate wet leather more uniformly, and are absorbed more rapidly than natural oils are absorbed by dry leather, because the surface tension between oil and water is less than that between oil and air. Just as the oil having the lower surface tension emulsifies the more readily (i. e., produces the finer particles), so will such an oil penetrate wet leather most rapidly. The effect of increased temperature is that of lowering the surface tension of oils; hence, the higher the temperature employed in the fat-liquoring process, the more uniform and rapid will be the absorption of the oil by the leather.

In general, the oils most suitable for treating leather are those of the "semi-drying," or "non-drying" variety (i. e., oils which do not tend to harden or solidify on exposure to air). Oils of the "semi-drying" variety are castor, neatsfoot, and olive; of the "non-drying" oils, ordinary mineral, or paraffin oil is an example. Fish (e. g., cod or menhaden) oils belong to the class of "drying" oils; the latter,—being subject to atmospheric oxidation and hardening,—are, for this reason, not so well adapted as the oils in the first-named groups for the purpose of softening and nourishing leather. The disadvantage of neatsfoot oil is that—

[47] Thus, in the production of "patent" leather, the common practise is to degrease the leather after fat liquoring, and before applying the varnish.

unless very carefully "cold-pressed"—it tends to form "spue" on the surface of the finished leather with which it is incorporated. Mineral, or paraffin oils are quite inert substances; while lacking the nourishing and filling properties of castor, neatsfoot, and olive oils, mineral oils may, however, be freely and safely employed in the fat-liquoring of leather, **provided, always, they can first be brought into the form of a stable emulsion.** For use in fat-liquor, preference should be given to the heavier grades of mineral oil (e. g., those having specific gravities at 60° Fahrenheit of .88 to .92); on account of the fact that the lighter mineral oils are more or less volatile (i. e., tending to evaporate) at ordinary temperatures, the use of these is best confined to the "oiling-off" of the grain-surface preparatory to the glazing of the finished leather.

Degras is the oxidation-product of cod-liver oil, formed in the "chamoising" of sheep-skins, while wool-fat, or crude lanolin, is a natural wax extracted from raw wool. From crude wool-fat is obtained, by distillation, a liquid wax known as "oleine." The emulsifying property of these substances is shown by their capacity to mix with large volumes of water. In addition, however, to being excellent oil-emulsifiers, degras, wool-fat, and oleine possess in themselves filling and nourishing qualities in a high degree when used upon leather in the form of fat-liquor, either alone, or in combination with one or more of the natural oils.

Within very narrow limits only does the color of the oil, or oils used in the fat-liquoring process determine the color of the leather. The color which the fat-liquored leather will assume depends on the amount of oil that is left in the surface-layer of the leather; in other words, the better the penetration of the fat-liquor into the interior, the lighter will be the color of the leather, and vice versa.

Of the different emulsifying-agents cited above, the effect of water-soluble gums and protein-substances (see 1, and 2 in the list) is not only to form a protective coating around the oil-globules, but also to counteract the upward movement of the oil-globules due to the force of gravity. Gums and proteins, however, have the disadvantage of decomposing in solution rather easily, and for this reason, are seldom employed as oil-emulsifiers. Modern fat-liquors, on the other hand, are of two kinds: namely, "acid fat-liquors," and "alkaline fat-liquors." "Acid" fat-liquors are those prepared with sulfonated oils, while "alkaline" fat-liquors are made from soap, wool-fat, or degras. The emulsifient used in preparing "acid" fat-liquors, namely, sulfonated oil, is made by treating any fatty oil, such as castor, corn, neatsfoot, or fish oil, with concentrated sulfuric acid, the effect of the acid being to convert a portion of the oil into its sulfo-fatty acid; the sulfo-fatty acid thus produced forms the emulsifying principle of the sulfonated oil, enabling the latter to mix with water, and to carry along with it into solution other natural oils with which it may be incorporated. Properly-made "acid" fat-liquors are seldom, if ever, more than faintly acid in reaction; more often than not they are quite "neutral," and may even show an alkaline reaction. On account of the fact, however, that by nature they are inclined to be "acid", sulfonated oils are particularly well-adapted to the fat-liquoring of chrome-leather, which, when wet, is always slightly "acid" by nature. On the other hand, the nearer the reaction of the "acid" fat-liquor approaches neutrality, the lower will be the surface tension of the oil, and the better, therefore, will the fat-liquor be enabled to penetrate the leather with which it is in contact. "Alkaline" fat-liquors, having soft or hard soap as their base, and often containing wool-fat, degras, or moellon, are, as a rule, much heavier (i. e., more viscous) in body than "acid" fat-liquors. The simplest way to make an "alkaline" fat-liquor is to heat any fatty oil, and then to stir into it a very small quantity of caustic potash (sufficient to saponify only a small portion of the oil) dissolved in water, and after this to add warm water until the emulsion is of the desired consistency. This method of preparing an "alkaline" fat-liquor is, of course, equivalent to that in which the oil is added in a fine stream to a hot soap solution, the product obtained in either case being quite the same. The quantity of soap used in making "alkaline" fat-liquors should be just sufficient to produce a stable emulsion with the oil. A correct proportion of soap will impart to the leather a feeling of "fulness" not obtained without the use of soap, while an excess of soap will produce a leather that is difficult to finish. In the preparation of "alkaline" fat-liquors, potash, or soft soap, finds preference over soda, or hard soap, for two reasons: viz., first, potash soap is a more powerful oil-emulsifient than soda soap; secondly, the use of potash soap permits the leather to be afterwards glazed, while hard soap—on account of its action in cementing together the fibres of the leather—renders glazing difficult, and is quite apt to produce "flat" and dull-appearing leather. By reason of the fact that "alkaline" fat-liquors produce a greater degree of "fulness" than "acid" fat-liquors, the former are extensively used in the fat-liquoring of chrome and combination-tanned split leathers, while "acid" fat-liquors find their principal application in the production of the more closely-grained shoe-upper leathers.

Inasmuch as salts, in general, interfere with the fat-liquoring treatment (causing the oil-emulsion to break up), chrome leather should invariably be washed after being "neutralised," and immediately before it is fat-liquored. The washing of the leather is carried out in a drum with warm water (at 120° to 140° Fahrenheit), and lasts for a period of fifteen to thirty minutes, or until the goods are free from salts. After the washing of the goods the wash-water is run off, sufficient fresh water at 130° Fahrenheit to submerge the leather is run into the drum, the latter set into motion, and the warm fat-liquor then fed through the hollow axle to the contents of the drum. By thus conducting the washing and the fat-liquoring in a single drum, the goods will be of the proper temperature to receive the fat-liquor when this is added, and the necessity of heating the drum prior to fat-liquoring is hence avoided.

In order to insure success, the following points must be observed in the "acid"-fat-liquoring of chrome-tanned leather: viz.,

(1) that neither the wet leather nor the fat liquor is more than **faintly acid** in reaction;

(2) that the temperature during the fat-liquoring treatment is 130° Fahrenheit or higher;

(3) that a sufficient quantity of water be used to allow a portion of it to remain in the drum at the conclusion of the treatment.

When insufficiently neutralised, chrome leather is fat-liquored, the oil-emulsion will not penetrate, but, instead, the excess acid in the leather will cause a "splitting-up" of (i. e., liberation of the fatty acids in) the oil; thus, in place of the oil being deposited within the interior, the

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fatty acids will remain on the surface of the leather in the form of "spue." In order to counteract the acid-reaction of a sulfonated-oil fat-liquor, a small quantity of aqua ammonia is commonly added to the liquor before it is fed to the drum. The effect of temperature upon oil-emulsions has already been described; the fact may be stated here that a large percentage of failures are due to the use of too low temperatures in the fat-liquoring treatment. With chrome leather, temperatures up to 160° Fahrenheit may safely be employed. The volume of fat-liquor in contact with the leather must be large enough to enable the fat-liquor to reach all parts of the leather, and to allow the oil-emulsion to penetrate completely. Dark spots appearing in the finished goods are due to excess oil on the surface, the fat-liquor not having been absorbed by reason of employing an insufficient volume of water, or because the temperature during the fat-liquoring process was kept at too low a point.

On account of the difficulty in obtaining even coloring of fat-liquored leather, leather which is to be finished without the use of pigments is usually dyed before it is fat-liquored. When dyed leather is to be fat-liquored, the volume of the liquor is kept as small as possible in order to prevent excessive "bleeding," or stripping of the color from the goods. "Bleeding" of the color may, however, be checked by the addition to the fat-liquor of a suitable quantity of dye[38]. When employed upon dyed leather, the fat-liquor should be made as nearly neutral in reaction as possible.

The proper quantity of oil for use upon chrome leather depends on the purpose to which the leather will be put in service, and, in practise, will vary between rather wide limits. Shoe-upper leather, for instance, may contain anywhere from three to 15 per cent of oil, the lower limit being for leathers that are to receive a high polish, such as kip and side, the higher values for the softer kid, and so-called "elk" leathers. In all cases where the leather is to be glazed or polished, an excessive amount of oil is to be avoided. Where it happens that—due to too much oil in the surface-layer—the leather will not glaze, the leather may first be brushed over with a dilute solution of formic, acetic, or lactic acid, after which the goods will usually be found to glaze quite readily. Lack of enough oil in the finished leather is not always responsible for the "cracking" of the grain so often observed in the case of shoe-leathers that have been in warehouse storage for a period of some months. "Cracking" of the grain is quite frequently the result of loss of moisture which leather stored in a dry or heated atmosphere suffers; in order, therefore, to prevent the grain thereon from cracking, leather must be preserved in a cool place where the atmosphere is not too dry.

Analytical Control. Inasmuch as, in the fat-liquoring process, practically the entire quantity of oil fed to the leather becomes absorbed by it, the process itself will require but little control of an analytical nature. The analytical work in connection with fat-liquoring is, therefore, confined to the testing of the raw materials (viz., the natural oils employed, sulfonated oil, degras, sod-oil, wool-fat, soap, etc.) which enter into the preparation of the fat-liquors, and to that of the condition of the leather that is to be fat-liquored.

The examination of the natural oils should include such determinations as specific gravity, degree of cold-test, acid-nnmber, iodine-number, and quantity of unsaponifiable oil present. The specific gravity and iodine-number usually serve to identify the oil under examination, while the presence of over five per cent of unsaponifiable oil will indicate admixture with mineral oil, wool-oil, or sperm-oil. The iodine-number (i. e., the percentage of iodine that the oil is capable of absorbing), moreover, measures the "drying-power" of the oil; thus, the iodine-number of "non-drying" oils will range from zero to 65; that of "semi-drying" oils, from 65 to 120; while the iodine-number of "drying" oils will vary from 120 or 130, in the case of the fish oils, to 180, which is that of linseed oil. The degree of cold-test (i. e., the temperature at which the oil becomes solid) is indicative of the solid fatty-acid (e. g., stearin) content of the oil; thus, for example, the more stearin an oil contains, the higher will be the temperature at which the oil will freeze or become solid, and the more apt such an oil would be to form "spue" upon leather. The acid-number of natural oils is equivalent to the percentage of "free" fatty-acids present. A freshly-expressed oil will show a very low acid-number (e. g., not over 5), but as the oil is exposed to the action of moisture, air, and light, the acid-number will increase, and may reach the figure 50 in the case of such products as degras and moellon. A high acid-number does not necessarily indicate "rancidity" of the oil; since "rancidity" is produced, however, by atmospheric oxidation, any increase in the acid-number of the oil usually means a corresponding increase in the "rancidity." In the fat-liquoring of leather, "free" fatty acids must be considered an advantage, insofar as they help to emulsify the oil; the excellent emulsifient properties of degras and moellon, for example, are in part thus due to the high content of free fatty-acids possessed by these materials. Finally, it should be explained that a high percentage of unsaponifiable oil occurring in the oil under examination may not always represent so much mineral oil; thus, unsaponifiable oil may consist of liquid waxes (of the type of wool-oil, or "oleine") which, in combination with sulfonated oil, as a rule, yield fat-liquors of a very high grade.

The analysis of sulfonated oils is made to determine the percentages present of water, ash, admixed unsaponifiable oil, if any, and combined sulfuric acid as (SO_3). Sulfonated oils, as a rule, contain from 20 to 25 per cent of water. The percentage of ash will vary from 1.5 or less in the case of sulfonated oils neutralized with ammonia, to 5 or 6 in the case of oils finished with soda. The percentage of combined SO_3—found by determining the percentage of total SO_3, and subtracting from this that of the SO_3 present as Glauber's Salt—will indicate the degree of sulfonation to which the oil was subjected in the process of its manufacture; it varies from one per cent in the case of lightly-sulfonated oils, to five per cent in that of the highly sulfonated oils. In order to compare the sulfonation-values of two sulfonated oils, it will be necessary to first calculate their percentages of combined SO_3 on the basis of the quantity of total fatty oil present in either oil.

The degras, or moellon, that is to be used upon leather is first tested for melting-point, and for the percentages present of water, ash, unsaponifiable oil, "free" fatty-acids (i. e., acid-number), and oxidized fatty-acids. Degras will contain up to 15 per cent of oxidized fatty-acids; the latter substances possess a great affinity for leather, combining with it to produce a sort of additional tannage, and are hence considered a very valuable adjunct to the fat-liquoring treatment. Sod-oil is an inferior grade of degras, showing, as a rule, free mineral acid, and a high percentage of ash; these arise from the sulfuric-acid and lye-treat

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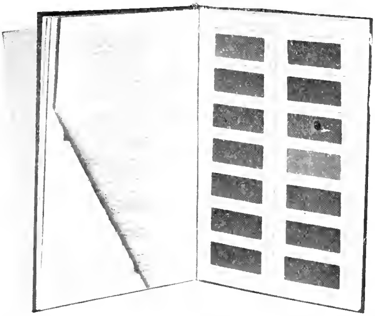
[38] According to the suggestion of M. C. Lamb.

ments which sod-oils receive in the course of their manufacture. Commercial degras and sod-oils are usually admixed with natural oils and tallow, which must hardly be regarded as adulterants. Degras and sod-oil, however, often contain mineral oil and wool-grease, which, if present, will be found in the unsaponifiable portion extracted from the former substances.

Soaps used in the preparation of "alkaline" fat-liquors should contain no "neutral" salts, inasmuch as the latter tend to break up oil-emulsions in general. The nature of the fat or oil (i. e., whether a solid or a liquid fat), and that of the alkali (i. e., whether soda or potash) of which the soap was made may be determined by chemical analysis. The analysis of soap may also include the determination of the water-content, and that of the presence or absence of rosin, filler, and free caustic alkali.



Appendix to Nature and Control of Tannery Processes

CONTENTS

The Coloring of Leather

LEATHER is colored with dye woods, coal tar dyestuffs or pigments. The most important dye woods used are logwood, fustic and hypernic. Besides possessing a high degree of coloring properties, these dye woods have tanning qualities and also mordanting properties for basic dyes.

Many vegetable tanning agents which are used to give the grain of the leather some particular quality, or to fill the fibres of the leather, also have some slight dyeing properties, but are more generally used as mordants for the basic dyes. The most important method of dyeing leather, however, is by the use of coal tar dyes, and these are usually considered under the following divisions:

Basic dyestuffs
Acid dyestuffs
Direct dyestuffs
Dyestuffs oxidized on fibre
Alizarine or mordant dyestuffs
Sulfur dyestuffs
Dyestuffs diazotised and developed on fibre

Dyestuffs commonly known as vat colors, such, for example, as indigo, are not suitable for leather.

BASIC DYESTUFFS are most commonly used because leather was formerly made almost entirely with vegetable tanning materials. These colors are also suitable for chrome leather, after it has been properly mordanted with a vegetable tanning material.

Basic dyes are best dissolved by mixing them thoroughly with cold water and then raising the solution to nearly a boil with a steam jet. Cold water is most advantageously used because basic dyes frequently contain material which is likely to cake if the dyes are put into hot water. Auramine, for instance, should not be dissolved in water over 175° F. If the water is hard the basic dyes should be wet with one-half their weight of acetic acid before the water is added. Phosphines which are not affected by the hardness of the water may be dissolved without the addition of acetic acid, even in very hard water. Dyes were formerly made by the purification of a byproduct of magenta, but the new phosphines, such as phosphine G N, are made synthetically and are much purer compounds.

Basic dyes as a class are not very fast to light, and in this respect many acid, direct and alizarine dyes are superior to basic dyes. It should be remembered that it is practically impossible for the dyer of leather to secure such excellent results as are possible for the textile dyer, because the tanner cannot boil the leather. National Phosphine G N, Bismarck Brown 53, Safranine A, Methyl Blue BD and New Blue D A conc. are faster to light. National Auramine O, Chrysoidine Y Ex. and 3T, Fuchsine N B Cry. Methyline Violet 2B and Victoria Green W B. Cry. possess the greatest penetrating qualities of the basic dyes.

Basic dyes are much improved in their fastness to fat liquor and finishing if they are after-treated with tartar emetic, potassium titanium oxalate or bichromate of potash. These salts also give more level results with basic dyes if the bottom is fixed with them before dyeing.

ACID DYES are used on all kinds of tannages. They readily dissolve in hot water and do not require a mordant. The depth of color obtained by their use is much improved by the addition of sulfuric or formic acid to the dye bath. Best results are obtained by adding the acid towards the end of the dyeing operation. The use of an acid is, however, undesirable, especially on chrome leather, if after dyeing the leather has to be fat liquored with an alkaline emulsion of oils, because the acid is liable to cause grease spots by curdling of the fat liquor.

Whenever acid is used the leather should be thoroughly washed afterwards. Some of the best levelling acid dyes are National Wool Yellow EX Con. Wool Orange A Conc; Wool Orange GG Cry., Fast Crimson G R, Fast Crimson 8 B L, Alphazurine 2 G, Alizarine Sapphire F S, and Acid Fast Violet B G.

These colors are reasonably fast to light and are also easily dissolved, which causes them to penetrate the leather and to produce very level shades.

They are excellent for making light pearl and ecru shades, but are not suitable for dark shades. Acid colors which are in the most common use are National Metanil Yellow 1955, Azo Yellow A5W, Resorcine Brown R and R W, Wool Scarlet B R, Croceine Scarlet MOO, Fast Red S Conc. Acid Bordeaux, Wool Violet 4 BN, Pure Soluble Blue, Induline N T, Durol Blue H R, Buffalo Black N B R, Buffalo Black A R, Acid Green L Conc. and Nigrosines.

The most important of these colors for leather dyeing is the line of Nigrosines which is used to produce blue-blacks on vegetable and chrome tanned leather and for making black seasons for finishing leather and for blackings and shoe polishes. The Nigrosines most commonly used for dyeing leather are:

National Nigrosine 128 (bluish)
National Nigrosine 27722 (greenish jet)

Those used for seasonings and blackings:

National Nigrosine 2011 conc. (bluish)
National Nigrosine 4523 conc. (jet)
National Nigrosine 3099 conc. (greenish jet)

Those Nigrosines which are ammonia proof are:

National Nigrosine 51457 (bluish)
National Nigrosine 19903 (bluish black)

There is also to be considered Spirit Nigrosine SG, which is soluble in alcohol, but not soluble in water, and which is related to the above nigrosines.

Acid dyes are used extensively on vegetable and chrome tanned leather as a bottom for basic dyes which are precipitated by the acid dyes and produce full level colors. Their greatest usefulness in fancy shades has been to produce brown glazed kid where they are used on chrome tanned goat skins, bottomed with fustic and logwood.

Acid dyes are not firmly fixed on leather by any process; they have a tendency to bleed off in the fat liquor, wherein lies one of the greatest objections to their use.

DIRECT DYES have created an important place for themselves in the dyeing of chrome leather. They attach themselves directly on to this material without any mordant, but they have only a slight affinity for vegetable leather. For this reason they give better results on chrome leather after it has not been retanned with any vegetable tanning agent.

There are, however, some direct dyes which are suitable for producing very light and level shades on vegetable tanned leather.

Direct dyes are readily soluble in water and, unlike

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The qualifications of the above dyestuffs on chrome tanned leather are as follows:

1. They penetrate thoroughly;
2. They dye absolutely level;
3. They produce a mild tanning action;
4. They improve the feel and strength of the grain;
5. In consequence of the above, they are applied to give the necessary grounding for aniline colors so that uniform shades may be produced with regularity.

FOR DYEING AND FINISHING, WE RECOMMEND

Russett Phosphine for tan base, Russett Brown for dark and brown base; Russett Mahogany; Russett Red for Russia red base; Ebonite for blacks; etc., etc.

For Other Shades
Write for Leather Shade Cards

Liquid Extracts sold in barrels of 500-550 lbs. Crystals sold in barrels of 350-400 lbs. Solid Extracts sold in boxes of various sizes, 25-60 lbs. Also in special weights as ordered.

AMERICAN
DYEWOOD COMPANY

New York — Boston — Philadelphia — Hamilton, Ont.
Works at Chester, Pa.

basic dyes, they are less soluble in acid solutions and become more soluble when an alkali is added to the dye bath. Because of this characteristic, chrome leather should be as nearly neutral as possible before dyeing, in order to secure the most level results, and it is not necessary that the dye bath should be acidified, even at the end of the dyeing operation, as the colors exhaust completely unless there is an undue excess of the dyestuff.

Direct colors most suitable for chrome tanned leather are:

National Erie Fast Yellow WB
" " Yellow Y
" " Orange CG
" " Fast Orange A
" " Scarlet 8 BA
" " Red F D
Niagara Sky Blue 6 B
Diazine Black H. Ex.
Erie Black GXOO

Direct dyes are often improved in respect to their fastness to fat liquor by after treatment with bichromate of potash or copper sulphate. They seem, however, to be affected detrimentally by iron salts. Some direct dyes work better in the dye bath if 2-3% of salt is used. National Erie Black GXOO is the most important of the direct colors used by leather manufacturers. It has come into successful competition with logwood and Nigrosine on chrome leather. It does not yield a black as cheaply as logwood, but on the other hand it does not make the leather as tender or as harsh feeling as logwood. National Erie Black GXOO does not bleed in the fat liquor as much as Nigrosine. If it is used in connection with logwood, it should be dyed on the leather before the logwood, in order to give the deepest black result. A good black on chrome leather is obtained by dyeing the neutralized leather as follows:

> For 100 lbs. wet weight, work for twenty minutes at 120° F. with 12 oz. National Erie Black GXOO, then for twenty minutes at 120° F. with 1 lb. of logwood crystals, 2 oz. bicarbonate of soda. Fix for ten minutes at 100° F. with 2 oz. of copperas. The material is then fat liquored in the usual manner.

The direct dyes give excellent colors on chrome leather which can be finished without glazing on the grain or on chrome leather finished in ooze. They are much faster to light than basic dyes. When topped with basic dyes they produce colors which are fairly fast to light, and have the fullness and brightness of the basic dyes themselves.

ALIZARINE OR MORDANT DYES have been used to some extent on chrome leather, as they are the fastest colors to light which are known. Many of this class of dyes, however, are unsuitable for general use, because the full value of the color is not developed except at a boiling temperature. For instance, Alizarine Red is actually yellow until it is developed by chrome at a boiling temperature. Different chemicals, such as bichromate of potash and potassium titanium oxalate, have been proposed as substitutes for a boiling temperature, but they have been only partially successful. There are some mordant colors, however, which develop cold, while others give shades which are useful although undeveloped. These colors as a class are usually dull and are much improved if topped with basic dyes. National Superchrome Yellow B N is the most important mordant dye.

Dyes which are developed on the leather have become important for making black ooze, which requires a very intense black. Other developed colors could be used when fullness is especially desired, but the process is long and tedious and does not give colors any faster to light than the basic dyes, which are applied much more simply. They are used at present only on chrome leather. The practice of diazotizing and developing seems to increase the softness of the leather, which is particularly beneficial in making ooze. The process is carried out as cold as possible with the exception of the dyeing at the beginning, so that the leather has small chance of being damaged. The following is a good formula for making black ooze calf skins with developed dyes:

The chrome tanned calf skins are sorted for good flesh. They are then washed and neutralized, shaved, fat liquored for thirty minutes at 120° F. with 5% egg yolk and 10% flour, drained, hung up and dried, damped in sawdust, staked and buffed. The buffing must be done very clean so that they will not need to be buffed after dyeing.

The percentages of dyes used in this formula are calculated on the dry weight. Wet the skins thoroughly at 120° F, dye 30 minutes at 120° F., with 7% National Diazine Black H. G. Extra, dissolved in enough water to cover the skins. Add to dye bath 5% muriatic acid diluted with water at 90° F. Run 15 minutes, drain off and add 10% muriatic acid diluted with enough cold water to cover the skins and run 10 minutes. Add to the same bath 5% sodium nitrate dissolved in cold water; run 15 minutes. Drain off and wash absolutely clean. Develop 15 minutes cold with 1% National Developer B D, 2% Soda Ash, dissolved together in enough cold water to cover the skins, and drain off and rinse. Fat liquor 30 minutes at 120° F., with 1% acid neatsfoot oil fat liquor. The skins are then dried on the hooks, damped in sawdust, staked, dry milled and tacked out.

SULPHUR COLORS are dyestuffs which are soluble only in sodium sulphide or some other similar reducing agent. They have never found much use on chrome or vegetable tanned leather, because they have a tendency to make the leather tender. They have been recommended for dyeing oil tanned chamois leather. For this purpose equal parts of sulphur dye and sodium sulphide crystals are dissolved in boiling water. After the solution is cooled add one-tenth of formalin and one-fifth of soap. The chrome leather is drummed in this solution and then again fat liquored. These colors are very fast to washing. Another use for sulphur dyes is for making grays on chrome tanned ooze calf skins.

Colors produced by oxydation on the fibres are used for fur dyeing. For this purpose two coal tar chemicals, Fur Black Superior and Fur Brown Base, are used. The tanned wool or fur skins are treated with a strong lime solution to remove grease and dirt and open up the hairs so that they will be prepared to absorb the mordants and dyes when they are applied. The lime is washed off and the wool or fur is mordanted. To insure a more rapid and intense absorption of the coloring matter developed in the dye bath, bichromate of potash sulphate or iron or copper in an acid or alkaline bath, are used for mordants and produce different shades with the fur dyes. The furs are then squeezed and immersed in the dye solution and peroxide of hydrogen, or sodium perborate, or peroxide neutralized with formic acid, is added. Various shades of brown, gray and black can be obtained; the process is carried out cold, so as to avoid damage to the skin. These colors have good fastness to light and washing.

Dyestuffs for leather finishes must be selected to mix properly with the other materials in the finish. It is in the leather finishes that pigments are mostly used. The pigments are merely suspended in the finishes, but the dyestuffs are usually in solution, at at least they should be if they have been properly selected and dissolved. The pigments give a body of color to the finishes, while the dyes give the brightness required. The finishes contain, besides pigments and dyes, various mixtures of albumen, casein, gelatin, gums, seeds and moss, soaps, oils, waxes and shellac. When the finishes are dissolved in alkaline, aqueous solution, acid or direct colors must be used; when dissolved in alcohol, basic dyes or spirits soluble dyes must be used. Collodion varnishes require spirit soluble colors such as National Amyl Black or Acetyl Brown.

In coloring the different kinds of leather for special purposes, if the best results are to be obtained the following points should be observed:

(1) Leather must be properly prepared to receive dyestuffs.

(2) Dyestuffs must be selected which are best suited to the kinds of leather used and for the shade required.

(3) The processes through which the leather must pass after dyeing must be chosen and arranged to cause the least possible injury to the color.

(4) Great care must be taken with every process.

Since the introduction of so-called pigment finishes, a great deal of carelessness has been shown in regard to the four above requirements. Pigments have covered a multitude of sins, but the connoisseur of fine leathers wants to see the characteristics of the grain of the leather. The result is that the best manufacturers are dyeing their leather with great care, so as to use only the smallest amount of pigment finish necessary.

CHROME TANNED CALF SKINS are finished into several grades of fancy leather; the most important are the smooth and boarded grain colors and ooze leather in black and fancy colors. The skins are sorted after tanning. The grain colors are prepared for dyeing directly after tanning and while they are still wet. The ooze colors are washed and neutralized, fat liquored with 5% egg yolk and 10% flour, then dried out and bathed in the same way as described for black ooze. Fancy ooze colors can be made by bottoming with sumac or fustic extracts and fixing with sulphate of iron, tartar emetic or potassium titanium oxalate, then coloring with basic dyes or with acid or direct dyes and sometimes topping with basic dyes. Some light shades are made with pigments. Besides the developed black method for black ooze, a combination of logwood crystals and copperas, National Nigrosine 4523 conc. and National Basic Table Black is used.

Three of the most common colors on chrome tanned calfskins finished on the grain, can be obtained as follows:

Chippendale	100 lbs. wet weight.
Bottom	3 lbs. Sumac ext.
20 min. 110°F.	1½ lbs. cutch.
Fix	1½ oz. potassium titanium oxalate.
10 min. 110°F.	
Dye	8 oz. National Resorcine Brown R.
20 min. 110°F.	
Top Dye	
20 min. 110°F.	11 oz. National Bismarck Brown 53.
	¼ oz. Victoria Green W. B. Crystals.
	1 oz. Safranine A.

Fat liquor with acid fat liquor.

Gold Brown	100 lbs. wet weight.
Bottom	2 lbs. Sumac ext.
20 min. 110°F.	1½ lbs. cutch.
Fix	1½ oz Potassium Titanium Oxalate.
10 min. 110°F.	
Dye	
20 min. 110°F.	8 oz. National Resorcine Brown R.
Top Dye	6 oz. National Chrysoidine Y ex.
20 min. 110°F.	4 oz. National Phosphine W T.
Fix	
10 min. 110°F.	1½ oz. Bichromate of Potash.

Fat liquor with acid fat liquor.

Morocco	100 lbs. wet weight.
Bottom	3 lbs. Sumac ext.
20 min. 110°F.	1½ lbs. Hypernic paste.
Fix	1½ oz. Bichromate of Potash.
10 min. 110°F.	
Dye	10 oz. National Acid Bordeaux.
20 min. 110°F.	
Top Dye	4½ oz. National Safranine A.
20 min. 110°F.	7½ oz. National Bismarck Brown 53.
	⅜ oz. National Methyl Violet 2 B. Conc. Cry.

CHROME TANNED GOATSKINS are mostly finished into black and colored glazed kid or patent kid. Black glazed kid or patent kid are colored as follows:

Bottom	1% Logwood Crystals.
20 min. 110°F.	¼% Bicarbonate of Soda.
Fix	
10 min. 110°F.	⅛% Chloride of Iron.

Drain off and dye 20 min. at 110° F. with

¾% National Nigrosine 27722

or ¾% National Erie Black GXOO

and 1/16% National Methyl Violet 2B

The glazed kid manufacturer is very firm in his conviction that he must have a vegetable retannage on his skins in order to obtain a good glazed finish, but to make a full black with logwood and iron alone would give a harsh grain.

CHROME TANNED SIDE LEATHER is tanned the same as chrome tanned calf skin, but about one-third less dye is required because of the greater thickness of the side leather.

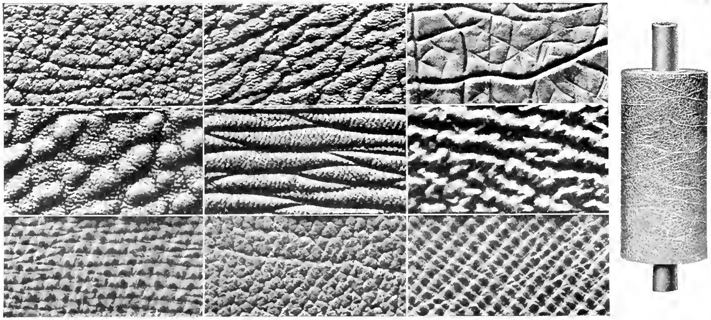
VEGETABLE TANNED SIDE LEATHERS are usually dyed with basic or acid dyes. The dyeing operations should never be carried out at a temperature higher than 110° F. The sides should be cleared in sumac and tartar emetic.

Light Tan Shade

For 30 bark tanned hides—750 sq. ft.
Dye in a paddle wheel pit 20 min. at 110 F. with
7½ oz. National Resorcine Brown R
1½ oz. National Resorcine Brown RN
¼ oz. National Buffalo Black N B R
Then add 3 oz. Sulphuric Acid and run 10 min.

Dark Coffee Shade

For 30 bark tanned sides—750 sq. ft.
Dye in a paddle wheel, put 60 min. at 110 F.
16 oz. National Bismarck Brown 53



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6 oz. National Safranine A
1 oz. National Methylene Blue B B
1 pint Acetic Acid
Then fix 15 minutes with 6 oz. Bichromate of soda

When dyeing bark tanned side leather on a brushing machine or on a table, acid dyes give the most satisfactory results.

BROWN GLAZED KID is most successfully made with acid dyes on a vegetable bottom. The skins are first carefully washed and neutralized.

For 100 lbs. wet shaved weight
Bottom 20 min. at 110 F. with
1½ lbs. Fustic Ext.
2 oz. Logwood Cry.
Fix 15 min. at 110 F.
1¾ oz. Chloride of Iron
Drain off and dye 30 min. at 110 F.
4½ oz. National Resorcine Brown R
4½ oz. National Leather Mahogany C M Y
2 oz. National Fast Acid Red T K C
2 oz. National Induline N T
Drain and wash. Fat liquor with 4% Acid Fat liquor

Mahogany Glazed Kid

For 100 lbs. wet shaved weight
Bottom 20 minutes at 110 F. with 1½ lbs. Sumac ext.
½ lns, Hypernic paste
Fix 15 minutes at 110 F.
2 oz. Bichromate of Potash
Drain off and dye 30 minutes at 110 F.
16 oz. National Mahogany Brown BL
2 oz. National Fast Red S. Conc.
2 oz. National Induline N T
Drain off, wash, fat liquor with 4% Acid fat liquor.

Vegetable Tanned Sheepskins and Goatskins are dyed with acid or basic dyes. The principal difference in treating the different kinds of vegetable tanned leathers is made in the method of preparation for coloring. The dyeing operations should be carried out at about 110 F.

India tanned sheep and goat skins contain considerable grease as well as vegetable tanning material. The grease must be removed from the surface of the leather before it can be dyed a clear even color. This is done by washing the skins first in soda to free the grease, then retanning with sumac, then clearing with sulphuric acid, then finally the skins are rinsed with plenty of water. The skins to be colored black on the grain leaving the black white, are stained on the grain by brushing with 8 oz. National Basic Table Black, 2 oz. Acetic acid and 2 quarts gum Tragacanth solution to one pail of water.

Pickled sheepskins tanned in sumac, are simply cleared with sulphuric acid and rinsed in water. Pickled sheepskins tanned in quebracho, for fancy colors, are washed up in sumac, which is then fixed with tartar emetic.

India sheep skins and pickled sheep skins are colored similarly and can be considered together. Whenever good fastness to washing is required, the skins should be dyed with basic dyes and the color set with bichromate of potash. On very light shades which must be slightly saddened, bichromate of potash must be used intead of blue or green, when possible. When full shades are made with acid dyes, such as bright reds, dyed with National Croceine Scarlet MOO, about 2 quarts of formic acid to 30 dozen skins should be added toward the end of the dyeing operation. Formic acid is generally chosen because it is quite as strong as sulphuric acid and will evaporate while sulphuric acid is stable. Dyes for ooze leather should be selected for their penetrating qualities. The best acid dyes for this purpose are National Wool Yellow Ex. con. Wool orange A Conc. Croceine Scarlet MOO add Induline N T, the best penetrating basic dyes are National Auramine O. Chrysoidine Y Ex. and 3 R, Fuchsine N. B. Cry, Methyl Violet 2 B cry.

Coffee Brown

30 dozen Quebracho tanned sheepskins 85 ft. per dozen
Dye 20 min. at 110 F.
6 oz. National Wool Orange A Conc.
12 oz. National Fast Brown BN
Dye 20 min. at 110 F.
42 oz. National Phosphine W T
34 oz. National Bismarck Brown 53
7 oz. National Methylene Blue BB
Fix 15 min. 110 F.
2 lbs. Bichromate of Potash
12 oz. Blue Stone.

Tan

30 doz. Quebracho tanned sheepskins 85 ft. per dozen
Dye 20 min. at 110 F
24 oz. National Wool Orange A Conc.
12 oz. National Resorcine Brown R
Dye 20 minutes at 110 F
72 oz. National Phosphine W T
1½ oz. National Methylene Blue BB
Fix 15 min. 110 F.
2 lbs. Bichromate of Potash

Chrome Tanned White Leather

In addition to the usual process for making white leather, namely, by the use of alum and formaldehyde, chrome tanned white leather is commercially produced according to one of the following methods: namely,

(1) For "soft" white leather (i. e., lining splits): Use of the ordinary two-bath process with an excess of acid and sodium thiosulfate in order to effect the maximum deposition of sulfur within the goods. The sulfur so deposited renders the resulting leather very light in color.

(2) For "firm" white leather: Use of a one-bath bisulfite chrome-liquor, followed by treatment with acid and sodium thiosulfate. In this process the deposited sulfur again acts as a "bleaching" agent. The leather is rendered perfectly white by the application of whiting (magnesium carbonate).

(3) By a combination of the one-bath process and of the alum-formaldehyde process. The goods are first run in the chrome-liquor until "struck through," when they are neutralized with borax and entered into an alum-liquor containing alum, salt and flour. After being drummed in this liquor until tanned, the leather is treated with formaldehyde, and subsequently fat-liquored in an emulsion of starch, egg-yolk and sulfonated neatsfoot oil.

The processes outlined above are typical of those employed by well-known tanning concerns in this country.

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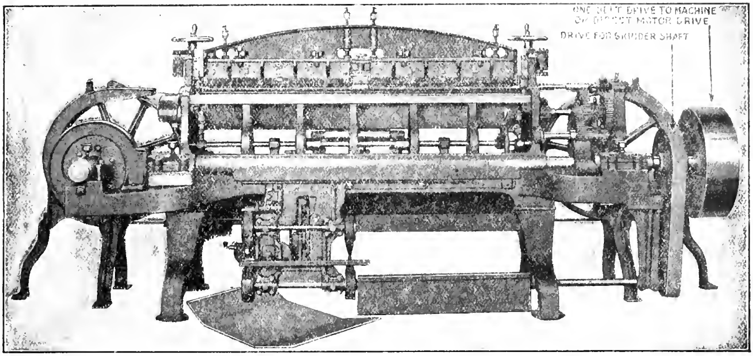
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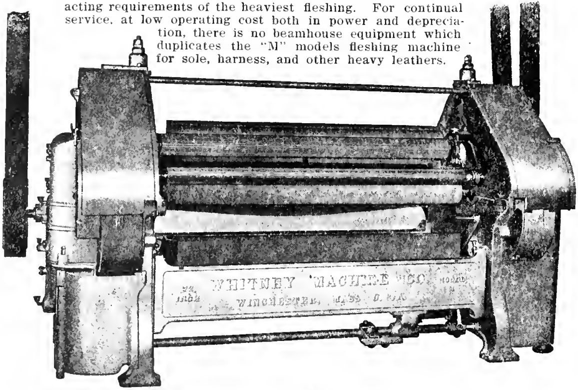
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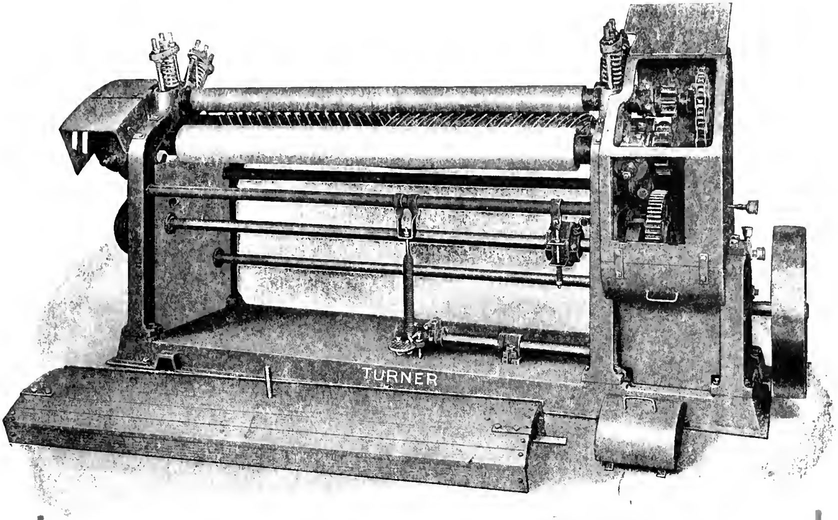
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