# The Use of Surface Active Agents in Tanning of Leather[1]

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## ABSTRACT

There are about 25 operations in the process of converting hides and skins into leather. Surface active agents are important in a number of these and find wide use in the leather-making industry. Both anionic and nonionic types are widely used while cationics have more specialized use. Sulfated oils (especially cod, sperm and neatsfoot), soaps, sulfated higher alcohols and alkylbenzene sulfonates are the main anionic surfactants used. The nonionics are principally condensation products of ethylene oxide with a secondary alcohol of 11-15 carbons or with octyl and nonyl phenol, introducing 7-10 oxyethylene units. Examples of the cationic type are the quaternary ammonium salts, i.e., lauryl, cetyl and stearyl dimethyl benzyl ammonium chloride. Surface active agents are used at various stages of the leather-making process. They are used in soaking, unhairing, bating, pickling, tanning and coloring, where they serve principally as processing aids. Thev find more important use in fatliquoring, impregnation and finishing, where they become a part of the leather composition. Certain surfactants, namely, chrome complexes of fatty acids and perfluoro acids, and long chain alkenyl succinic acid have been used to impart water repellent properties to leather. Recent research shows promise of developing new uses for surfactants in the tanning industry. Long chain quarternary ammonium salts have shown promise as a short term preservative for freshly flayed hides and skins. An amphoteric surfactant, i.e., a long chain fatty amino acid of the structure $RNHCH_2CH_2CO_2H$, has shown promise as leather lubricant with improved resistance to drycleaning solvents.

## INTRODUCTION

### Leather—The Natural Nonwoven Fabric

Leather is a unique flexible sheet material somewhat analogous to textiles. It can be called the first and only natural nonwoven fabric. However, leather is a very unusual fabric. It is strong, durable, supple, soft, warm and porous. It is also a product with beauty and appeal. These properties arise because of leather's unique structure, an intricate, interwoven, three-dimensional network of fibers inherent in the natural raw material, hides and skins. This natural raw material is mainly a fibrous protein known as collagen and is composed of one continuous network of fibers. Figure 1 is a vertical cross section of steerhide showing the structure of this natural product. At least four distinct structures are evident. The various structures are as follows: a, the thin outermost layer termed the epidermis; b, the grain layer; c, the juncture between the grain layer

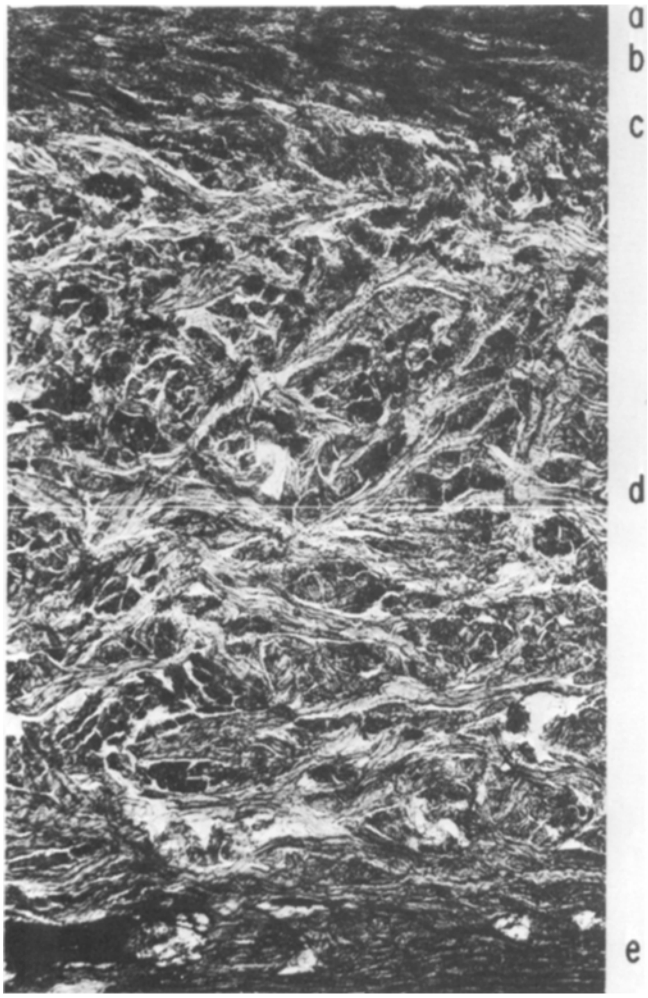

FIG. 1. Photomicrograph of vertical cross section of steerhide. (A.L. Everett, J. Amer. Leather Chem. Ass. 62:25-44 (1967), Fig. 4b.)

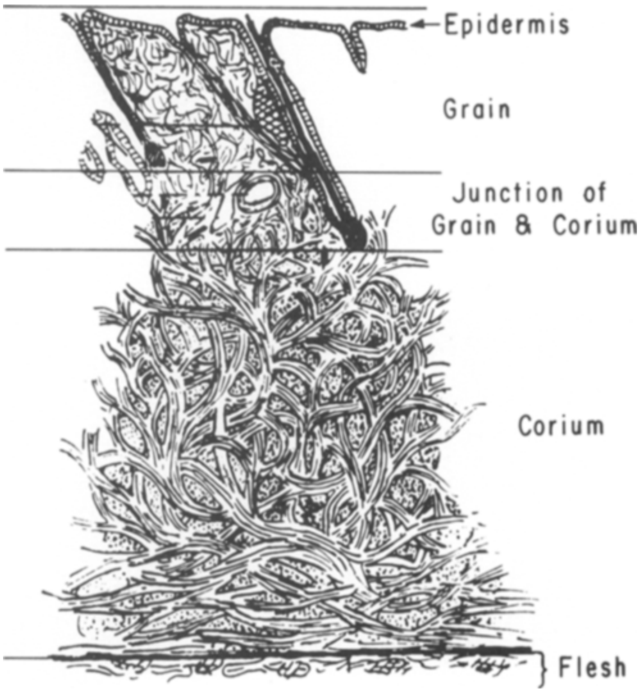

FIG. 2. Schematic diagram of cross section of cattlehide. (Fig. 13 in "Hides, Skins and Leather Under the Microscope, 1957" British Leather Manufacturers' Research Association.)

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[1] One of eight papers to be published from the Symposium "Surface Active Agents in the Textile Industry."

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TABLE I

Hides and Leather Statistics, 1967[a]

| Type | Skins tanned, millions | Estimated value: Raw material[b] $1,000,000 | Estimated value: Leather[c] $1,000,000 |
|---|---|---|---|
| Cattlehide | | | |
| Shoe upper | 15.8 | --- | --- |
| Sole | 4.3 | --- | --- |
| Other | 3.3 | --- | --- |
| Total | 23.4 | $175.5 | $510.0 |
| Calfskin | | | |
| Total | 4.0 | 20.0 | 42.0 |
| Goatskin | | | |
| Total | 8.7 | 10.9 | 25.2 |
| Sheepskin[d] | | | |
| Total | 30.4 | 45.6 | 115.0 |
| | | $252.0 | $692.0 |

[a] Data from Tanners' Council of America and U.S. Tariff Commission, T.C. Publication 281 (1969).

[b] Assuming average cost as $7.50 per hide, $5.00 per calfskin, $1.25 per goatskin and, $1.50 per sheepskin.

[c] Assuming average leather prices per square foot as $0.55 (steer), $1.00 (calf), $0.60 (goat) and $0.50 (sheep).

[d] Includes two million cabretta skins.

and the corium; d, the major portion of the pelt known as the corium; and e, the flesh layer or the structure adjacent to the body tissues. Figure 2, a schematic diagram of cattlehide, shows the structure and essential features of this natural product more clearly.

In converting the pelt to leather the tanner removes the epidermis as well as the hair, minor noncollagenous proteins and some fat. The epidermis and hair are proteins of the keratin type. Removal of the epidermis exposes the second layer immediately below, referred to as the grain layer, which becomes the leather surface. The grain contributes to leather's beauty and appeal. It is composed of very fine fiber bundles that appear to be quite dense. Elastin and collagen, predominately the latter, are the fibrous proteins comprising this layer. The grain layer merges into a third and the major portion of the skin known as the corium, which is characterized by coarse fiber bundles. The corium is composed almost entirely of large bundles of collagen fibers whose structure varies from one area to another in a hide. The corium contributes to the strength and suppleness of the leather. This organization of interwoven protein fibers is stabilized by tanning so that the product is no longer putrescible and remains soft and supple.

### Leather and Its Raw Materials

Practically all of the world's supply of animal hides and skins, which are a by-product of the meat packing industry, is tanned into leather. 85% of which goes into footwear. Leather is produced mainly by two tanning processes, chrome tanning and vegetable tanning. The former is affected with basic chromium sulfate and the latter with extracts of vegetable matter, principally the bark and wood of trees. Today there is practically no end to the variety of leathers commercially available.

The most important raw materials used in the U.S. for tanning of leather are shown in Table I. In 1967 we tanned 23 million cattlehides into leather valued at about $500 million. Production of calfskin leather was considerably less, valued at about $42 million. Goatskins, practically all of which are imported, were tanned into $25 million worth of leather. Sheepskins ranked second to cattlehide in importance with about $115 million worth of leather.

Cattlehides are our most important raw material for leather production. When tanned in their full thickness, the leather is used mainly to make soles, insoles, belting and packings. For this leather the preferred tanning agents are the vegetable tannins. In current practice, however, most cattlehides are tanned with chrome and are split horizontally into two pieces. The most valuable portion contains the grain and is known as top grain leather. It is used for shoe and boot uppers, upholstery, garments, work gloves, linings, bags, cases, belts, luggage and sporting goods. The portion toward the flesh is less valuable and is termed split leather. This is used to make all kinds of lower priced leather goods containing an embossed artificial grain or a sueded surface.

Calfskins, goatskin and sheepskin are also chrome tanned. The first produces our highest quality leather, ideal for shoe uppers, slippers, handbags and billfolds. Goatskin leather is very suitable for shoe upper, lining, gloves, garments and bags. In sheepskins the fiber bundles in its structure are loosely packed and this leather is very soft and supple, well suited for grain and suede garments, shoe linings, slippers and dress and work gloves.

Similarly the pelts of other mammals, such as horsehide, buffalo hide, deerskin, and kangaroo skin, are also tanned into leather, but they comprise only a small fraction of the leather market. Reptile leathers are a small volume specialty item which require some modification in the tanning process as compared to mammalian leathers.

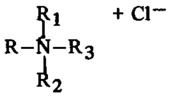
TABLE II

Estimated Tanning Chemical Market, 1966

| Product | Millions of dollars |
|---|---|
| Tanning agents | $30 - 40 |
| Leather finishes | 25 - 30 |
| Dyestuffs | 10 - 18 |
| Oils | 10 - 12 |
| Heavy chemicals | 8 - 15 |
| Surface treatment | 4 - 5 |
| Bates, adhesives, etc. | 3 - 4 |
| Surfactants | 1 - 2 |
| Other | 5 - 10 |
| Total | $96 - 136 |

TABLE III

Surface Active Agents Used in Leather

| Type | Formula[a] | Examples |
|---|---|---|
| Anionic | $RCOOM$<br>$ROSO_3M$<br>$RSO_3M$ | Soaps<br>Sulfated oils and alkyl sulfates<br>Alkyl benzene sulfonates |
| Cationic |  $R-\overset{\overset{R_1}{\vert}}{\underset{\underset{R_2}{\vert}}{N}}-R_3 \quad + Cl^-$ | Cetyl dimethyl benzyl ammonium chloride |
| Nonionic | $R(OCH_2CH_2)_nOH$<br>$RC_6H_4(OCH_2CH_2)_nOH$ | Alkanol ethoxylate<br>Alkylphenyl ethoxylate |

[a] R is a long chain alkyl group and M represents a metal or ammonium.

## LEATHER–A MARKET FOR CHEMICALS

An estimate of the value of the tanning industry as a consumer of chemicals is shown in Table II. In 1966 tanners were customers for roughly $125 million worth of chemicals. Tanning agents, finishes, dyes and oils comprise the major portion of these sales. Surfactants as such amounted to sales of 1-2 million dollars. Most of these are the nonionic type surfactants which are condensation products of ethylene oxide with long chain alcohols or alkyl phenols. However, surface active agents are also important ingredients of the oils, leather finishes and surface treatment chemicals which total 39-47 million dollars. All three types of surfactants, anionic, cationic and nonionic are used by the tanning industry. The chemical industry plays a key role in its relationship to the leather industry. It provides not only chemicals but also new developments and technical service to the tanner.

## SURFACE ACTIVE AGENTS IN TANNING OF LEATHER

Surface active agents are classified according to the charge residing on the fatty portion of the molecule. The types used in the tanning industry are indicated in Table III. Common examples of anionic surfactants are soaps, sulfated oils and alkylbenzene sulfonates.

Well known examples of the cationic type of surfactant are the quaternary ammonium salts such as lauryl, cetyl and stearyl dimethyl benzyl ammonium chloride. The nonionics are neutral compounds with a long chain hydrocarbon radical at one end and a hydrophilic structure at the other end. Nonionics commonly used in the leather industry are of the structure shown in Table III. In one type we have an ethoxylate of a secondary alcohol of 11 to 15 carbons. The hydrophilic portion is a polyethylene glycol chain of 7 to 10 oxyethylene units. The other type is derived from octyl or nonyl phenol by condensation with ethylene oxide, introducing 7 to 10 oxyethylene units. These ethylene oxide type condensation products are by far the more important of the nonionics used in the leather industry. These nonionic surface active agents may be sulfated to produce anionic surfactants. Both anionic and nonionic surface active agents are used broadly in the tannery while cationics have more specialized applications.

## USES OF SURFACE ACTIVE AGENTS IN TANNING

The leathermaking process is unrivaled for pure craftmanship and chemical ingenuity. The conversion of animal hide into leather is a long, complicated and interrelated series of mechanical and chemical operations requiring 7 to 45 days depending on the type of leather produced. Surface active agents are used at various stages of this series of operations. In most instances they serve as processing aids, but in some they become a part of the composition of the leather. While the overall process is general and common to all leather manufacture, details of various operations, including use of surface active agents, will vary from tanner to tanner.

By means of a process flow sheet in outline form, I would like to take you on a tour of a typical tannery processing cattlehides into shoe upper leather and point out where surface active agents may be used. The leathermaking process may be conveniently divided into wet and dry processes as shown in Table IV. The former comprise pretanning, tanning and post tanning processes and the latter the post tanning or finishing processes.

### Pretanning Processes (Wet)

Surface active agents are used at the very beginning of hide processing. The second operation noted here (the first chemical treatment) is soaking, which is the process for complete hydration of the hide or skin. Because animal hide is a perishable material, the packers must prepare it for market by curing with salt. This replaces the water in the

TABLE IV

Outline of Tanning Processes

| Wet processes | | Dry processes |
|---|---|---|
| Pretanning | Tanning and post tanning | Post tanning |
| 1. Trimming and sorting | 7. Tanning | 14. Drying[a] |
| 2. Soaking[a] | (a) chrome[a] | 15. Conditioning |
| 3. Fleshing | (b) vegetable[a] | 16. Staking |
| 4. Unhairing[a] | 8. Wringing | 17. Buffing |
| 5. Bating[a] | 9. Splitting | 18. Impregnation[a] |
| 6. Pickling[a] | 10. Retanning | 19. Finishing[a] |
| | 11. Coloring[a] | 20. Plating |
| | 12. Fatliquoring[a] | 21. Measuring |
| | 13. Setting out | 22. Grading |

[a] Surface active agents used in these steps.

hide with a nearly saturated salt solution which effects a dehydration as well as preservation. The tanner must restore the water content before processing.

This is done by treatment with water containing about 0.2% (on hide weight) of a nonionic surface active agent such as described above to assist penetration of water. This results in faster rewetting and also in removal of some grease. With very greasy skins the amount of nonionic used may be increased. The nonionics (7 to 10 ethylene oxide units) are most effective for general use because of their ability to form stable emulsions in the present of salt.

The fourth step in our flow sheet is unhairing. In this step the tanner treats the hide with lime and an unhairing agent such as sodium sulfide which attacks the keratin proteins present in epidermis and hair. The addition of nonionic surfactants to lime liquors helps to hold the lime in suspension and gives more effective unhairing and removal of scud, which is debris from the epidermis. The dispersing and detergent effect of these agents permits use of about 10% less sodium sulfide and aids grease removal. Nonionics are preferred because of their effectiveness at this high pH. In a hair-saving process, nonionics, such as those mentioned above, are used when washing the hair after removal from the hide. It is important to remove grease from hair before drying and baling in order to prevent spontaneous combustion.

The very next step is bating which involves treatment of the hide, after removal of the hair, with ammonium sulfate and a proteolytic enzyme. The former neutralizes the lime bringing the pH to about 8 and the latter removes noncollagenous protein, protein degradation products and scud. Nonionics (0.25%) are used to assist in removal of scud and also to obtain some aqueous degreasing. Nonionics are most suitable here because anionics may inactivate some enzymes.

After bating, the stock is ready for pickling, in preparation for chrome tanning. Normally tanners of cattlehide do not use surface active agents at this stage of the leather-making process. However, certain skins, noteably sheepskin, pigskin and goatskin, have a very high fat content which introduces serious problems to the tanner. Therefore, these skins are degreased at this stage. One method is to treat the pickled skins with kerosene or Stoddard solvent with up to 0.5% of a nonionic surfactant. The surfactant permits the solvent to penetrate the wet pelt by emulsification and thereby extract the grease. Anionic surfactants such as the sulfates may also be used; however, stability of the emulsified system to salt and low pH is essential. However, it is important to recover solvent and grease and this may dictate the choice of surface active agent used in this step. Some of the nonionics produce relatively stable emulsions which makes recovery difficult. Removal of grease at this stage, i.e., in the pickle and with solvent, is best for very greasy skins such as sheepskin.

### Tanning and Posttanning Processes (Wet)

This completes the pretanning wet operations of leather-making. This is followed by the important step of tanning itself, also a wet operation, and the normal post tanning wet processes outlined in Table IV. Tanning stabilizes the fibrous structure of the collagen and converts hides and skins into the useful product, leather. As you will note, there are two major tanning processes used for this purpose. The process used depends on the type of leather being made. Chrome tanning, which employs basic chromium sulfate (a cationic complex) as the tanning agent, is by far the most important tanning process. It is used for producing what is termed light leather, suitable for shoe upper, gloves, garments, etc., which accounts for about 80% of the total leather production. The vegetable tanning process is used for producing heavy leather, i.e., cowhide tanned in its full thickness, useful for soles, insoles, belting, etc.

Surface active agents are used in the chrome tanning step. Requirements are that the agent shows surface activity in the presence of salt and at low pH. Also they should not interact with the chrome complex. Nonionics and cationics meet these requirements. Their function is to further remove grease from the hides. This is a good place to remove grease since the tanning operation generally ends up at a temperature of about 120 F. The grease then is in a molten state and the surface active agent disperses and removes it from the hide. Generally about 0.25% of a nonionic (ethoxylate type) is added with the chrome. The use of 0.1% of a neutral naphthalene syntan with the nonionic improves grease removal further. Removal of grease is a growing problem because of today's practice of forced feeding of cattle at the feed lot which results in a higher economic return for the livestock. However, the higher grease content in the byproduct, hide, works to the disadvantage of the tanner.

Vegetable tannins are polyphenols, which are anionic in nature. Nonionic surfactants (as well as cationic) interact with these tannins to form a precipitate and for this reason cannot be used in the vegetable tanning process. Certain anionics, particularly dioctyl sodium sulfosuccinate, are used in the vegetable tanning process to effect some grease removal. The anionics also promote penetration and prevent precipitation of vegetable extracts.

We now come to the last steps in the wet operations, steps 8 to 13 in Table IV, generally grouped under the term wet post tanning processes. When a tanner uses a surfactant in the bating and/or chrome tanning step as mentioned above, he gains an additional advantage in the first two post tanning steps listed here. At the wringing step the life of the felts on the wringing machine is approximately doubled because of prior removal of grease from the stock. In splitting, the leather is more uniformly split because it is drier and contains less grease which aids in overcoming slippage on the feed rolls of the splitting machine and this results in closer tolerance to the desired thickness of the leather.

After retanning, the next step in our process is coloring. Here surface active agents are used to aid and control penetration of the dyes. All three types of agents may be useful. Surface active agents with the same charge as the dye will compete with it for oppositely charged sites on the leather thus assisting in levelness of dyeing. Agents with opposite charge to the dye are used to reduce dye penetration and promote surface dyeing through coprecipitation. Dyeing of leather is a complicated process and many other materials, such as syntans, which are synthetic tanning agents, are used extensively in this process as dyeing assists.

After coloring we come to the step known as fatliquoring. This is probably the most important operation using surface active agents. In fatliquoring, oils are incorporated into the leather fiber to serve as a lubricant. Fatliquors are emulsions of oil in water. The components are (a) the oil, which lubricates the leather; (b) water, which carries the oil into the leather; and (c) an emulsifying agent, which stabilizes the oil in water emulsion. All three types, i.e., anionic, cationic and nonionic surface active agents, are used in preparing the fatliquors. They may be used singly to emulsify the raw oil or blends of the surface active agents may be used. The latter are termed multicharged fatliquors. Both types find wide use in fatliquoring; however, the sulfated oils, used either singly or in multicharge blends, are by far the most important surface active agent for this function. The quaternary ammonium salts, when used as cationic surface active agents, are not especially good emulsifiers. The amphoteric long chain derivatives, how-

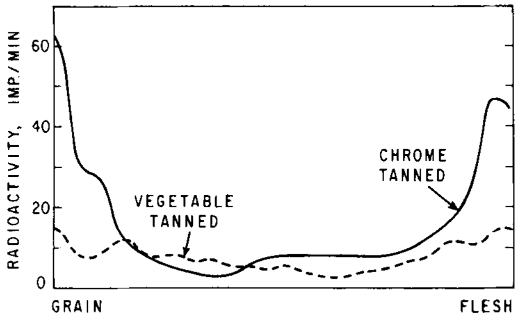


FIG. 3. Distribution of sulfated oils in leathers (8). (Das Leder.)

ever, when used at lower pH serve as cationic surface active agents and are more efficient emulsifiers and more useful in cationic fatliquors. Oils commonly used in the tanning industry are neatsfoot, cod, sperm, castor, coconut and palm oil and wool grease. The first three account for about 90% of the 40 million pound usage of oils.

The fatliquor becomes a part of the composition of leather. The amount of fat incorporated depends on the type of leather produced, varying from about 5% fat for firm leathers, such as for shoes, to about 25% fat for soft leathers, such as for gloves and garments. This lubrication gives strength, suppleness and stretch to leather.

The ionic charge of the particles in the fatliquor emulsion as well as the charge on the leather are important in considering its combination with the leather. The sulfated oil (anionic) imparts a negative charge to the fat particles in the emulsion. Figure 3 shows how the sulfated oil portion of this fatliquor, which was labeled with radioactive sulfur, is distributed through leather. The solid curve is chrome-tanned leather which is a cationic substrate.

FIG. 4. Photomicrograph of vertical cross section of fatliquored chrome-tanned leather stained with oil stain. (A.L. Everett.)

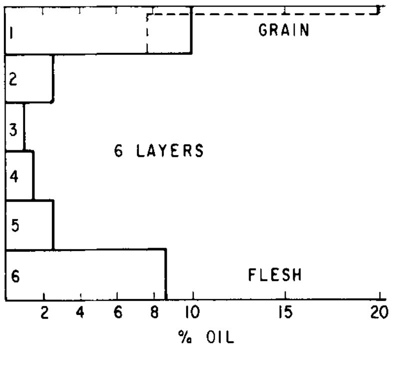


FIG. 5. Stratigraphic analysis of fatliquored chrome leather (17). (J. Amer. Leather Chem. Ass.)

You can see that the sulfated oil is bound to a much greater extent at the grain and flesh surfaces of the leather due to the interaction of opposing charges. Vegetable tanned leather, which is an anionic substrate, on the other hand, shows almost uniform distribution of the sulfated oil. Figure 4 is a photomicrograph showing penetration of fatliquor (total oil, including raw and sulfated oil) into chrome-tanned leather. This was stained with an oil stain to show penetration. It is quite evident that most of the oil is in the grain and flesh portions.

Figure 5 presents this same information in a quantitative way. The total oil content was determined by stratigraphic analysis. Again we note that the leather has much more oil deposited in the grain and flesh portions than the center portion. The dotted line in the six-layer stratigraph of Figure 5 indicates the oil distribution in finer detail, i.e., if the leather were to be split into more layers as with a microtome. Thus the oil is more concentrated at the surface of the grain layer than in the remainder of layer one (grain layer).

Leather being a protein fiber is naturally hydrophilic. In applications such as footwear and garments this is undesirable. In a limited way substances have been found useful in overcoming this deficiency. In a broad sense some of these may be considered surface active agents. Some garment suede leather has been made water repellent with a stearato chromic chloride complex. Also some suede leather has been made water and oil repellent by treatment with chrome complexes of perfluoro fatty acids. Alkenyl succinic acids with 14-20 carbon atoms in the chain have been suggested as a water repellent. The first two types are substantive by virtue of the trivalent chrome in the structure. The alkenyl succinic acids are fficient water in oil emulsifiers and may be effective by virtue of this property.

These treatments are quite limited and would be applied as the last wet operation after fatliquoring. However, they leave much to be desired. They are expensive, not long-lasting and complicate the conventional finishing processes.

### Post Tanning Dry Processes

Table IV also outlines the eight remaining steps in the leathermaking process and these are dry processes. Chrome leather is commonly retanned with vegetable tannins. This makes the surface anionic and highly absorptive. Hence, a cationic fatliquor may be used as a topping oil back in the fatliquoring step. This treatment is an aid in the drying of leather by preventing the paste from penetrating the grain. This aids the release of the dry leather from the pasting plate.

Impregnation is the deposition of polymeric materials into the grain layer of leather to improve its break, scuff resistance and appearance and to upgrade the leather. Break refers to the grain pattern caused by flexing leather. The polymers may be applied in either an organic solvent or in an aqueous system. The latter is more widely used and in general the impregnants are aqueous emulsions of acrylic copolymers containing about 10% polymer and up to 25% on the polymer weight of an anionic or nonionic surfactant. The emulsion is applied to the grain of buffed leather and penetrates about 35% of the thickness. The surfactant serves to suspend the latex particles and to obtain optimum rate of penetration and depth of polymer deposition. The particle size of the emulsion is of the order of 0.05 $\mu$ or less.

Finishing is the application of polymers as base and color coats to the grain surface of leather to increase its beauty. The use of surfactants in these polymer coating materials is extensive and the manufacturer uses nonionic or anionic surfactants in preparing these emulsions. In finishing, wetting, also termed leveling, and penetration, which is termed water release, are required of these aqueous emulsions. These are functions of the surfactants used in the emulsion. Since the finish is designed for surface coating only, the latex particles do not penetrate significantly except into the hair follicles. However, the water does release from the finish coating and penetrates into the leather pores.

The total effect of the surfactant in the finish coating must be balanced to produce leveling and water release. The best leveler choice would be an anionic surfactant which plasticizes less than nonionics and is not likely to migrate into subsequent top coats. The particle size of emulsion for finishing is in the range of 0.05 to 0.8 $\mu$.

We conclude the leathermaking process after measuring and grading of the finished leather. Before concluding I would like to mention some research from our laboratory that offers promise of new applications for surface active agents. We showed that a cationic surfactant, such as a long chain alkyl dimethyl benzyl ammonium chloride, was effective as a short term preservative for freshly removed hides at the packinghouse. By treating with a 0.4% solution of the benzalkonium chloride, the hide was stable to microbial attack for about three days. This permitted trucking the hides to nearby tanneries or to a hide processing plant.

Another report from our laboratory described results obtained with the use of an amphoteric surface active agent such as N-lauryl-$\beta$-amino-propionic acid. These long chain fatty amino acids were substantive to chrome-tanned leather and served as lubricants for the leather. Tests with the common drycleaning solvents revealed that this lubricant was more resistant to extraction by a factor of about three. Thus the amphoteric surfactant appears to offer promise from the standpoint of drycleanable leather garments.

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