This invention relates to a process for treating leather to strengthen its defenses against damage by water, perspiration, chemicals and scuffing. More particularly the invention is directed to a process of applying to side leather a water-soluble complex compound of the Werner type in which trivalent nuclear chromium atoms are coordinated with carboxylic acid groups having at least 10 carbon atoms. The invention is also directed to fat-liquoring compositions comprising a water-soluble compound composed of the Werner type in which trivalent nuclear chromium atoms are coordinated with carboxylic acid groups having at least 10 carbon atoms.

This application is a continuation-in-part of my copending application Serial No. 520,162, filed July 5, 1955, and now abandoned, which in turn is a continuation-in-part of my parent application Serial No. 351,471, filed April 27, 1953, and now abandoned.

For the purposes of this invention, the term "chrome complex" shall mean any water-soluble complex compound of the Werner type in which trivalent nuclear chromium atoms are coordinated with carboxylic acid groups having at least 10 carbon atoms.

In the drawing:

FIGURE 1 is a semi-diagrammatic illustration showing the fibrils of a swatch of leather in section which has been treated with a chrome complex according to the invention.

FIGURE 2 is a perspective view showing a single, greatly enlarged fibril 1 modified in accordance with a process of the invention, different portions of the coated fibril 1 shown being cut away.

FIGURE 3 shows in step-wise progression, viewed from left to right, how the two fibrils 1 and 11 of FIGURE 4 are modified by the preferred practice of the invention.

FIGURE 4 is a diagrammatic illustration of the two fibrils 1 and 11 in section showing the juncture between them. The small circle A in FIGURE 4 is the basis for the sectional views shown in FIGURE 3.

The mere conversion of raw skin into leather does not generally make it suitable for the various purposes for which leather is used. For some kinds of leather more work is required in the operations following the actual tannage than in the tanning and all preceding operations put together. Each of the innumerable kinds of finished leather requires a special series of operations after tanning. One of the most important of these is an operation known as fat-liquoring.

It is upon the efficiency of the fat-liquoring and other after-tanning processes that the feel and appearance of the finished leather as well as the strength depends. Too much fat, particularly if it is sulfonated, makes the leather cloth-like, raggy and in some cases greasy or liable to throw off the excess in the form of spue as the leather ages. Too little fat-liquor will cause the leather to dry but harsh and to crack when stained or finished in the ordinary way, or at least be too firm even after staining.

In the processing of most leathers, particularly chrome-tanned leathers, fat-liquoring is absolutely essential. The main purpose of fat-liquoring is to lubricate the small fibers or fibrils 1 and 11 and so smooth them to move over one another freely and easily. This causes the leather to be more flexible. Fat-liquors are also believed to cause a splitting up of the larger fibers into finer ones.

Hereofore, it has not been possible to dry clean fat-liquored leathers without a deterioration in general leather properties, such as color, feel, nap characteristics, drape and general overall water resistance.

I have now found that a water-repellent, pliable leather product can be readily obtained which retains its desired leather characteristics even after solvent dry cleaning or mild soap and water washings by using in place of the fat-liquors well known to those skilled in the art a fat-liquoring composition containing a chrome complex.

I have further found that a water-repellent, pliable shoe leather product, which is both acid and alkali resistant, can be obtained by applying a chrome complex to side leather after the leather has been conventionally fat-liquored or concurrently with a conventional fat-liquoring oil, or, less preferably, before a conventional fat-liquor has been applied to the leather.

Leathers treated with fat-liquoring compositions containing a chrome complex but free of the conventional fat-liquoring oils retain their desirable characteristics after solvent dry cleanings, water washings or even acid dyes, effectively preventing the complex to react with the free carboxylic acid groups (or amino groups) of the collagen lattice through the coordinate valences of the chrome complex. After further polymerization of the complex-protein reaction product (olation) which takes place on heating or aging of the chrome complex-treated, oil-free leather, this stable chemical combination is no longer affected by solvent extraction or by emulsifying agents.

The long chain hydrocarbon end of complex 3, by virtue of its hydrophobic properties, resists the penetration of liquid water 4 into the leather, but allows the passage of water vapor. These hydrocarbon ends sticking up from the surface of the leather, as shown in the drawing, also give improved adherence for leather finishes. A more complete discussion of the mechanisms of the invention will follow.

When conventionally fat-liquored, chrome-tanned side leather is treated in accordance with a process of this invention, the fat-liquor 2b (12b) becomes permanently anchored to the fibrils 1 and 11. The tenacity of this union is remarkable. From a theoretical standpoint, it appears that the water resistance and other beneficial properties resulting from this novel chrome complex treatment may be due to the long chain hydrocarbon group present in the complex 3 (13), or to improved bonding of the fat-liquor 2b (12b) to the leather fibrils 1 and 11 due to a reaction between the fat-liquor 2b (12b) and the chrome complex 3 (13), or to both.

Not only may there be a reaction between the complex 3 (13) and the collagen or leather protein of the fibrils 1 and 11, but also between the complex 3 (13) and the fat-liquor 2b (12b). This second reaction may account for the large amount of chrome complex 3 (13) that may be added to conventionally fat-liquored leathers before the leathers become greasy to the hand.

It is believed that the chrome complex may rearrange in contact with the anionic fat-liquoring oils 2b (12b), sulfated or sulfonated, or even acid dyes, effectively pro-
ducing a water-resistant, anchored fat-liquoring oil 2b (12b) as well as a dye system. Additionally, chrome complexes 3 and 13 of differing carbonic contents may have varying degrees of reactivity with anionic fat-liquor-
ing oils 2b and 12b in the leather. It will be understood, however, that applicant does not limit in any way his in-
tention to this explanation of the mechanism of the inven-
tion.

The nature of this invention and more particularly its manner of operation will be more fully discussed fol-
lowing a description of the complexes and other reactants
used in the processes of the invention, the leathers which can be treated, and the process conditions which are to be
employed.

By the term “fat-liquoring oil” I mean to include not
only the raw oils, but also the emulsified and/or sulfated
oils used in conventional fat-liquoring of leather. Among
the fat-liquoring oils frequently encountered in the pro-
duction of leather there may be named neat’s-foot oil, co-
cconut oil, fish oil, sperm oil and castor oil. All of these
oils may be coproducts with anionic or cationic type
emulsifiers. Sulphated forms of such oils can be employed.
Other types of oils which fall within may definition of
fat-liquoring oils are the non-ionic type such as, for in-
stance, mustard seed oil, teasled oil, lard oil, corn oil,
olive oil, linseed oil, rapeseed oil, soya oil and tallow oil.
These non-ionic oils can also be emulsified and/or sul-
fated for use in the processing of leather.

The cromium compounds of the Werner type useful for
the purposes of my invention are the complex compounds
produced by processes in which contact is effected between
carboxylic acids having at least 10 carbon atoms and
basic salts of trivalent chromium, the basicity of the chro-
nium salt being no greater than about 50%.
The general methods disclosed in United States Patents Nos.
2,273,040, 2,356,161 and 2,683,156 are suitable for the prepa-
ration of the complexes useful herein.

Carboxylic acid groups having at least 10 carbon
atoms will for convenience of reference hereafter be
designated as “functional” acid groups. They may be
present as simple coordinated groups held by either prin-
cipal or auxiliary valences or they may be present as
bridging groups between two nuclear chromium atoms.
Particularly useful functional groups may conveniently be
designated by adding the suffix “-ato” to the first part of the name
of carboxylic acids corresponding to the acid group.
For instance, lauric acid gives “laurato” groups, stearic
acid gives “stearato” groups, abietic acid gives “abietato”
groups, oleic acid gives “oleato” groups and napthenic
acids give “naphthenato” groups.
The functional carboxylic acid groups coordinated
with the nuclear chromium atom to make up the prin-
cipal ingredient of the fat-liquoring compositions of the
present invention can be acyclic, carbocyclic, saturated
or unsaturated.
The term “acyclic” is here used in its ordinary chemi-
cal meaning to indicate organic compounds which con-
tain no ring system. For instance, the functional acyclic
acid groups can be negative groups found in the satu-
rated normal fatty acid having at least 10 carbon atoms.
Particularly useful functional groups include capric, un-
decanoic, lauric, tridecanoic, myristic, pentadecanoic, palmitic,
margaric, stearic, nonadecanoic, or arachidic acids, or high
acids of this homologous series.

Similarly, the functional acyclic acid groups may be
the negative groups of olefinic carboxylic acids having
at least 10 carbon atoms. Thus, such acids as unde-
cyanoic, crotonic, and butadienoic or oleic may be used.
The functional acid groups may also be derived from
carboxylic acids having more than one unsaturated link-
age such as linoleic, linolenic, elaesthesric or clupano-
donic acids. The functional acid groups may also be
derived from carboxylic acids having branched carbon
chains in which the total number of carbon atoms in the
chain is at least 9.
tanned leather, such as aluminum, titanium, zirconium, iron, etc.; leather tanned with so-called syntan or sulfonated and sulfated hydrocarbon oils and leather tanned with copolymers of styrene and maleic anhydride, and combinations of the above.

It will naturally be necessary to adapt the fat-liquoring process to the type of leather to be treated. For instance, the period of drumming sheepskin suede leather with the fat-liquoring compositions of the invention will be substantially less than that required for drumming side leather. Such adaptations as this can be readily made by those skilled in the art in order that the compositions of this invention meet the specific needs of specialized problems.

Leather to be fat-liquored according to the processes of this invention may be prepared in accordance with any of the conventional tannery practices. For instance, raw sheepskin may be put through the conventional steps of de-greasing, chrome tanning, fleshing, wet wheeling, moldanting (with extract) and drying preparatory to being dyed and fat-liquored. Raw hide such as cowhide can be put through the customary processing steps of soaking, liming, unhairing, baking, pickling, chrome and/or vegetable tanning, sorting, splitting to weight and shaving to even. The side leather is then ready to be fat-liquored and colored if necessary.

It is also possible to add after the moldanting step a intermediate drying step preparatory to being dyed and fat-liquored with a complex chromium compound.

It is also possible to add after the moldanting step a synthetic resin such as styrene-maleic anhydride tanning agent as a filler and also eliminate the conventional time-consuming drying step, going directly to the fat-liquoring processes of this invention.

In the processing of side leather a retannage involving a small amount of vegetable extract 2b (12b) or a resin 2b (12b) after the chrome tanning 2a (12a) step is preferred. This assures better penetration of the chrome complex 3 (13) and exhaustion of it from the fat-liquoring composition. Most fat-liquors except possibly those of the alkaline types can be employed without difficulty. However, it will be understood that wetting agents should not be used.

While I have described sheepskin and side leather, it will be readily recognized that the processes of this invention can be applied to other types of skins being processed into finished leather such as calf skin, kidskin, horse, pigskin, deer skin, kangaroo, chamos, kip and the like.

While leather prepared in any manner may be treated according to the processes of this invention, the pH of the leather is important. It is generally found desirable to have the leather at a pH of from about 4 to 5 although leathers having pH as low as 2.5 or lower can be satisfactorily fat-liquored in accordance with my invention.

It will be understood that the leather may be fat-liquored with the chrome compositions prior to, or subsequent to dying, or partially at each of these times.

The considerations as to the type of apparatus to use, the time to be allowed for fat-liquoring, the temperature of fat-liquoring, and the amounts of fat-liquoring composition are substantially those known to the art in connection with prior art fat-liquoring processes.

The time allowed for fat-liquoring with a complex chromium compound should be sufficient to permit substantial exhaustion of the fat-liquoring composition. With sheepskin suede, for example, a period of at least 30 minutes is recommended for practical usage. Generally the period for fat-liquoring will not exceed 1½ hours. The preferred time for fat-liquoring side leather with a carboxylate chromic chloride is from about ½ hour to 2½ hours.

The fat-liquoring can best be effected at temperatures of from about 70° to about 130° F. but temperatures outside this preferred range could suitably be employed if desired. In the case of suede leathers, the leather following dyeing is preferably washed at 70°-130° F. prior to treatment in accordance with the present invention in order to eliminate foam, to improve dye leveling by removing unreacted dye, and to adjust the leather to the proper temperature.

The leather is floated in water according to conventional practice following washing and drainage. The exact amount of water to use can best be determined by a few simple tests under the specific conditions of the process selected and with the specific leather to be treated. High floats such as 8 parts of water per 1 part of leather (over 100 gal. percent) may be used. Low floats, say 4 parts of water to 1 part of leather, are also satisfactory.

The exact amount of the fat-liquoring composition to use is readily determined by a few simple experiments under the precise conditions selected and with the specific leather to be treated. For fat-liquoring sheepskin suede the preferred amount of fat-liquoring composition containing about 30 percent of the Werner-type chromium complex to be used ranges from about 10 to about 25 percent by weight based on dry leather. On a basis of wet weight of the leather the chromium complex is applied in concentration of from about 5 to 15 percent. For side leather, 10 to 40 percent by weight of the fat-liquoring composition is preferably employed. In general, enough of the fat-liquoring composition must be used to effect the fat-liquoring desired but unduly large amounts should not be used as they will not be taken up by the leather in a reasonable period.

In order to avoid local action and waste, the fat-liquoring compositions are generally diluted with water before they are added to the leather.

It will be understood that fat-liquoring compositions containing a chromium compound of the Werner-type may be used together with raw oils such as, for instance, mineral and neat's foot oil to enhance color value, or in the case of side leather to supplement the fat-liquoring effect of the Werner type chrome complex. The Werner type chrome complexes in my fat-liquoring compositions serve as cationic emulsifying agents for the raw oil. The raw oil is added to the chrome complex and the resulting mixture then added to the water system.

As already indicated, acid and alkali resistant, water repellent leather can be produced by first treating the tanned skins with conventional fat-liquor compositions and applying a chrome complex of the type described above. In this fat-liquoring operation the range of concentrations of the fat-liquoring oils is from about ½ to about 6 percent. However, in some instance the total concentration of fat-liquors may be as high as 20 percent based on the wet weight of the leather. The limiting factors on oil concentration is maintenance of water resistance and softness of the leather. An excessive amount of oil causes the leather to be too soft.

A typical operating procedure for applying chrome complex to a conventionally fat-liquor side leather consists of the following three steps:

1. After the last wet operation (dyeing or fat-liquoring) the drum is drained and a new float is introduced at about 100° F. and adjusted to a pH of from 3 to 3.5 with a monobasic acid such as formic acid. These conditions are necessary to limit the reaction rather than to allow the proper penetration of the complex throughout the hides.

2. The chrome complex is then added in an amount equal to 6 to 10% of the weight of the skins after splitting and shaving.

3. The skins are drummed for from 30 minutes to 1 hour. The time actually required will be dependent upon the type of drainage employed.

Alternatively, the chrome complex can be applied to the tanned leather prior to, or concurrently with, conventional fat-liquors. Such fat-liquors may be of the cationic, anionic or nonionic type. The resulting leather is water-repellent, alkali and acid resistant.
Upon exhaustion of the chrome complex composition, it is preferred to wash the leather with room temperature water. The purpose of this washing is to remove unreacted chrome complex compound, dye and any possible side reaction product between dyestuff and chrome complex. If foam is present, it is readily removed by such washing.

As indicated above, the leather to be fat-liquored with a chrome complex may be dyed with any of a wide variety of dyestuffs customarily used in the art and treated with conventional finishing compositions to obtain commercially acceptable leathers.

Leather treated in accordance with the processes of my invention finds wide use in leather garments, shoes, gloves, gaskets, belting, luggage and the like. The leather obtained according to the present invention has a satisfactory handle or feel comparable to leather produced solely with conventional fat-liquors. The leather is not greasy. Further, the leather is water resistant but still permeable to moisture vapor.

Leather obtained using a Werner type chrome compound of at least 10 carbon atoms as the sole fat-liquoring agent is also resistant to dye bleeding both in water and solvents, the former being of importance in the normal wear of the garment; while the latter is of importance in preventing dye fading or washout when the garments, particularly those of suede, are dry-cleaned. Thus, leather fat-liquored without use of conventional fat-liquoring oils retains its good appearance and feel after solvent dry cleanings.

The water resistant properties of the leather produced by the process of the present invention were measured by a dynamic absorption test involving a 20-minute immersion in water at 80°F. Conventionally fat-liquored leather absorbs approximately 150–200 percent water in this test, but leather fat-liquored with the compositions of the invention absorb only 20–50 percent water. The water absorbent capacity of leather fat-liquored with chrome complexes alone remains substantially unchanged after 3 cleaning cycles with dry cleaning solvent or neutral soap and water at 120°F.

Side leather produced by a process comprising (1) chrome-tanning hides of steer, cow, or kip, (2) re-tanning with from 3 to 50 percent of quebracho crystals or extract (or wattle, chestnut or combination of syants such as styrene-maleic anhydride, and wood extracts), (3) fat-liquoring with conventional fat-liquors, (4) dyeing, and (5) applying a chrome complex of at least 10 carbons, is outstanding in its resistance to chemicals. For example, such leather is resistant to 98 percent sulfuric acid, 70 percent nitric acid, 85 percent lactic acid, 36 percent hydrochloric acid, 25 percent caustic, concentrated ammonia, nitrobenzene and the like. The resistance of such leather to lactic acid, which is present in perspiration, makes the leather of particular value in the inner sole field and in the manufacture of white shoes such as those worn by nurses. Such side leather is also useful for safety shoes and for farmer shoes and boots in view of their repeated exposure to manure and urine.

Actual wear-tests of matched pairs of shoes—one made of leather treated with a chrome complex in accordance with the invention and the other of untreated leather—clearly shows that a chrome complex having at least 10 carbon atoms imparts properties to side leather which are more important than water resistance alone.

Leather treated with a chrome complex in accordance with the invention gives consistently a tighter grain structure. This factor of tighter grain structure promises to enable the tanner to produce a higher percentage of high-quality and shoes made of this leather keep their good appearance longer.

Shrinkage or dimensional stability is another characteristic common to side leather treated in accordance with this invention. A chrome complex treated shoe keeps its shape and fit, while the untreated shoe stretches, tears out stitches, and loses its fit, comfort and appearance. In the shoe factory dimensional stability promises to reduce rejections and to increase the efficiency of workmen.

Still another characteristic common to side leather treated with chrome complex according to the invention is better finish. In wear-tests, this shows up as less tendency to scuff. Polishing tends to give the leather a more pleasing appearance, even after severe wear. In the tannery, finish adheres better to leather treated with chrome complex, and the leather appears to take less finish to give desired coverage. In manufacturing shoes, improved adhesion of the finish promises fewer rejections and better efficiency.

As has already been indicated, resistance to chemicals such as strong acids and bases is particularly conspicuous in leather treated with a chrome complex according to the present invention.

Resistance to perspiration is another feature of such leather. When swatches of chrome-tanned, vegetable tanned leather were subjected to 9 cycles of synthetic perspiration by a procedure recommended by the Tanners’ Council Research Laboratory, the swatch without chrome complex treatment broke when flexed the first time, while the treated one remained pliable and strong even after 8,000,000 flexes. Likewise, in the Gustafson perspiration test, the leather which was processed with a chrome complex in accordance with the process of my invention maintained its original properties, while the untreated material was destroyed when subjected to one cycle of the aforementioned test procedure.

As already indicated, water resistance is an important characteristic of the side leather which has been treated with a chrome complex. Shoes made from leather treated with a chrome complex absorbed only 14 to 18% of their dry weight. In contrast, shoes made of comparable leather without the complex absorbed 80 to 100%. In manufacturing shoes, the factor of water resistance carries with it the promise of greater stability as to moisture content, fewer rejections and higher efficiency.

The processes of the invention can be more fully understood by further reference to the drawings. There is shown in FIGURE 1 a cross section of a swatch of leather which has been subjected to one of the processes of the invention. The wavy lines represent fibrils or small leather fibers. It will be noted that there are many more fibrils near the surface or top of the leather. But regardless of their particular position in the swatch, the individual fibrils are substantially identical.

As has already been indicated, FIGURE 2 is an enlarged view of a typical fibril of FIGURE 1. It illustrates a modified fibril in which the collagen (leather protein) of the fibril 1 has been chrome-tanned, optionally retained, fat-liquored with a conventional oil, and then with a chrome complex 3 according to the invention. The collagen core 1 is surrounded with a chrome-reactive layer 2, which in turn may be composed of several distinct sublayers or envelopes—chrome tan layer 2a and layer 2b resulting from a vegetable extract retannage or from fat-liquoring with an anionic agent. Finally, an outer coating of chrome complex 3 surrounds intermediate shell 2 which in turn envelops the fibril 1.

The circles in FIGURE 3 give a diagrammatical comparison of fibrils 1 and 11 before and after treatment according to processes of the invention.

The circle at the extreme left of FIGURE 3 is an enlarged view of the inner circle of FIGURE 4 and shows the two individual fibrils 1 and 11 in section near the juncture of the two. The fibrils in this circle have not been tanned or treated in accordance with the invention. The small space 5 between the fibrils 1 and 11 is a void into which only a very limited amount of air or water vapor can penetrate. Hides composed of bundles of such fibrils are unworkable.
The second circle of FIGURE 3 shows two fibrils 1 and 11 of A of FIGURE 4 in a similar position but this time the skin substance has been tanned with chrome and the fibrils 1 and 11 are coated with chrome layers 2 and 12. Water 4 is shown to have penetrated into the void between the two fibrils 1 and 11. Accordingly, this circle illustrates the prior art.

The center or middle circle of FIGURE 3 is a view of two fibrils 1 and 11 which have been tanned and the chrome-tanned layers 2 and 12 coated with chrome complexes 3 and 13 according to the invention. No aqueous layer is present between fibrils 1 and 11 but there is still sufficient space between fibrils 11 and 11 for water vapor to pass thru. In other words, the leather containing such fibrils is water-repellent but it can breathe.

The chromium in the chrome complexes 3 and 13 is shown as a circle at the end of the black bar, the solid-linked bar representing the organic tail or hydrocarbon end of the complex. The chromium is chemically bound to the collagen of the fibrils 1 and 11 thru the chrome or chrome-reactive layer 2. The bond is so firm that the complex 3 stays anchored to layer 2 which in turn permanently envelopes the fibril core 1. This chemical union of chromium to the chrome-reactive layer 2 (shown in the fourth circle of FIGURE 3 as chrome-tan layer 2a and anionic modifier layer 2b) aids in the penetration and lubrication of the leather fibrils. This means the fibrils move smoothly when the leather is flexed and hence cracking is reduced. The organic portions of the chrome complex 3 or 13 are long chain hydrocarbon groups that stick out from the surfaces of fibrils 1 and 11, giving them water resistance and better adherence for leather finishes. By virtue of their hydrophobic properties these hydrocarbon ends resist the penetration of liquid water into the void between fibrils 1 and 11 but allow for the passage of water vapor therebetween.

In the fourth circle of FIGURE 3, viewed from left to right, there is shown in cross section fibrils 1 and 11 which have been treated in accordance with a preferred process of the invention. The fibrils have been tanned with chrome 2a and 12a and then subjected to a treatment with an anionic fat-liquor 2b and 12b preferably after retanage with a vegetable extract.

The remaining circle of FIGURE 3 illustrates the non-water repellency of the two fibrils 1 and 11 which have been tanned 2a and 12a, retanned and fat-liquored with conventional oils 2b and 12b but not treated according to my invention. Instead of the fibrils 1 and 11 being enclosed in an outer shell of a chrome complex, they are merely covered with chrome-tan layers 2a and 12a and chrome-reactive (anionic modifying) layers 2b and 12b. These fibrils possess none of the beneficial properties of the fibrils of circles three and four which are enclosed in a unique chrome complex layer such as 3 or 13.

It will be understood that the above explanation of the mechanism of the preferred processes of the invention is based on the best data available to the applicant. The results of the invention are, however, independent of such explanation.

Reference should now be had to the following illustrative examples:

Example 1
Chrome tanned sheepskin suede leather in a crusted condition without fat-liquor is wet back with water and in some cases wetting agent and dye according to standard leather practices. The final pH of the leather is about 4.0.

After the washing operation is completed following dyeing the leather is allowed to drain completely. The temperature of the wet leather is about 120°F.

The wet but drained colored sheepskin leather is floated in water using four gallons of water per ½ dozen skins. The water used is at room temperature. The ½ dozen skins weigh about 6 pounds dry. One and one-half pounds of fat-liquoring composition containing 30% by weight stearato chrome chloride is diluted with 1 gallon of "room temperature" water and added to the floated leather in a drum or paddle wheel.

The leather is drummed in the stearato chrome chloride solution for a period of about 30 minutes. Optionally, it can be run until maximum exhaustion takes place.

After exhaustion, the leather is drained, washed at room temperature, drained again, set out and dried in the conventional manner. Following drying, the leather is finished in a conventional fashion to give dry-cleanable, water-resistant, pliable leather product.

Example 2
Six parts by dry weight of chrome tanned side leather following splitting and shaving is treated with quebracho extract in water according to standard leather practice. The leather is allowed to drain. The drained extract-treated side leather, adjusted to pH 2.5 with hydrochloric acid, is floated in water.

About 2 parts by weight of fat-liquoring composition containing about 30% stearato chrome chloride and 6% raw neat's-foot oil are diluted with 4 parts of water and added to the floated leather. The leather is drummed in the stearato chrome chloride solution for about 2 hours. After the solution is exhausted, the leather is drained, set, dried and finished in a conventional manner. The resulting leather is water-resistant.

Example 3
Sheepskin suede leather is fat-liquored in a manner identical with that described in Example 1, except that a fat-liquoring composition containing palmitato chrome chloride is employed instead of stearato chrome chloride. The resulting leather is dry-cleanable and has bleef resistance in water and solvent.

Example 4
Fat-liquoring of sheepskin suede leather is effected in a manner similar to that described in Example 1 using oleato chrome chloride. The resulting leather is water-repellent, pliable and mellow.

Example 5
Ten parts by weight of conventional army retan leather at pH 2.5 (after vegetable retan but before conventional stuffing) in fat-liquored as follows:

About 2 parts by weight of a fat-liquor composition containing about 30% stearato chrome chloride are diluted with 80 parts of water at room temperature and added to the drained wet leather in a suitable drum. The leather is drummed in this fat-liquoring composition for about 2 hours in which period exhaustion of the complex occurs. The leather is drained, set out, pasted and finished according to conventional practice. The resulting leather is water resistant.

Example 6
Fat-liquoring of sheepskin suede leather is effected in a manner similar to that described in Example 1 using abietato chrome chloride. The resulting leather is very water resistant and pliable. Similar results are obtained with fat-liquoring compositions containing individually or jointly such Werner type complexes as for instance capratoo chrome chloride, laurate chrome chloride and a complex prepared by reacting basic chrome chloride with a mixture of saturated fatty acids having 20 or more carbon atoms.

Example 7
Cowhide is chrome tanned by drumming the hide with 7 percent basic chrome sulfate containing 22.5 percent Cr₂O₃ for a period of four hours. Sodium bicarbonate (1½ percent) is added to the hide to fix the chrome in the hide. The hide is then drummed for one hour to obtain penetration of the sodium bicarbonate. The hide is drained, washed and pulled out of the drum. The
leather is split to the desired thickness. The skins are wet back. Twelve percent of quebracho extract based on the split shaved weight of the skins is added. The resulting mixture is drummed for a period of one hour. Ten percent based on split shaved weight of a composition consisting essentially of sulfated near-foot and sulfated cod oil is added as a fat-liquoring agent. Fat-liquoring requires about one hour. One percent egg yolk is added, and the mixture run 20 minutes. After drainage the leather is dyed, the dying being added in amount of 2 percent based on split shaved weight. The leather is then run and set with formic acid. It is dried and rinsed to adjust the temperature to 100°F. An isopropanol solution of steararic acid chloride having a water content of from 3 to 6 percent by weight of the solution is added in an amount based on split shaved weight of about 10 percent. The leather-chrome complex solution is drummed for one hour. The leather is removed and found to be water-resistant, acid-resistant and alkali-resistant.

Example 8

In a manner substantially identical with that described in Example 7, cowhide is chrome tanned with 8 percent Tanolin R, retained with 12 percent quebracho extract, fat-liquored with a composition containing 10 percent by split shaved weight of sulfated near-foot combined with sulfated fish oil and 1 percent egg yolk. The fat-liquored leather was dyed and finally treated with stearic acid chloride in isopropanol. Based on the split shaved weight of the leather, the amount of chrome complex modicity (isopropanol solution of steararic acid chloride containing 6 percent chromium) applied to the leather was about 10 percent. The resulting leather is well suited for shoe uppers.

Example 9

Using a tanning process related to that described in Example 7, steer hide is tanned with 6 percent Tanolin R, retained with a mixture consisting of 7 percent quebracho and 7 percent wattle, dyed, fat-liquored with a composition consisting of 2 percent cationic sperm oil, 4 percent sulfated fish oil, and 2 percent emulsified fish oil. To this fat-liquored leather, 7 percent "Quilon" chrome complex is added to render the leather water-resistant, acid- and alkali-resistant.

1. In an after-tanning process for treating leather the step which comprises lubricating the leather by applying thereto a composition containing as an essential ingredient a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms at a temperature and for a time sufficient to effect lubricating of said leather.

2. In an after-tanning process for treating leather, the step which comprises applying to the leather a fat-liquoring composition containing as an essential active fat-liquoring ingredient a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms at a temperature and for a time sufficient to effect lubricating of said leather.

3. In an after-tanning process for treating leather, the step which comprises applying to already tanned leather a fat-liquoring composition containing as an essential active fat-liquoring ingredient a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms at a temperature and for a time sufficient to effect fat-liquoring of said leather.

4. In an after-tanning process for treating leather, the step which comprises applying to the previously tanned leather a fat-liquoring composition comprising a fat-liquoring oil in an amount up to about 20% based on the wet weight of the leather and, in an amount up to about 40% based on the wet weight of the leather, a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms, at a temperature from about 70 to 130°F. for a period of one-half to two and one-half hours.

5. In an after-tanning process for treating leather, the step which comprises applying to the already tanned leather a fat-liquoring composition containing as an essential active fat-liquoring ingredient a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms, at a temperature from about 70 to 130°F. for a period of one-half to two and one-half hours.

6. In an after-tanning process for treating leather, the steps which comprise as a first step applying to the already tanned leather a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms and, as a second step, applying to the treated leather a fat-liquoring oil, the two-step treatment being carried out at a temperature and for a time sufficient to effect fat-liquoring of said leather.

7. The method for effecting the fat-liquoring of already tanned leather wherein the compound comprises applying to the leather a fat-liquoring composition containing as an essential active fat-liquoring ingredient a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms, the two-step treatment being carried out at a temperature and for a time sufficient to effect fat-liquoring of said leather.

8. In an after-tanning process for treating leather, the step which comprises applying to the already tanned leather a fat-liquoring composition containing as an essential active fat-liquoring ingredient a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms, at a temperature and for a time sufficient to effect fat-liquoring of said leather.

9. In an after-tanning process for treating leather, the step which comprises applying to the already tanned leather a fat-liquoring composition containing as an essential active fat-liquoring ingredient a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms, at a temperature and for a time sufficient to effect fat-liquoring of said leather.

10. In an after-tanning process for treating leather, the step which comprises applying to the already tanned leather a fat-liquoring composition containing as an essential active fat-liquoring ingredient a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms, at a temperature and for a time sufficient to effect fat-liquoring of said leather.

11. In an after-tanning process for treating leather, the step which comprises applying to the already tanned leather a fat-liquoring composition containing oleic acid chloride, at a temperature and for a time sufficient to effect fat-liquoring of said leather.

12. In an after-tanning process for treating leather, the step which comprises applying to the already tanned leather a fat-liquoring composition containing oleic acid chloride, at a temperature and for a time sufficient to effect fat-liquoring of said leather.

13. In an after-tanning process for treating leather, the step which comprises applying to the already tanned leather a fat-liquoring composition containing as an essential fat-liquoring ingredient a Werner complex compound in which a trivalent nuclear chromium atom is coordinated with a carboxylic acid group having from 10 to about 25 carbon atoms, at a temperature from about 70 to 130°F. for a period of one-half to two and one-half hours.
ing from 10 to about 25 carbon atoms, at a temperature and for a time sufficient to effect fat-liquoring of said leather.

14. In an after-tanning process for treating leather, the step which comprises applying to the already tanned leather a fat-liquoring composition containing abietato chromic chloride, at a temperature and for a time sufficient to effect fat-liquoring of said leather.

15. A composition of matter comprising a fat-liquoring oil and as an essential fat-liquoring ingredient a Werner complex compound in which trivalent nuclear chromium atoms are coordinated with carboxylic acid groups having from 10 to about 25 carbon atoms, said fat-liquoring oil and said Werner complex compound together being present in a total amount sufficient to effect the fat-liquoring of already tanned leather, and said fat-liquoring oil and said Werner complex compound being mutually compatible.

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