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TANNING

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This invention relates to the production of leather. It is more particularly directed to the tanning of skins by first subjecting them to an acidic polymeric material in which the acidity is due to carboxyl groups attached to aliphatic carbon atoms and thereafter treating the skins with a soluble salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium. The invention is also directed to the leather produced.

The conversion of skins into leather is accompanied by profound changes in their physical characteristics. They become opaque, and a distinct fibrous structure becomes apparent. The stiffness characteristic of dry rawhides disappears to a great extent and they become comparatively flexible. They assume a characteristic attractive appearance and soft "feel." Tanning also renders the product imputrescible. For useful tanning these changes must be relatively permanent, and the leather should be resistant to de-tanning by water, at least at ordinary temperatures.

The ancient and well-developed art of tanning customarily effects the conversion of skins into leather by the use of vegetable preparations that contain tannins. Vegetable tanning materials, such as quebracho extract, are quite slow in their action, and tanning processes employing them require excessively long periods of time for completion. The leather produced using vegetable tanning materials is characteristically colored, and it is difficult to obtain good true colors upon dying. It is particularly difficult to produce satisfactory light-colored leather.

Tanning processes employing metal compounds, such as chromium sulfate, are also known. Such processes are, however, subject to a number of disadvantages in operation, and the leather produced is characteristically colored. White leather, so-called, can be produced by employing bleaching if required, but this leather is not truly white since it has a distinct blue, yellow, green, or gray tint.

Numerous synthetic tanning materials have been proposed, but these are markedly inferior to the vegetable or metal compound tanning agents mentioned. In some instances the leather produced with known synthetic tanning agents is not sufficiently resistant to de-tanning by water, and in other cases the leather lacks the necessary "fullness" and "plumpness." Therefore, these synthetic tanning materials of the prior art are customarily used in conjunction with a vegetable tanning material or a metal compound tanning agent, and they are useful principally because of properties apart from their characteristics as tanning agents.

Recently there have been developed greatly improved tanning processes involving the use of an acidic polymeric material in which the acidity is due to carboxyl groups attached to aliphatic carbon atoms. These processes produce leather of good color and the leather is additionally of good character, being opaque, soft, "full," and flexible.

While the leather produced by these recently developed processes employing an acidic polymeric material is of good character, it has some undesirable characteristics including a tendency to become detanned by the alkaline finishes commonly used in the art and it sometimes displays a "papery" quality and a lack of water repellence.

It is an object of this invention to improve these recently developed processes involving the use of an acidic polymeric material. It is a further object to provide processes which are rapid, simple, and easily controlled and which do not greatly increase the difficulty of employing the recently developed tanning processes. It is a still further object of this invention to provide tanning processes by means of which there may be produced a very high quality of leather. It is a still further object of this invention to provide processes which produce a quality of leather suitable for finishing with alkaline materials frequently used for the treatment of white leather. It is another object of this invention to produce a good quality of white leather. Still further objects will become apparent hereinafter.

These and other objects of my invention are attained by processes involving first tanning skins with an acidic polymeric material in which the acidity is due to carboxyl groups attached to aliphatic carbon atoms and then after tanning is thus effected treating the leather produced with a water-soluble salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium. In the preferred embodiments of the invention the leather is treated with aluminum sulfate or ferric sulfate. The leather produced resists detanning by alkaline finishes and it has excellent general character, being considerably improved as to water repellence and being "fuller" and "plumper."

The processes of this invention may be used for the treatment of any type of skin adapted to be converted into leather or fur. It is to be observed that the term "skin" is used generically

to include heavy skins such as cowhide, lighter skins such as goatskin and calfskin, and also skins of fur-bearing animals. It will naturally be necessary to adapt the processes to the type of skin to be treated. For instance, goatskin may be more rapidly tanned than calfskin, but those skilled in the art are well aware of such factors and may readily adapt the agents of this invention to the specific needs of particular specialized problems.

Skins to be tanned according to the processes of this invention may be prepared in any of the manners customary in the art. They may suitably be unhaired, limed, delimed and bated, and pickled. The skins may if desired be de-pickled. They may also be given a salt liquor treatment to soften them up and to render them of more uniform condition as is the practice in prior art tanning processes.

While skins prepared in any manner may be treated according to the processes of this invention, the pH of the skins is important. As will be observed below, the tanning is effected at certain conditions of acidity and the skins may tend to change these conditions. The tanning solution may suitably be controlled to compensate for any variance of the pH of the skins from that of the tanning solution. It may sometimes be found advantageous to adapt the processes for preparing the skins so that a skin prepared for tanning is approximately at the pH of the tanning solution.

Too rapid reaction of the tanning agent with the skin in the first stages of the process should be avoided in order to prevent surface hardening of the skin. In tanning with acidic polymeric tanning agents this result is accomplished by careful adjustment of the pH of the tanning solution. The exact acidity of a tanning solution containing a polymer according to this invention may be widely varied depending upon the specific type of skin to be treated and depending upon the specific type of leather to be produced. While a wider range of acidity may be used, it will generally be found desirable to have the tanning solution initially at a pH from about 4.7 to 5.0. Still more specifically, it will be found that under many conditions of operation a pH of about 4.75 is optimum. At a pH much below 4.7 the affinity of skins for the polymerization products becomes so great that surface hardening takes place, while at a pH much above 4.7 the affinity of the hides for the tanning agent is so decreased that penetration is not sufficiently rapid for the best results.

The acidity of the polymerization products may suitably be adjusted by the use of such alkalies as alkali metal hydroxides or carbonates, ammonium hydroxide, and organic bases such as ethanolamines. As has been observed before, the pH of the hide should be considered in adjusting the pH of the tanning solution so that the tanning solution will be employed at an acidity within a desired range. To assist in maintaining the tanning solution at about the optimum acidity a suitable buffer salt such as sodium acetate or sodium phosphate may be included in the tanning solution.

After satisfactory penetration of skins by the tanning agent has been effected the rate of tanning may be accelerated by lowering the pH of the solution. The pH to which the solution should be brought to effect complete tanning will vary considerably with the specific type of skin being treated. It will not generally be desirable to go to a pH below about pH 3 since, at a higher hydrogen ion concentration, hydrolysis of the skin may take place. As a practical matter it will be found that the pH should be lowered to about 3.4 to 4.2, while more specifically it will be found that in many processes a pH of about 4 will be most satisfactory.

The lowering of the pH of the tanning solution may suitably be effected by the use of any acidic material such as lactic, hydrochloric, sulfuric, acetic, phosphoric, sulfamic, and formic acids.

The considerations as to the type of apparatus to use, the time to be allowed for tanning, the temperatures of tanning, and the amounts of tanning agent are substantially those known to the art in connection with prior art tanning processes. The time allowed for tanning must be sufficient to permit complete penetration of the tanning agent and the pH should not be lowered too rapidly or there may be puckering and apparent over-tannage of the grain surface. The tanning can best be effected at room temperature, say 20° to 30° C., but temperatures somewhat higher than those used by the art can successfully be employed if desired. The exact amount of the tanning agent to use can best be determined by a few simple tests under the specific conditions of the process selected and with the specific skin to be treated. In general, enough of the tanning agent must be used to effect the tanning desired but unduly large amounts should not be used as they will not be taken up by the leather in a reasonable period of time.

The recently developed tanning agents with which a skin is treated as a first step in the processes of my invention are composed of an acidic polymeric material in which the acidity is due to carboxyl groups attached to aliphatic carbon atoms, that is, carbon atoms which are not a part of an aromatic nucleus. It is preferred to use as tanning agents acidic polymers of alpha-unsaturated aliphatic carboxylic acids, while still more specifically, it is preferred to use an acidic polymer of alpha-methacrylic acid.

The expression "acidic polymeric material in which the acidity is due to carboxyl groups" includes a wide variety of polymers all generically suited for use as tanning agents. Included are not only polymers in which the polymeric structure is built up by synthetic means, but also those in which the polymeric molecule is built up by nature, such as cellulose glycolic acid, alginic acid, and pectic acid. The suitable acidic synthetic polymers include, not only the self-polymers and interpolymers of polymerizable aliphatic carboxylic acids, but also acidic condensation polymers, e. g., those in which an aliphatic polycarboxylic acid, such as citric acid or tricarballylic acid, is reacted with a polyhydric alcohol, such as glycerol.

As already indicated, best tanning results are obtained with polymerization products of alpha-unsaturated aliphatic carboxylic acid. Examples of such are the self-polymers of acids of the acrylic series such as polyacrylic acid, polyalpha-ethylacrylic acid, and polyalpha-methacrylic acid. Still other suitable polymerization products of alpha-unsaturated aliphatic carboxylic acids are the interpolymers of acids of the acrylic series with polymerizable materials, for example, styrene and methyl methacrylate. Mixtures of such polymerization products may of course be used.

The term "polymerization products of alpha-

unsaturated aliphatic carboxylic acids" also includes interpolymers of alpha-unsaturated dicarboxylic acids such as maleic acid or of maleic anhydride, its equivalent, with polymerizable materials such as styrene. Products obtained by interpolymerizing the alpha-unsaturated carboxylic acids with each other such as interpolymers of methacrylic acid with acrylic acid or with maleic anhydride, may be used. There is no particular restriction on the type of added polymerizable material except that it be one which does not destroy the free acidity of the final polymer, to which it is believed the tanning effect is largely attributable.

These recently developed tanning agents are preferably used in aqueous media. The preferred agents are water-soluble initially, as is polyacrylic acid and polymethacrylic acid, or are capable of being brought into solution with aqueous alkali metal hydroxides, amines, or other bases, as are the interpolymers of maleic anhydride with styrene. For best results the solubility in either instance should be such that the solution may be brought to the proper pH for tanning without precipitation of the tanning agent. In some instances, however, agents that are moderately or even only slightly soluble can be used with some degree of success, due possibly to the fact that, as the small amount in solution is used up, a small additional amount of the polymer in turn goes into solution, and so on.

As examples of acidic polymeric materials which may be used for the tanning of skins there may be mentioned heat-polymerized polymethacrylic acid prepared by heating methacrylic acid with benzoyl peroxide as a catalyst, polyacrylic acid prepared by heating acrylic acid with benzoyl peroxide in toluene, a polymeric polycarboxylic acid which is a hydrolysis product of methylacrylate polymer and is prepared by heating methylacrylate polymer with toluene and adding potassium hydroxide in ethyl alcohol, acrylic acid-methacrylic acid interpolymer prepared by heating acrylic acid with methacrylic acid in toluene with benzoyl peroxide catalyst, and maleic anhydride-styrene interpolymer prepared cautiously heating together equal parts of styrene and maleic anhydride.

As will be apparent from the list of illustrative polymeric materials the acidic polymers suitable for use as tanning agents may be made in a number of ways. The polymerization may be effected by any of several well-known procedures, such as at elevated temperatures with benzoyl peroxide as a catalyst and in the presence of solvent or dispersion media such as acetone, toluene, or water, or by heating in the presence of a solvent and in the presence or absence of a catalyst, or by exposure to ultra-violet light.

Tanning action is affected to a certain extent by degree of polymerization and the latter in turn, as is well known, by polymerization conditions. It is known, for example, that in the polymerization of acrylic acid the temperature at which the reaction is carried out markedly influences the molecular weight of the polymer. As shown by Staudinger, comparatively low temperature reactions tend to produce high molecular weight products whereas high temperatures have the opposite effect. In the work leading to the present invention it was found that these relationships were correct and that the tanning results vary somewhat with the different types of polymers. For example, when polymerization of acrylic acid was effected at room temperature by exposure to ultra-violet radiations, the product was a glassy, brittle, solid which was difficult to dissolve in water. This agent tanned only slowly and yielded a product lacking in opacity and fullness. Polymerization in a low-boiling solvent such as acetone, at a temperature of 60° C. or less, also yielded an agent which produced relatively inferior leather. The poorer tanning effect of these high molecular weight polymers may be due to the relatively poorer penetration of the polymer into the skin.

On the other hand, as shown in the examples, polymerization by heating to high temperatures without a solvent or in a high-boiling solvent such as toluene at a temperature above 100° C., yielded readily water-soluble products which produced good leather. Whereas these superior materials were polymerized to high molecular weight as shown by the fact that they are amorphous solids, their ready solubility in water indicated that they were much lower in molecular weight than the agent produced, for example, by polymerizing acrylic acid at room temperature by means of ultra-violet light.

It is understood that the above applies chiefly to acrylic acid and merely illustrates one of several instances in which somewhat different tanning results may be expected with polymers prepared by different methods.

In addition to the polymers above listed, the following polymerization products are also illustrative of polymeric tanning agents suitable for use in the processes of this invention. These are given in tabular form for convenience.

The proportions given in parentheses in the table refer to proportions of the constituents found in the polymers upon analysis; the other figures given under the heading "Materials polymerized" indicate the initial proportions of the starting material.

Polymerization products of alpha-unsaturated acids

Material polymerized	Method of preparing polymer	Appearance of product	Solubilities
Alpha-ethyl acrylic acid	Monomer exposed to ultra-violet light for five days.	Opaque, white solid.	Soluble in dilute sodium hydroxide.
Acrylic acid 75:styrene 25 (82:18)	15 percent solution of monomers in toluene at 100° C. for 30 minutes with 1 percent benzoyl peroxide.	White powder	Do.
Alpha-ethyl acrylic acid 83:styrene 17.	Monomers exposed to ultra-violet light for four days.	do	Do.
Methacrylic acid 50:maleic anhydride 50 (92:8).	15 percent solution of monomers in toluene at 100° C. for 14 hours with 1.25 percent benzoyl peroxide.	do	Soluble in water.
Maleic anhydride 50:methacrylic acid 25:stryene 25.	15 percent solution of monomers at 90-100° C. for four hours with 1.25 percent benzoyl peroxide.	do	Soluble in dilute alkali.

Also illustrative of the broad type of polymeric compound above illustrated are the acidic polymers obtained by partial or complete hydrolysis of polymers or interpolymers of derivatives of alpha-unsaturated acids such as the esters, amides, or nitriles. One such polymer, the hydrolyzed methacrylate polymer, is mentioned above.

As has been noted above, one particularly satisfactory group of polymeric tanning agents are the acidic polymerization products of methacrylic acid. Among the tanning agents of this specific group there may be mentioned as illustrative polymethacrylic acid prepared by heating methacrylic acid in water with a small amount of benzoyl peroxide catalyst, polymethacrylic acid prepared by heating methacrylic acid in toluene with benzoyl peroxide as a catalyst, polymethacrylic acid prepared by exposing methacrylic acid to the action of ultra-violet light, partially hydrolyzed methyl methacrylate prepared by dissolving methyl methacrylate polymer in benzene and heating with potassium hydroxide in absolute alcohol, methacrylic acid-styrene interpolymer prepared by polymerizing five parts of styrene with thirty-five parts of methacrylic acid in toluene with benzoyl peroxide as a catalyst, methacrylic acid-methyl methacrylate interpolymer prepared by dissolving methylated starch in water, adding 87.5 parts of methacrylic acid and 12.5 parts of methyl methacrylate and effecting polymerization in the presence of a small amount of benzoyl peroxide.

In addition to the methacrylic acid polymers listed there is set out in tabular form for convenience a number of still further illustrative tanning agents of this group. All of these polymers, with the exception of the interpolymer of methacrylic acid with methacrylamide, which is a yellowish friable resin, are obtained as white powders of varying degrees of water and alkali solubility.

Methacrylic acid polymers

Material with which interpolymerized	Method of preparing interpolymer	Proportions*		Solubilities
		Original	By analysis	
Diethyl fumarate	15 percent toluene solution of monomers heated at 100° C. for 16 hours with 1.33 percent benzoyl peroxide.	50:50	83:17	Readily soluble in water.
Butadiene	25 percent solution of monomers in mixture of 14 parts of toluene and 1 part carbon tetrachloride heated for 24 hours at 65° C. with 1 percent benzoyl peroxide.	80:20	----------	Partly soluble in water. Readily soluble in dilute sodium hydroxide.
Vinyl acetate	15 percent toluene solution of monomers heated at 90–103° C. for 30 minutes with 1.25 percent benzoyl peroxide.	75:25	83.5:16.5	Soluble in water.
Unsym-dichlorethylene	15 percent toluene solution of monomers heated at 90–100° C. for 15–16 hours with 1.25 percent benzoyl peroxide.	75:25	86:14	Partly soluble in water. Readily soluble in dilute sodium hydroxide.
Indene	15 percent toluene solution of monomers heated at 90–107° C. for 1 hour with 1.25 percent benzoyl peroxide.	87.5:12	94:6	Do.
Vinyl chloride	25 percent toluene solution of monomers heated in autoclave at 65° C. for 24 hours with 1.0 percent benzoyl peroxide.	80:20	----------	Difficultly soluble in water. Readily soluble in dilute sodium hydroxide.
Vinyl chloroacetate	25 percent benzene solution of monomers heated 26.5 hours at 65° C. with 0.5 percent benzoyl peroxide.	50:50	72:28	Insoluble in water. Soluble in alkali.
Methacrylamide	15 percent toluene solution of monomers heated 16 hours at 90–100° C. with 1.25 percent benzoyl peroxide.	75:25	74:26	Difficultly soluble in water. Readily soluble in dilute sodium hydroxide.

*In both columns, the percentage of methacrylic acid is given first.

After a skin has been tanned with an acidic polymeric material as above described, it is then treated according to the present invention with a salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium. The treatment is effected by subjecting the leather to the action of a solution of the metal salt, the treatment being continued long enough to assure penetration of the hide by the metal salt solution.

While any soluble salt such as the sulfate, chloride, lactate, or acetate of aluminum, iron, titanium, copper, or chromium may be used, it is preferred to use salts of inorganic acids, particularly those which are neither strongly oxidizing nor reducing. More specifically, it is preferred to use a salt of an acid selected from the group consisting of nitric acid, sulfuric acid, hydrochloric acid, and sulfamic acid, and by far the best results have been obtained with the sulfates.

The polymers employed for tanning skins apparently form, probably through their free carboxyl groups, some kind of chemical complex with skins, and it is believed that the leather produced according to these methods comprises a reaction product of the acidic polymer with skin substance.

I believe that there is a great excess of carboxyl groups present, however, and it is impossible for all of these carboxyl groups to become tied up directly to the hide substance with the result that certain parts of the acidic polymer molecule are present as more or less active groups. I believe that the presence of these active groups accounts for the detanning of the leather by alkalies, for the lack of water repellence, and for the other undesirable characteristics heretofore noted.

When tanned skin is treated with a salt of aluminum, iron, titanium, copper, or chromium, I believe that the active carboxyl groups are rendered inactive without becoming separated from the hide substance and without separating carboxyl groups previously linked to the hide substance. The metal salt treatment of this invention, therefore, is not a neutralization of excess tanning agent but is rather a tying up of only those carboxyl groups in the molecule which have not become associated with the hide substance. The decrease in pore character of the leather, that is its decreased tendency to imbibe water after the treatment, tends to support this theory. The carboxyl groups unassociated with the skin substance thus are sequestered by the metal salt. I believe that the leather produced according to the present invention comprises a reaction product of the acidic polymer with skin sub-

stance, carboxyl groups unassociated with the skin substance being sequestered with a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

It will be understood that the acidic polymers may if desired be used together with other tanning agents or tanning assistants in manners known to the art. They may, for instance, be used in conjunction with vegetable tanning materials such as quebracho extract, with chrome tans, or with synthetic tanning agents containing sulfonic acid groups. The tanning assistants used in conjunction with the acidic polymers may be used simultaneously or may precede or follow the treatment with the polymer.

It will be found particularly satisfactory to effect tanning and subsequent treatment with metal salts in the presence of surface-active agents of the type often used as fatliquoring assistants. Particularly excellent results have been obtained using chlorosulfonated straight chain hydrocarbons, the treatment tending to improve the quality of the leather and having no deleterious action on the resistance of the leather to ultra-violet light.

The treatment with a metal salt may frequently be modified to advantage by the joint use of a soluble lactate, acetate, citrate, or tartrate or by using lactic, acetic, tartaric, or citric acids themselves.

The leather obtained according to the preferred processes of this invention is white but it may if desired be treated with white pigment or may be colored during or after the tanning process by the inclusion of any of the common leather dyes and pigments. The dyeing may be effected during the treatment with a metal salt.

Leather produced according to the processes of this invention may be subjected to any of the various kinds of finishing treatments customarily used. The leather if desired may be suitably filled or given any of the numerous surface treatments customary to the art. As has been observed above, the alkaline surface sizes such as the alkaline casein finishes commonly used in the art to treat white leather may satisfactorily be employed without undue difficulty.

In order that my invention may be better understood, reference should be had to the following illustrative examples:

Example 1

To a solution made up containing 9.5 pounds of sodium chloride, 13.5 pounds of sodium acetate, and 23 gallons of water contained in a tanning drum, is added 192 pounds of drained pickle weight of pickled kipskin. These skins are run in this solution for forty minutes. The tanning agent used is prepared by polymerizing a 10 per cent solution of methacrylic acid in water with 1.5 per cent of benzoyl peroxide (based on the weight of methacrylic acid) at about 80 to 100° C. The polymethacrylic acid produced is partially neutralized with sodium hydroxide to a pH of 5.2 and the partial sodium salt is then dried. Twelve pounds of this partial sodium salt is dissolved in 108 pounds of water, the solution added to the drum and the drum is run for three hours. The pH of the tanning solution is then adjusted to pH 3.5 by adding 10 per cent sulfuric acid at fifteen minute intervals during the course of four hours, with drumming. The skins are then piled down overnight.

Careful examination of the skins at this point shows that they have been completely tanned.

The tanned skins are placed in the tanning drum with the spent tanning liquor and 12 pounds of aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, is added. The drum is run one-half hour. The pH of the solution is adjusted to 3.9 by adding sodium bicarbonate. The skins are then removed, wrung out, shaved and neutralized to pH 4.7. The skins are then washed and fatliquored with a neat's-foot-sulfonated oil mixture of conventional character.

When the finished skins are compared with specimens of tanned skins without the alum treatment, it is found that the alum-treated leather is fuller, plumper, and has no tendency to be papery. The alum-treated leather shows less tendency to imbibe water, and in general, has decidedly improved leather characteristics.

Example 2

A maleic anhydride-styrene interpolymer tanning agent is prepared by mixing 50 grams of maleic anhydride with 50 grams of styrene and dissolving the mixture in 450 grams of xylene. To the solution is added 1 gram of benzoyl peroxide and the solution is then heated to the boiling point. Polymerization is rapid and is largely complete in about one minute. The product is isolated by filtration and dried.

Fifty parts by weight of pickled calfskins (drained pickle weight) is prepared for tanning by drumming for about one-half hour in a solution containing 5 parts of sodium chloride and 3 parts of sodium acetate in 83 parts of water. There is then added 20 parts by weight of a 1 per cent solution of the maleic anhydride-styrene interpolymer which has previously been hydrolyzed by boiling a 10 per cent solution of the polymer with 20 parts of sodium hydroxide per 100 parts of polymer. The skins are drummed in this maleic anhydride-styrene solution for about four hours. The pH of the solution is then lowered to 3.5 by the addition of 5 per cent sulfuric acid solution at one-quarter hour intervals over a period of four hours.

To the tanned skins contained in the spent tan liquor, there is added 2 parts by weight of aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$. The skins are drummed three-quarters of an hour, and then neutralized with sodium bicarbonate additions in small portions at one-quarter hour intervals until the pH has been raised to 4.7. The total time required for this neutralization is about three hours. The treated skins are then removed from the solution, washed, fatliquored with a neat's-foot oil-sulfonated oil mixture and dried in the usual manner.

When specimens of the tanned leather with and without the alum treatment are compared, it is apparent that the alum treatment has effected substantial improvement in the plumpness and feel of the leather and has reduced tendency to be papery and to imbibe water. The general leather characteristics of the treated material are also greatly improved.

Example 3

A tanning agent is prepared by dissolving 20 parts of maleic anhydride and 20 parts of vinyl isobutyl ether in 170 parts of toluene and then adding 1 part of benzoyl peroxide. After heating the solution to the boiling point, polymerization begins and proceeds vigorously. After the reaction mixture is cool the product is isolated and dried. Thirty-five parts of tanning material is obtained.

A quantity of calfskins is prepared for tannage by drumming 63 parts (drained pickle weight) of the calfskin for one-half hour in a solution containing 4.65 parts of sodium acetate and 4.65 parts of sodium chloride in 93 parts of water. Tannage of the skins is then effected by adding 15.4 parts of a 10 per cent solution of the above described, drumming for one-quarter hour, adding another 15.4 parts by weight portion, drumming for another one-quarter hour and continuing the addition until a total of 4 portions is added. The total weight of interpolymer thus added is 10 per cent of the drained pickle weight of the skin. After the last addition of the interpolymer, the skins are drummed for four hours. The solution is then acidified to pH 3.5 by adding successive portions of 5 per cent sulfuric acid solution and drumming after each addition, the total time required for the additions being four hours.

The tanned skins are then subjected to an alum treatment by adding to the skins in the spent tan liquor 1.6 parts of aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, (equivalent to 5 per cent of the drained pickle weight of the skin); 2.33 parts of sodium acetate; 100 parts of water; and 5 parts of sodium chloride. The skins are drummed for one hour and then neutralized to pH 3.9 by the addition of sodium bicarbonate, after which the skins are drummed for about fifteen minutes and are then removed, shaved, washed and neutralized to the desired pH suitable for fatliquoring. The skins are then fatliquored in a mixture of neat's-foot and sulfonated oils and dried.

The skins which have been treated with alum after tanning are strong, full, and well tanned and are in general of improved quality over those which have not received the alum treatment.

Example 4

A quantity of calfskins is prepared for tannage by drumming for twenty minutes, 970 parts (drained pickle weight) of the calfskin in a solution containing 68 parts of sodium acetate, 73 parts sodium chloride and 1455 parts of water. Tannage of the skins is then effected using a partial sodium salt of polymethacrylic acid prepared by polymerizing a 16 per cent solution of methacrylic acid in water with 2 per cent based on the weight of methacrylic acid of ammonium persulfate as a catalyst at a temperature of about 75 to 100° C. The polymethacrylic acid is partially neutralized with sodium hydroxide to a pH of about 5.2. Sixty parts of the sodium salt of polymethacrylic acid (equivalent to 6 per cent of the drained pickle weight of skins) is added to the drum and the skins are then drummed for two hours. The solution is then acidified to pH 4.25 by adding portions of 10 per cent acetic acid over a period of four hours with drumming. The skins are then removed from this liquor and placed in a solution made up with 1500 parts of water, 75 parts of sodium chloride, and 25 parts of 10 per cent acetic acid. The pH of the solution is then adjusted to pH 3.5.

To the tanned skins contained in the acidified solution there is added 35 parts by weight of aluminum chloride. The skins are drummed for one hour, after which the pH of the solution is adjusted to 3.8 by adding 30 parts of sodium acetate ($NaC_2H_3O_2 \cdot 2H_2O$). The solution is then neutralized to pH 5.1 with sodium bicarbonate, after which the skins are removed, washed, shaved, and fatliquored with a neat's-foot oil-sulfonated oil emulsion mixture.

When leather made without the aluminum chloride treatment is compared with that made with the aluminum chloride treatment, it is seen that a substantial improvement in the quality of the leather has been effected by the treatment.

Example 5

A quantity of kipskins is prepared for tannage by drumming 2070 parts (drained pickle weight) of the kipskins for twenty minutes in a solution containing 155 parts sodium chloride, 145 parts sodium acetate, and 3105 parts water. Tannage of the skins is effected by adding 1101 parts of an 8.93 per cent solution of the polymethacrylic acid tanning agent of Example 1 and drumming for three hours. The solution is then acidified to pH 3.5 by the addition of 10 per cent of sulfuric acid during the course of four hours.

To the drum containing the polymethacrylic acid tanned leather and the spent tan liquor is added 103.5 parts of ferric sulfate (as a 10 per cent ferric sulfate solution in water) equivalent to 5 per cent on the drained pickle weight of the skin. The skins are drummed for one-half hour, after which the pH is raised to pH 5.0 with 10 per cent sodium bicarbonate solution during the course of one hour of drumming.

When untreated leather is compared with that treated with the iron salts, it is found that a considerable improvement in plumpness of the leather has been effected by the iron salt treatment and the strength of the leather has been greatly improved. The iron-heated leather has a pleasing, uniform brown color.

Example 6

Twelve hundred twenty-one parts of pickled calfskin (drained pickle weight), is drummed for fifteen minutes in a solution made up by dissolving 85.5 parts sodium acetate, 146.5 parts of sodium sulfate in 1831 parts of water. To this solution is added 58.1 parts of the partial sodium salt of polymethacrylic acid of Example 4. The skins are drummed in this solution for three hours. The pH of the solution is then adjusted to pH 3.5 in the course of four hours of additional drumming.

To the tanned skins in the drum in the presence of the spent tan liquor is added 217 parts of a titanyl sulfate solution (9.5 per cent TiO_2 equivalent) equivalent to 1.68 per cent of TiO_2 on the drained pickle weight. The leather is drummed for two hours in this solution. It is then neutralized to a pH of approximately 4.5 with 10 per cent sodium bicarbonate during the course of aproximately four hours. The skins are then removed from the tanning drum, wrung, shaved and re-neutralized to pH 4.7 and fatliquored with an emulsion of neat's-foot oil and sulfonated oil and dried.

Example 7

A quantity of pickled calfskins is prepared for tannage by drumming 100 parts of pickled calfskins (drained pickle weight) in a solution of 150 parts water, 7.5 parts sodium acetate, 7.5 parts sodium chloride for twenty minutes. The skins are then tanned by adding to the solution 4.5 parts of the partial sodium salt of polymethacrylic acid of Example 1 and drumming for three hours. The solution is then adjusted to pH 3.5 by the addition of dilute sulfuric acid, during the course of four hours drumming. To the drum is added 5 parts of copper sulfate,

$CuSO_4 \cdot 5H_2O$, dissolved in 50 parts of water, and the drum is run for two hours, after which the solution is neutralized to pH 5.0 with 10 per cent sodium bicarbonate during the course of three hours drumming. The skins are then shaved, washed and fatliquored with neat's-foot oil-sulfonated oil emulsion in the usual manner. By comparison of treated and untreated skins, it is found that the treatment with copper sulfate improves the fullness of the leather and improves the general leather characteristics. The color of the treated leather is a pastel shade of green.

Example 8

A quantity of pickled calfskins is tanned with polymethacrylic acid as in Example 3 and is finished off at a pH of 3.4. A portion of this leather is then treated with alum in the following manner: To a solution containing 108 parts of a 10 per cent aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) solution, 13 parts of sodium chloride and 400 parts water contained in a tanning drum, there is added 180 parts of the polymethacrylic acid tanned leather. The pH of the solution is then adjusted by the addition of sodium bicarbonate to 5.08 over a period of twenty-six hours and a portion of the leather is removed. The pH is then sucessively adjusted to 5.98, 6.55, and 7.02 over about five hour intervals, and a sample of the leather at each pH is taken off. These pieces are shaved, washed and fatliquored in the usual manner.

The leather finished off at the various pH's is all found to be of good quality and to show a decided improvement in leather characteristics over the polymethacrylic acid-tanned leather before alum treatment.

Example 9

A quantity of kipskins is prepared for tannage by drumming in a tanning drum 136 parts drained pickle weight of kipskins in a solution comprising 9.5 parts of sodium acetate, 16.3 parts sodium sulfate and 204 parts water (this amount of sodium sulfate is equivalent to 12 per cent of the drained pickle weight of the kipskins). The The skins are then tanned with polymethacrylic acid by adding to the solution 8.4 parts of the polymethacrylic acid tanning agent of Example 4 in the form of the partial sodium salts containing the equivalent of 80.7 per cent polymethacrylic acid. The skins are drummed for one and one-half hours and then acidified to pH 3.4 by addition of dilute sulfuric acid in the course of five hours drumming. At this point the skins are completely tanned.

The tanned skins are then subjected to an alum treatment by adding to the spent tan liquor 6.8 parts of aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, (5 per cent of the drained pickle weight of the skins) and drumming for forty-five minutes. The solution is then neutralized to pH 4.8 with 10 per cent sodium bicarbonate during the course of four hours drumming, after which the skins are piled down overnight. The skins are then washed, shaved, and fat-liquored in the usual manner.

It is found that by this procedure the alum treatment exerts all its beneficial effect as previously noted and in addition, the grain of the treated leather is improved as compared with leather tanned and alum treated in substantially the same manner except that no sodium sulfate is used.

Example 10

A quantity of kipskins is prepared for tannage by drumming 136 parts drained pickle weight of kipskins in a solution comprising 204 parts water, 9.5 parts sodium acetate, and 10.2 parts sodium chloride for fifteen minutes. The skins are then subjected to the polymethacrylic acid tanning agent of Example 4 in the presence of 6.8 parts of a sodium salt of a chlorosulfonated straight chain hydrocarbon containing an average of sixteen carbon atoms, and 8.4 parts of polymethacrylic acid in the form of a partial sodium salt containing 80.7 per cent acid equivalent, equal to 5 per cent polymethacrylic acid on the drained pickle weight of the skins. The solution is then acidified to pH 3.5 with 10 per cent sulfuric acid during the course of four hours drumming.

The leather so produced is then treated with alum according to processes shown in the foregoing examples. The leather produced is found to be benefited by the alum treatment as above described and in addition, shows a much improved grain characteristic.

If in the above procedure the chlorosulfonated hydrocarbon is added along with the alum, a similar result is obtained.

While in most of the examples shown the concentration of alum used was 6 per cent based on the drained pickle weight of untanned skins, it has been found that from about 4 to 7 per cent of alum may be used to advantage. The preferred amount of alum to use is dependent to a certain extent upon the amount of polymeric carboxylic acid material used to effect the tannage, varying in direct proportion. With maleic anhydride-styrene interpolymers it appears that the amount of alum required is slightly less than for the corresponding amount of polymethacrylic acid. Whereas for 4 per cent polymethacrylic acid one would use 4 per cent alum and for 6 per cent polymethacrylic acid one would use 6 per cent alum, if maleic anhydride-styrene interpolymer were used as the tanning agent, one would use for 4 per cent of the tanning agent about 3 per cent alum and for 6 per cent maleic anhydride-styrene one would use about 4.5 per cent alum. In general, enough of the metal salt should be used to effect satisfactory sequestration of any free carboxyl groups in the leather and the exact amount required in any instance can most readily be determined by inspection of the results obtained with increasingly larger amounts. In general, the amount of salt is not critical provided there is sufficient present to effect sequestration and to be on the safe side one may use an excess of the metal salt. It will be understood that the considerations above given as to the use of metal salts will be generally applicable to any of the metal salts which may be used such as chromium sulfate, double salts of iron and aluminum such as ferric alum, aluminum chloride, and other suitable compounds falling within the group previously hereinabove described.

While I have shown certain specific acidic polymer tanning agents and certain specific metal salts and certain specific processes, it will be understood that one skilled in the art may readily employ numerous processes and related compositions without departing from the spirit of this invention.

I claim:

1. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of

an acidic polymeric material in which the acidity is due to carboxyl groups, and then subjecting the skin to the action of a soluble salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

2. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of an acidic polymeric material in which the acidity is due to carboxyl groups attached to aliphatic carbon atoms, and then subjecting the skin to the action of a soluble salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

3. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of a polymerization product of an unsaturated aliphatic carboxylic acid, and then subjecting the skin to the action of a soluble salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

4. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of a polymerization product of an alpha-unsaturated aliphatic carboxylic acid, and then subjecting the skin to the action of a soluble salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

5. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of the polymerization product of maleic anhydride and styrene, and then subjecting the skins to the action of a soluble salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

6. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of an acidic polymerization product of methacrylic acid, and then subjecting the skins to the action of a soluble salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

7. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of polymethacrylic acid, and then subjecting the skins to the action of a soluble salt of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

8. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of a polymerization product of an alpha-unsaturated aliphatic carboxylic acid, and then subjecting the skin to the action of aluminum sulfate.

9. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of a polymerization product of an alpha-unsaturated aliphatic carboxylic acid, and then subjecting the skin to the action of ferric sulfate.

10. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of a polymerization product of an alpha-unsaturated aliphatic carboxylic acid, and then subjecting the skin to the action of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium, the skin being treated with a chlorosulfonated straight chain hydrocarbon.

11. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of a polymerization product of an alpha-unsaturated aliphatic carboxylic acid, and then subjecting the skin to the action of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium, the treatment with the metal salt being effected in the presence of a compound selected from the group consisting of tartrates, citrates, and tartaric and citric acids.

12. In a process for the tanning of skins, the steps comprising subjecting a skin to the action of a polymerization product of an alpha-unsaturated aliphatic carboxylic acid, and then subjecting the skin to the action of a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium, the treatment with the metal salt being effected in the presence of sodium sulfate.

13. The leather which comprises a reaction product of skin substance and an acidic polymeric material in which the acidity is due to carboxyl groups attached to aliphatic carbon atoms, carboxyl groups unassociated with skin substance being sequestered with a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

14. Leather which comprises a reaction product of skin substance and a polymerization product of an alpha-unsaturated aliphatic carboxylic acid, carboxyl groups unassociated with skin substance being sequestered with a metal selected from the group consisting of aluminum, iron, titanium, copper, and chromium.

15. Leather which comprises a reaction product of skin substance and a polymerization product of an alpha-unsaturated aliphatic carboxylic acid, carboxyl groups unassociated with skin substance being sequestered with aluminum.

16. Leather which comprises a reaction product of skin substance and a polymerization product of maleic anhydride and styrene, carboxyl groups unassociated with skin substance being sequestered with aluminum.

17. Leather which comprises a reaction product of skin substance and an acidic polymerization product of methacrylic acid, carboxyl groups unassociated with skin substance being sequestered with aluminum.

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