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MANUFACTURE OF LEATHER

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This invention relates to the production of improved hides, skins and leather. More particularly, it relates to the treatment of hides and skins with a vinyl ether-maleic anhydride copolymer.

There is a demand on the part of tanners of lightweight skins such as calfskins and goatskins for a product or a method which will permit the use of chromium salts as tanning agents but which will avoid the empty unfilled character of chrome tannage and yet not retract from the clear neutral color of chrome leather and its normal affinity for acidic type dyestuffs. It is recognized by the tanning art that salts of chromium have many virtues which are desired both by the tanners and the users of leather. Chief among these are the high degree of stability of the leather, the simplicity of the tanning operation and high degree of substantivity to all acidic type dyestuffs. Chrome leather has the disadvantage, however, in being empty and unfilled, lacking the roundness and body which is generally desired of leather. This is of particular disadvantage to tanners of light-weight skins.

Vegetable-tanned leather, or the leather produced by subjecting skins to the action of the natural plant tanning extracts, has most of the attributes of fullness and body required of leather. It lacks the extreme resistance to deterioration of chrome tanned leather, and in addition is frequently dark-colored and has generally poor affinity for the direct or cotton-type dyestuffs. In addition, vegetable-tanned leather is less resistant to reversal by alkalis and hot water than is chrome tanned leather. For these reasons special precautions must be observed in the manufacture of leather by vegetable-tanning processes.

In order to improve the body and fullness of chrome tanned leather, many materials have been tried. Among these are the sulfonated aromatic condensates, various organic acids (masking agents) styrene-maleic anhydride copolymers and other agents. The sulfonated aromatic condensates as a rule are sensitive to light, becoming discolored upon exposure to light, and in addition have a strong retarding action on the absorption of acidic dyestuffs, causing weak and washed out shades. The organic acids such as formic, acetic and phthalic acids etc. have a modifying action on the deposition of the chrome in the skin but do not materially contribute to the filling and bodying action. They have no pronounced effect on the dyeing characteristics of the leather.

Styrene-maleic anhydride copolymers, while imparting an acceptable body and nap to the finished leather, have been found to render the treated skins extremely difficult to color, whereby the finished leather is frequently spotty in appearance and weak in shade. Only pastel colors could be produced. The decrease in colorability of the treated skins varied inversely with the amount of copolymer applied, whereby tanners have been faced with either a leather with a desirable body and nap but without good colorability, or a dyeable leather which did not have sufficient increase in quality to justify the added cost of applying the styrene-maleic anhydride copolymers.

It is an object of this invention to provide a method for

fulling, plumping, stuffing and improving the dye receptivity and other properties of hides and skins before or during tanning. A further object is the provision of improved hides, skins and leather. Other objects will appear as the description proceeds.

These objects are attained by the instant invention which comprises treatment of hides and skins with a vinyl ether-maleic anhydride copolymer. The use of the aforementioned copolymers results in the following unique properties and advantages which are of great value to the leather trade:

When used in conjunction with chrome tannage they impart body and fullness to the leather. They may be applied either prior to or during chrome tanning. When applied to hides and skins as above, they cause no appreciable alteration in their receptivity to dyestuffs, in contrast to previously employed expedients. Full uniform shades and blacks are easily obtained on subsequent dyeing operations. They are insensitive to any concentration of salt or acid used in tanning and they are not precipitated from solution by 10% salt or 2% sulfuric acid. They may accordingly be used on bated stock prior to pickling operations. They require no special alteration of procedure from customary methods of chrome tanning. They may be applied to pickled skins at pH 2.5–4.0, and after absorption by the skin, chrome tanning solutions may be applied directly to it. They are only mildly astringent and do not cause "case hardening" of the surface of the leather. Their use has been found to enable the production of suede leather having improved body, feel and fullness and a fine uniform nap. This latter characteristic is of extreme importance to suede manufacturers.

The copolymers of the instant invention may be produced in a manner well known in the art. Suitable methods for producing the copolymer by condensation between the maleic anhydride and the vinyl ether are described in U. S. Patent No. 2,047,398 and others. While the preferred copolymer for use in the instant invention is the vinyl methyl ether-maleic anhydride copolymer, other vinyl ether-maleic anhydride copolymers may be used which are sufficiently water-soluble and resistant to the action of salts and acids, as for example, those derived from n-butyl, isobutyl, 2-methoxyethyl (from vinylation of methyl Cellosolve), 2-ethoxyethyl (from vinylation of Cellosolve) and especially vinyl ethyl ethers.

Methyl vinyl ether-maleic ahydride copolymer is a bulky, dusty white powder. It disperses rapidly in water, and when dispersed in water at 180° F. or above, passes in a few minutes into a viscous, starch-like mass which upon further heating dissolves to a clear but quite viscous mucilagenous solution of approximately pH 2.5. Under these conditions, a major portion of the anhydride linkages is opened. Neutralization of the solution from a pH of 2.5 to a pH of 4.5 produces a pronounced rise in viscosity.

The sensitivity to acids and salts increases as the aliphatic chain of the ether group increases. Thus extreme care must be taken in using n-butyl and isobutyl vinyl ether copolymers since they are more sensitive to acidification and may tend to separate from solution as viscous sticky masses. Substantivity to dyes is at a maximum in the lower aliphatic vinyl ether copolymers and decreases as the length of the aliphatic chain increases.

The copolymers of the invention possess the additional advantageous properties of dissolving in aqueous media to produce a pH within the operative range for producing the desired results, which is from about 2.5 to 4.0. Accordingly, in many cases no pH adjustment of the resulting solution with its attendant disadvantages is necessary. However, in some cases other factors such as the

acidity of the hides and skins being treated, presence of other agents and assistants, etc. may render such adjustment necessary. In such cases, the pH may be adjusted by use of alkaline materials such as alkali metal hydroxides and carbonates, ammonium hydroxide, organic bases and the like. Buffer salts such as sodium acetate and phosphate and the like may be made use of to maintain the acidity of the treating bath within the desired pH range, which is preferably from 3.0 to 3.5.

In general, the copolymers of the invention may be incorporated in amounts of about 0.5 to 6% based on the weight of the hides and skins. Impregnation is generally accomplished from aqueous media at any sutiable temperature and for a period of time sufficient to allow impregnation in the desired amount. Since the process proceeds by way of exhaustion, the amount incorporated into the hides and skins will depend essentially on the total amount of copolymer in the treating bath and the duration of treatment, and not on the concentration of the treating bath. The concentration of the treating bath may, accordingly, range from the saturation point down to that sufficient to supply the total amount of copolymer desired to be incorporated. The bath is usually at room temperature or slightly above. The temperature, duration, concentration, and other conditions of treatment will, of course, be somewhat dependent on the character of the hide or skin being treated and the results desired.

The amount incorporated will depend on the desired results. Too large an amount when used on drained, pickled skins, although readily exhausted, imparts more than the desired plumpness to the leather with resultant loss of footage. Obviously, the lowest amounts effective for producing the desired results are economically desirable. The aqueous medium containing the copolymers of the invention may also contain other common hide and skin treating additives, buffering agents and the like, which do not detract from the desired result.

While the copolymers of the invention may be employed in conjunction with any tanning agents such as alum, natural tanning agents and the like, it is especially advantageous in the production of chromed leather. In such production the converted copolymer may be used either prior to or during tanning with chrome. Excellent filling and plumping have been obtained by either method.

The hides and skins which may be treated in accordance with the instant invention may be from any of the common sources. The leather produced therefrom is plumped, fulled, bodied, stuffed, and has a soft and mellow feel. Because of the mild, non-astringent character of the treatment, it may be used in the production of grain leathers in order to increase the body. In the production of suede kid, the finished leather has a more uniform nap with much better buffing qualities than obtainable by other plumping agents or chrome alone. The color is not reduced as with other products, thus yielding full bloomy blacks on subsequent dyeing. In most cases the color is definitely superior to straight chromed leather. Light-weight goatskins are definitely plumped. Calf suedes and splits are likewise improved. Of course in the treatment of any of the hides and skins, their pH should be taken into consideration in order that optimum results may be obtained. Slight adjustment of the pH of the treating solution may be necessary to compensate therefor. The leather produced from the hides and skins treated in accordance with this invention may be subjected to any of the various kinds of finishing treatments customarily used.

The following examples are illustrative of the instant invention and are not to be regarded as limitative. Unless otherwise indicated, proportions recited are based on the weight of the hides and skins being treated.

Example 1

There were placed in a 50 liter flask equipped with stirrer, thermometer, gas inlet tube, and reflux condenser 2500 g. (25.5 moles) maleic anhydride; 19,500 cc. nitrative grade benzene; and 25 g. lauroyl peroxide. The mixture was then heated to reflux (78° C.) with stirring and at this temperature, technical grade vinyl methyl ether was bubbled into the reaction solution. Within 15 minutes a copolymer slurry was noted. The temperature was then lowered to 65° C. and the addition of vinyl methyl ether was continued at 65–67° C. for a period of 6 hours. (At the end of this time, sufficient vinyl ether had been added as indicated by bubbling occurring in a gas-bubble counter attached to the exit end of the reflux condenser.) Approximately 1700 g. (293 moles) of vinyl methyl ether was added altogether. The copolymer was separated by filtration and dried in vacuo to a white powder.

Example 2

To 100 lbs. of D. P. W. (drained pickle weight) suede kid stock, pH 2.5, were added 5 lbs of salt, 8 to 10 oz. of sodium acetate, and 1.5 to 3.0 lbs. of the product of Example 1 previously dissolved in water and at a pH of 3.3–3.5. After running for 1 to 2 hours, 5% aluminum sulfate was added. The batch was run for 30 minutes longer, after which 8 to 10% of Tanolin R (commercial chromium sulfate containing 25% Cr_2O_3) was added in 3 portions 30 minutes apart. After the last addition, the batch was run for 1 hour longer, neutralized with 3–4% sodium bicarbonate in 3 additions to a pH of 4.1 to 4.3 and the skins washed and horsed up. The leather from the treated skins had a more uniform nap, with improved buffing qualities, than was obtained by other plumping agents or chrome alone. On dyeing, full bloomy blacks were obtained, much superior to that obtained on straight chrome leather. The skins were definitely plumped and had a highly desirable body and feel.

Example 3

100 lbs. of D. P. W. suede kid were run for 20–30 minutes at 80–90° F. in 12 gal. water, 2 lbs. salt and ½–1 lb. sodium acetate. 1–2 lbs. of the product of Example 1, previously dissolved and adjusted to a pH of 3.3 were then added and the batch run for 1–2 hours longer. 3–5 lbs. of iron free aluminum sulfate were then added, the batch run for 10 minutes and 8–10 lbs. of Tanolin R added. After running for 1 hour longer, the batch was neutralized with sodium bicarbonate to a pH of 3.9 to 4.1 and the skins washed and horsed up. Improved properties, similar to those obtained in Example 2, were obtained.

Example 4

Skins treated in accordance with Example 3, were pearled, crusted and buffed in accordance with the normal practice of the art. They were wet back with 1% ammonia (28%) and ½% wetting agent in 7 times their weight of water at 135° F. The skins thus prepared for dyeing were divided into two parts.

One part of the skins were dyed in known manner in the regular developed black process using:

18% Diazo Black BHN Conc. (C. I. 401)
3% sodium nitrite
4% Metatoluylene diamine

After coloring the skins were fatliquored, crusted, staked, buffed and dry milled in the customary suede procedure. The finished skins were then compared with regular chrome suede leather dyed and treated by identical procedure and were found to have a shorter silkier nap and a fuller bloomier color.

Example 5

The other part of the skins prepared for dyeing in the previous example were, in known manner, colored black

by dyeing in a drum at 140° F. with 18% of a dyestuff mixture composed as follows:

40% Chrome Leather Fast Black SG Conc., Pr 371
15% Sulphon Cyanine 5RA Extra Conc., C. I. 284
15% Resorcine Brown, G, C. I. 234
20% Benzo Dark Green BA–CF, C. I. 583
10% Ethyl Acid Violet 4B Conc., C. I. 53

The dyestuff was applied in two additions using 10% and 8% respectively followed by two additions of formic acid of 3% each. The skins were processed after coloring as in Example 5. The finished skins were found to be of excellent suede having a deeper bloomier color than regular chrome leather dyed in a similar manner.

Example 6

The process of Example 3 was repeated except that a vinyl ethyl ether-maleic anhydride copolymer was employed in equivalent amounts. The treated skins had improved properties similar to those obtained in Example 3, including improved dyeing properties when dyed in the manner of Examples 4 and 5.

Various modifications and variations of this invention will be obvious to a person skilled in the art, and it is understood that such modifications and variations are to be included within the purview of this application and the spirit and scope of the appended claims.

What is claimed is:

1. A process comprising impregnating hides and skins with a methyl vinyl ether-maleic anhydride copolymer in an aqeuous medium maintained throughout the impregnation at a pH of about 2.5 to 4.0.

2. A process comprising impregnating hides and skins with a methyl vinyl ether-maleic anhydride copolymer in an aqueous medium maintained throughout the impregnation at a pH of about 2.5 to 4.0, and tanning such hides and skins in the presence of said copolymer with a tanning agent selected from the group consisting of alum, chromium compounds and natural plant extract tanning agents.

3. A process as defined in claim 2 in which the copolymer is applied before the tanning operation.

4. A process as defined in claim 3 followed by the step of dyeing the tanned hides and skins.

5. A process as defined in claim 2 in which the copolymer is applied simultaneously with the tanning operation.

6. A process as defined in claim 5 followed by the step of dyeing the tanned hides and skins.

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