These objects are attained by the instant invention which comprises treatment of hides, skins and leather with a vinyl ether-maleic anhydride copolymer in which from about 3 to 15% of the anhydride groups have been converted to the salt-half amide with a member of the group consisting of ammonia and lower aliphatic primary and secondary amines. The use of the aforementioned converted copolymers result 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 chrome tanning, during, or subsequent to it. When applied to hides, skins and leather as above they cause no appreciable alteration in their respective dyeability, 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 chroma-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 and the salt and acid added to the skins as in normal 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 astrigent and do not cause “case hardening” of the surface of the leather. Their use has been found to improve the body, feel and fullness of suede leather producing a fine uniform nap to the suede. This latter characteristic is of extreme importance to suede manufacturers.

The converted copolymers of the instant invention may be produced in a manner well known in the art. Suitable methods for producing the initial copolymer by condensation between the maleic anhydride and the vinyl ether are described in U.S. Patent No. 2,047,988 and others. The production of the full ammonium salt substantially complete conversion of anhydride groups) of a vinyl ether-maleic anhydride half amide copolymer is disclosed in U.S. Patent No. 2,313,565, but it is emphasized that no claim is made to the methods and compositions described therein since it has been found that copolymers in which more than about 15% of the anhydride groups have been converted to the salt-half amide with a member of the group consisting of ammonia and lower aliphatic primary and secondary amines are undesirable for the treatment of hides, skins and leather in accordance with the instant invention. They are taken up much more slowly by the hides, skins and leather, and produce decreased plumping, fulling and stuffing effects. On the other hand, at least about 5% of the anhydride groups should be converted to the salt-half amide since otherwise the solubility in aqueous media, speed of take-up, and plumping, fulling and stuffing effects are insufficient. Within the range of about 5 to 15% conversion the copolymers of the invention have been found to possess, as compared for example with the unconverted or initial copolymers, the highly desirable properties of increased solubility in aqueous media, faster take-up by the hides, skins and leather, increased plumping, fulling, and bodying action, and the like. The preferred range is from 8 to 12% conversion, and within this range a copolymer with an about 11% conversion has been found to give optimum results.

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-methyl...
oxyethyl (from vinylation of methyl Cellosolve), 2-ethoxyethyl (from vinylation of Cellosolve) and especially vinyl ethyl ethers. Dry ammonia is preferred for conversion of the requisite number of anyhydride groups in the copolymer into ammonium salt, half amide groups, but other amines may be employed which produce converted copolymers with the desired solubility, non-sensitivity and other properties. Such other amines are for the most part in the lower aliphatic group, such as dimethyl amine, ethanolamine and the like. It will be understood that, in addition to ammonia, other than ammonia, for the conversion will result in production of the corresponding amine salts of the corresponding half-substituted amides of the initial vinyl ether-maleic anhydride copolymers.

The converted 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, unless influenced by other factors, no pH adjustment of the resulting solution with its attendant disadvantages is necessary. Thus, for example, by merely dissolving a copolymer with about an 11% anhydride conversion in water a solution is obtained with a pH of about 3.8, whereby no adjustment of pH by addition of acids or bases need be made before treatment of hides, skins and leather therewith. The preferred pH range is from 3.0 to 3.8.

In general, the converted copolymers of the invention may be incorporated in amounts of about 0.5 to 6% based on the weight of the hides, skins or leather. Impregnation is generally accomplished from aqueous media at any suitable 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, skins and leather will depend essentially on the total amount of converted 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 temperature, duration, concentration, and other conditions of treatment will of course be somewhat dependent on the character of the skin or leather being treated and the results desired. In general, operating temperatures on raw skins are usually held below about 85°F. On chrome leather, after-treatment temperature as high as 140°F. may be used. Too large an amount of copolymer, when applied to blue chromed skins, is difficult to exhaust from solution and gives too much fullness, yielding a bloated, over-plump character to the skin. Likewise, 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 converted copolymers of the invention may also contain other common leather 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 tanning with chrome or may be applied on the shaved blue stock. Excellent filling and plumping have been obtained by either method. The use on blue shaved stock permits selection for weight at the end of the tannage and is definitely advantageous in building up light-weight stock. Use after tanning has the further advantage of not requiring any changes in the complex tanning formulations and procedures already being employed by the tanners. However, since at a pH of about 3.0 to 3.3 chrome solutions cause a rapid rise in the viscosity of solutions of the converted copolymers employed in this invention, with resultant decrease in the amount and speed of take-up by the skins and leather, care should be taken in applying such solutions to chromed, tanned to avoid the presence of appreciable quantities of uncombined or unneutralized chrome. This may be accomplished by washing.

The hides, skins and leather which may be treated in accordance with the instant invention may be from any of the common sources. The leather produced is plumped, fulled, bodied, stuffed, and has a soft and mellow feel. Because of the mild, non-antiregent 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 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 pigskin is definitely plumped. Call suedes and splits are likewise improved. Of course in the treatment of any of the hides, skins and leather 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 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 limiting:

**Example 1**

1330 grams of vinyl methyl ether-maleic anhydride copolymer (Naero® 76.76) were suspended in 6500 cc. of benzene. 35 grams of anhydrous ammonia were bubbled through the slurry over a period of 4 hours at 50-55°C. After all the ammonia had been added, the slurry was warmed for 30 minutes, filtered, and the filtrate washed with benzene and dried in vacuum to yield 1355 grams of dry powder. Nitrogen analysis indicated that about 11% of the initial anhydride groups in the copolymer had been converted to the ammonium salt of its half amide.

**Example 2**

375 grams of chrome tanned calf leather were thoroughly washed for 15 minutes, drained, and then immersed in 2000 cc. of water. The product of Example 1 was easily dissolved in warm water in an amount to produce a 10% aqueous solution, of which 112 cc. were added to the leather treating bath. The addition amounted to about 3% of the said product on the weight of the leather. After 15 minutes of working, the bath had a pH of 3.1. The leather was worked in the bath for 40 more minutes, after which 11.2 grams of Tanol® R (commercial chromium sulfate containing 25% Cr₂O₃) were added. The leather was then worked in the bath for another hour longer, at which time the measured pH of the bath was 3.0. 4 grams sodium bicarbonate were added to the bath and the leather worked therein for an hour longer, removed, washed and hosed up. The treated leather had a highly desirable plumpness and fullness of feel, somewhat like a vegetable-tanned product, and was a dense, dark shade. The converted copolymer was taken up by the leather from the bath in a comparatively rapid and complete manner.

**Example 3**

1000 grams of Nigerian skins, drained pickle weight, were worked for 15 minutes in a bath containing 20 grams of salt and 7.5 grams of anhydrous sodium acetate in 1000 cc. of water. There was then added a solution of 30 grams of the product of Example 1 (3% on the
weight of the skin) in 400 cc. of water. Said solution was previously made by dissolving the said product in hot water and had a pH of 3.8 without any adjustment with alkali being necessary. After running for 1½ hours, the pH was measured at 3.5 and 50 grams of iron free aluminum sulfate were added to the bath. After running for another 5 minutes, 7.5 grams of soda ash were added. After working the skins in the bath for 30 minutes longer, there was added a solution of 100 grams of Tunolin R (copperous chromite sulfate containing 25% Cr₂O₃) in 500 cc. of water. The skins were worked in the bath for 1½ hours longer, the pH measured at 3.2, and 15 grams sodium bicarbonate added. After working for 30 minutes longer, the pH was 3.6 and 10 grams of sodium bicarbonate added. The skins were worked in the bath for 30 minutes, at which time the pH was 3.95. The skins were then removed, washed and horset up. The treated skins were plump and solid, and were readily dyed in light or dark shades. The converted copolymer was taken up by the skins from the bath comparatively rapidly and completely.

Example 4

The process of Example 3 was repeated except that an 11% converted vinyl ethyl ether-maleic anhydride copolymer was employed. Improvements similar to those obtained in Example 3 were obtained.

Example 5

Skins treated in accordance with Example 3, were pearled, crust, 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 155°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% Diazob Black BHN conc. (C. I. 401)
3% sodium nitrite
4% metatolylene diamine

After coloring the skins were fatliquored, crust, 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 slicker nap and a fuller bloomer color.

Example 6

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 dye stuff mixture composed as follows:

40% Chrome Leather Fast Black SG conc., Pr 371
15% Sulphon Cyanine SRA Extra conc., C. I. 284
15% Resorcin 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 bloomer color than regular chrome leather dyed in a similar manner.

Example 7

The product of Example 4 was prepared and colored by the procedure of Example 5, producing an improved colored leather as compared with leather which had not been treated with the same.

Various modifications and variations of this invention will be obvious to a worker 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 treating hides, skins and leather with a lower alkyl vinyl ether-maleic anhydride copolymer in which at least about 5 and no more than 15% of the anhydride groups have been converted to the salt-half amide with a member of the group consisting of ammonia and lower aliphatic primary and secondary amines.

2. The process of claim 1, in which the vinyl ether is vinyl methyl ether.

3. The process of claim 2, in which about 11% of the anhydride groups have been converted to the ammonium salt-half amide.

4. The process of claim 1, in which the vinyl ether is vinyl ethyl ether.

5. The process of claim 4, in which about 11% of the anhydride groups have been converted to the ammonium salt-half amide.

6. A process comprising treating hides, skins and leather in an aqueous medium with a lower alkyl vinyl ether-maleic anhydride copolymer in which at least about 5 and no more than 15% of the anhydride groups have been converted to the salt-half amide with a member of the group consisting of ammonia and lower aliphatic primary and secondary amines.

7. A process comprising treating hides, skins and leather in an aqueous medium at a pH of about 2.5 to 4.0 with a lower alkyl vinyl ether-maleic anhydride copolymer in which at least about 5 and no more than 15% of the anhydride groups have been converted to the salt-half amide with a member of the group consisting of ammonia and lower aliphatic primary and secondary amines and then dyeing the treated hides, skins and leather.

8. Hides, skins and leather treated by the process of claim 1.

9. A process comprising treating hides, skins and leather with a lower alkyl vinyl ether-maleic anhydride copolymer in which at least about 5 and no more than 15% of the anhydride groups have been converted to the salt-half amide with a member of the group consisting of ammonia and lower aliphatic primary and secondary amines and then dyeing the treated hides, skins and leather.

10. The process of claim 1, in which the vinyl ether is vinyl methyl ether.

11. The process of claim 9 in which the vinyl ether is vinyl ethyl ether.

12. The products of the process of claim 9.

References Cited in the file of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Reference</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,976,679</td>
<td>Fikentscher</td>
<td>Oct. 9, 1934</td>
</tr>
<tr>
<td>2,047,398</td>
<td>Voss et al.</td>
<td>July 14, 1936</td>
</tr>
<tr>
<td>2,156,069</td>
<td>Schlack</td>
<td>Apr. 25, 1939</td>
</tr>
<tr>
<td>2,205,882</td>
<td>Graves</td>
<td>June 25, 1940</td>
</tr>
<tr>
<td>2,205,883</td>
<td>Graves</td>
<td>June 25, 1940</td>
</tr>
<tr>
<td>2,220,867</td>
<td>Kirk</td>
<td>Nov. 5, 1940</td>
</tr>
<tr>
<td>2,313,565</td>
<td>McDowell et al.</td>
<td>Mar. 9, 1943</td>
</tr>
<tr>
<td>2,456,177</td>
<td>Cuprey</td>
<td>Dec. 14, 1948</td>
</tr>
<tr>
<td>2,469,428</td>
<td>Beachell</td>
<td>May 10, 1949</td>
</tr>
<tr>
<td>2,469,437</td>
<td>Kirk</td>
<td>May 10, 1949</td>
</tr>
<tr>
<td>2,543,602</td>
<td>Rowland</td>
<td>Feb. 27, 1951</td>
</tr>
<tr>
<td>2,577,041</td>
<td>Seymour</td>
<td>Dec. 4, 1951</td>
</tr>
<tr>
<td>2,609,350</td>
<td>Spatt</td>
<td>Sept. 2, 1952</td>
</tr>
</tbody>
</table>