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Method for improving leather treatment.

A method of using a dispersion of a selected amphiphilic copolymer formed from a predominant amount of at least one hydrophobic monomer and a minor amount of at least one copolymerizable hydrophilic monomer in the pretanning and tanning step improves moisture release in the wringing step and improves thickness adjustment in the splitting and shaving steps of leather treatment is disclosed.

This invention relates to a method for improving the processes in leather treatment, and more particularly to the use of selected polymers to improve the wringing, splitting and shaving steps in leather treatment.

Animal hides and skins are converted into useful leather by processing involving both wet and dry operations. The wet operations include trimming and sorting, soaking, fleshing, unhairing, bating, pickling, tanning, wringing, splitting and shaving, retanning, coloring, fatliquoring and setting out. Some of these steps put the hide or skin into the proper condition for a subsequent processing step. Others of these steps affect major changes in the properties or appearance of the hide or skin. Each step in the processing is interrelated with one or more of the other steps in the processing.

Typically, leather is produced from hide which is first pickled and then tanned and neutralized. The tanned stock is subsequently wrung to remove excess moisture from tanned stock so that it can be properly handled on the splitting and shaving machines which follow to adjust the thickness of the tanned stock to that required for the end use.

Chromium salts are often used to tan hides because a stable hide is produced. When the chrome-tanned leather is subsequently split and shaved, however, residual waste is produced which contains some of the chromium salts. Some tanneries now attempt to complete the mechanical splitting and shaving operations before the hide is subjected to the chrome tanning so that the residual waste will not contain any chromium salts. These tanneries however experience difficulties because hides which have not yet been chrome tanned are characteristically sticky causing the hides to stick to the processing machinery used to split and shave them. Our invention permits the tannery to overcome this sticking problem if it chooses to split and shave the hides before chrome tanning. Furthermore, our invention improves the splitting and shaving steps even if the chrome tanning step is completed before the splitting and shaving steps.

We have discovered that the use of a dispersion of a selected amphiphilic copolymer formed from a predominant amount of at least one hydrophobic monomer and a minor amount of at least one copolymerizable hydrophilic monomer in the pretanning and tanning step improves moisture release in the wringing step and improves thickness adjustment in the splitting and shaving steps of leather treatment.

A method of the present invention involves the use of a dispersion of a selected amphiphilic copolymer formed from a predominant amount of at least one hydrophobic monomer and a minor amount of at least one copolymerizable hydrophilic monomer in the pretanning and tanning step in addition to the other pretanning and tanning agents used. The resulting tanned leather has improved moisture release in the wringing step and improved thickness adjustment in the splitting and shaving steps of the leather treatment.

The selected amphiphilic copolymer must contain at least one hydrophobic and at least one hydrophilic group. The copolymer is formed from greater than 10% by weight to less than 50% by weight of at least one hydrophilic monomer and greater than 50% by weight to less than 90% percent of at least one hydrophobic comonomer. It is preferred if the copolymer is formed from greater than about 15% by weight to less than about 45% by weight of at least one hydrophilic monomer and greater than about 55% by weight to less than about 85% by weight of at least one hydrophobic comonomer, and even more preferred if the copolymer is formed from greater than about 20% by weight to less than about 40% by weight of at least one hydrophilic monomer and greater than about 60% by weight to less than about 80% by weight of at least one hydrophobic comonomer.

The hydrophilic monomer used to prepare the amphiphilic copolymer is at least one monomer selected from water-soluble ethylenically unsaturated, preferably monoethylenically unsaturated, acidic or basic monomers or mixtures thereof. Examples of suitable hydrophilic monomers include acrylic acid; methacrylic acid; itaconic acid; fumaric acid; maleic acid; and anhydrides of such acids; acid substituted (meth)acrylates, such as for example, phosphoethyl methacrylate and sulfoethyl methacrylate; acid substituted (meth)acrylamides such as, for example, 2-acrylamido-2-methylpropylsulfonic acid; and basic substituted (meth)acrylates and (meth)acrylamides, such as for example, amine-substituted methacrylates including dimethylaminoethyl methacrylate, tertiarybutylaminoethylmethacrylate and dimethylaminopropyl methacrylamide and the like. The preferred water soluble hydrophilic monomers used to prepare the amphiphilic copolymer are acrylic acid and methacrylic acid.

The selection of the nature and concentration of the hydrophilic monomer was made to impart the amphiphilic copolymer with the ability to be well dispersed in the continuous phase, such as for example in water, and for the amphiphilic copolymer to be prepared at high polymer solids at a handleable or shearable viscosity without adversely affecting the ability of the copolymer to penetrate the leather.

The hydrophobic comonomer used to prepare the amphiphilic copolymer is at least one monomer selected from alkyl (meth)acrylates; primary alkenes, and vinyl esters of alkyl carboxylic acids, and mixtures thereof. Suitable hydrophobic monomers include C₄ to C₁₂ alkyl acrylates; C₄ to C₁₂ alkyl methacrylates; C₄ to C₁₂ 1-alkenes, and vinyl esters of C₄ to C₁₂ alkyl carboxylic acids. The preferred hydrophobic monomers which have been found to provide the amphiphilic copolymer with the best performance characteristics are the C₄ to C₁₂ alkyl (meth) acrylates and mixtures thereof, most preferably 2-ethylhexylacrylate.

The use of the term "(meth)" followed by another term such as acrylate or acrylamide, as used throughout the disclosure, refers to both acrylates or acrylamides and methacrylates and methacrylamides, respectively.

Minor amounts of other ethylenically unsaturated copolymerizable monomers at concentrations equal to or less than 50% by weight of the total hydrophobic comonomer concentration may be used in combination with a predominant amount (greater than about 50% by weight) of at least one of the above types of hydrophobic comonomers. These additional hydrophobic comonomers have been found to be useful as diluents for the other hydrophobic comonomers without adversely affecting the water release properties obtained upon treatment with the amphiphilic copolymer. Examples of such useful copolymerizable hydrophobic diluent comonomers include styrene, methylstyrenes, vinylacetate, (meth)acrylonitrile n-alkyl (meth) acrylamides and olefins.

The amphiphilic copolymer may be prepared by the polymerization of the hydrophilic and hydrophobic monomers by any conventional polymerization technique. We have found a preference for conducting the polymerization using standard emulsion polymerization procedures using a water soluble free radical initiator at a concentration of from about 0.1% by weight percent to about 3 % by weight based on total weight of the monomers. The polymerization is preferably conducted at a temperature of from about 40°C to about 100°C, preferably from about 50°C to 70°C, using a chain transfer agent, such as for example a mercaptan, to control the molecular weight. The weight-average molecular weight of the amphiphilic copolymer useful in the method of the invention can be as low as about 2500 to as high as about 100,000, preferably less than about 50,000. The polymerization may be conducted by polymerizing all monomers together or by the gradual addition of monomers until polymerization is essentially complete. Residual unreacted monomers can be incorporated into the polymer by the addition of subsequent initiator by techniques well known in the art. The polymerization produces a concentration of amphiphilic polymer solids in a non-organic solvent of from as low as about 20% solids to as high as about 60% solids.

The treatment process of the invention involves subjecting leather during the pretanning or tanning step to the selected amphiphilic copolymer dispersion. The amount of copolymer used to treat the leather is in the range of from about 0.09% solids by weight to about 20% solids by weight polymer on weight of leather, preferably in the range of from about 0.35% solids by weight to about 10% solids by weight and most preferably in the range of from about 1% solids by weight to about 5% solids by weight. We evaluated the amphiphilic copolymers by comparing the relative ease of wringing, shaving and splitting among leathers pretanned with and without the selected amphiphilic copolymer dispersions.

The following examples are intended to illustrate the invention.

EXAMPLE 1: PREPARATION OF AMPHIPHILIC COPOLYMER

70% by weight 2-ethylhexyl acrylate/30% by weight methacrylic acid

The polymerization was conducted under nitrogen atmosphere in a one liter, four-necked, round bottom flask equipped with a Teflon® blade stirrer in the center neck, a thermometer and a reflux condenser. Into the flask was charged 185 grams deionized water, 4 grams sodium lauryl sulfate, 1 drop of sulfuric acid and 0.3 grams of a 1% by weight solution of ferrous sulfate. This mixture was then heated to 60°C. The monomers (140 grams of 2-ethylhexyl acrylate and 60 grams of methacrylic acid) along with 10 grams of n-dodecane thiol chain transfer agent were emulsified with 95 grams of deionized water and 4 grams of sodium lauryl sulfate, and, simultaneously with the initiators, 0.6 grams ammonium persulfate diluted with 22 grams water and 0.6 grams sodium bisulfite diluted with 22 grams water, were fed to the reaction flask over a three hour period maintaining the temperature of the reaction mixture at 60°C. At the end of the additions, any remaining monomer was converted to polymer by the shotwise addition of 0.1 gram additional redox and free radical initiators. The polymer emulsion was then cooled and the pH was adjusted by the addition of 20.4 grams of 13% aqueous solution of sodium hydroxide. The final product contained 37.8% solids by weight and has a pH of 5.5. The weight-average molecular weight of the polymer, as measured by gel permeation chromatography using polyacrylic acid copolymer as the standard, was 8200 and the number average molecular weight was 6600.

EXAMPLE 2: PREPARATION OF LEATHER

The following procedure was used to prepare tanned leather for wringing and subsequent shaving and splitting. Two lime split cow hides were used for testing:

Wash 20 minutes at 32°C (90°F.)

Add: 1% ammonium sulfate -- run 15 minutes

Add: 1% ammonium sulfate

0.06% Bate

0.2% Triton N-101 surfactant -- run 45 minutes

Wash 15 minutes at 90°F

Wash 15 minutes at 65°F

Add: 6% sodium chloride

5 Add: 1% Leukotan 1042 acrylic syntan -- run 5 minutes

Add: 0.5% formic acid -- run 15 minutes

Add: 0.6% sulfuric acid -- run 2 hours -- pH 3.8

Add: 0.2% sulfuric acid -- run 30 minutes -- pH 3.5

Add: 3.5% Chromesaver A-31 pretan -- run 2 hours -- pH 3.2

10 Add: 0.5% sodium bicarbonate -- run 15 minutes

Add: 0.5% sodium bicarbonate -- run 30 minutes

To Hide 1

Add: 3% aqueous dispersion of 70% by weight 2-ethylhexyl acrylate/30% by weight methacrylic acid (37.8 % solids) -- run 15 minutes -- pH 4.2

15 To Hide 2 (*Comparative -- outside scope of invention*)

Add: 3% Leukotan 1028 acrylic syntan -- run 15 minutes -- pH 5.68

The hides were set out overnight. The hides were then wrung and shaved. Hide 1 wrung and shaved well -- comparable to normal full chrome tanned leather. Comparative Hide 2 did not wring and shave as well Hide 1. Typically hides not treated in the final step with an acrylic copolymer of the invention characteristically do not wring well. Consequently, because they are sticky, the hides do not shave and split adequately for subsequent processing.

Claims

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1. A method for improving wringing, shaving and splitting steps of leather processing comprising subjecting leather during pretanning or tanning to a dispersion of an amphiphilic copolymer formed from greater than 10% by weight to less than 50% by weight, preferably from greater than 15% and to less than 45% by weight, of at least one hydrophilic monomer and greater than 50% by weight to less than 90% percent, preferably greater than 55% by weight to less than 85% by weight, of at least one hydrophobic comonomer.

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2. The method of claim 1, wherein said copolymer is formed from greater than 20% by weight to less than 40% by weight of at least one hydrophilic monomer and greater than 60% by weight to less than 80% by weight of at least one hydrophobic comonomer.

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3. The method of claims 1 or 2, where said amphiphilic copolymer is formed by aqueous emulsion polymerization, and where said amphiphilic copolymer is present as a dispersion in water.

4. The method of claims 1, 2 or 3, wherein said amphiphilic copolymer has a weight average molecular weight of from 2500 to 50,000.

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5. The method of any one of the preceding claims, wherein said hydrophilic comonomer used to prepare the amphiphilic copolymer is at least one monomer selected from water soluble ethylenically unsaturated acidic or basic monomers or mixtures thereof; and wherein preferably said hydrophilic comonomer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, fumaric acid, maleic acid, and anhydrides of such acids; acid substituted (meth)acrylates, acid substituted (meth)acrylamides and basic substituted (meth)acrylates and (meth)acrylamides.

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6. The method of any one of the preceding claims, wherein said hydrophobic comonomer used to prepare the amphiphilic copolymer is at least one monomer selected from alkyl (meth)acrylates, primary alkenes, vinyl esters of alkyl carboxylic acids, and mixtures thereof.

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7. The method of claim 6, wherein said hydrophobic comonomer is further selected from the group consisting of C₄ to C₁₂ alkyl acrylates, C₄ to C₁₂ alkyl methacrylates, C₄ to C₁₂ 1-alkenes, and vinyl esters of C₄ to C₁₂ alkyl carboxylic acids.

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8. The method of claims 6 or 7, wherein said hydrophobic comonomer further comprises less than 50% by weight of one or more second hydrophobic comonomers selected from the group consisting of styrene, methystyrenes, vinyl acetate, (meth)acrylonitrile and n-alkyl(meth)acrylamides olefins.

9. The method of any one of the preceding claims, wherein said amphiphilic copolymer comprises from 20% by weight to 60% by weight of the solution or dispersion.
10. The leather produced by the method of any one of the preceding claims.

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