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TANNING COMPOSITIONS COMPRISING AQUEOUS SOLUTIONS OF UNSATURATED ACID-UNSATURATED SULFATED OIL COPOLYMERS

William J. Rau, Wyndmoor Valley, Pa., assignor to Rohn & Haas Company, Philadelphia, Pa., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

Tanning compositions are made by copolymerization of a mixture of (A) methacrylic acid, acrylic acid or mixtures of such acids with (B) a sulfated unsaturated oil. The unsaturated acid used is preferably 75 to 100% methacrylic acid and 25 to 0% respectively of acrylic acid, and generally the use of methacrylic acid exclusively is most practical from the standpoint of cost and effectiveness. The amount of sulfonated oil is from 10 to 25% by weight of the acid monomer.

The present invention is concerned with the tanning of leather.

It is already known that various skins or hides can be tanned by the application of polyacrylic acid, polymethacrylic acid or copolymers of these acids. These materials may be used as the sole tanning agents or they may be used as pretanning or retanning agents preceding or following respectively the application of other tanning agents such as chrome, zirconium, natural tannins, and synthetic tanning agents. The use of these agents has an important disadvantage, however, in that they frequently impart crackiness to the grain of the leather and this even occurs in some instances with heavily fat-liquored skins. Most synthetic tanning agents do not cause cracking in this fashion even when applied without fat-liquoring. Compositions made up with the tanning agent and a fat-liquoring agent such as an oil, have the disadvantage that there is gross separation of the oil from the composition on storage after a few days.

It is an object of the present invention to provide a new composition having advantageous tanning properties. It has been discovered that such tanning compositions can be made by copolymerization of a mixture of (A) methacrylic acid, acrylic acid or mixtures of such acids with (B) a sulfated unsaturated oil. The unsaturated acid used is preferably 75 to 100% methacrylic acid and 25 to 0% respectively of acrylic acid, and generally the use of methacrylic acid exclusively is most practical from the standpoint of cost and effectiveness. The amount of sulfated oil is from 10 to 25% by weight of the acid monomer. Preferably, the amount of such oil is about 15 to 20%, based on the weight of the monomer.

The sulfated oil with which the unsaturated acid is polymerized is one in which the extent of sulfation has not been so great as to completely eliminate points of unsaturation in the product. Thus, the extent of sulfation may be such as to remove all points except one of unsaturation in the oil. In those oils which also contain hydroxyl groups, the sulfation may be exerted exclusively on the hydroxyl groups leaving all of the points of unsaturation essentially untouched or the sulfation may convert both the hydroxyl groups and part of the unsaturated groups into sulfates. For example, in olive oil, which contains as a major constituent a glyceride of oleic acid, sulfation may introduce sulfate groups on one or two of the three points of unsaturation in the glyceride molecule leaving one or two of the unsaturated groups essentially untouched or unmodified. While olive oil is mentioned there may be used instead any of the other animal and vegetable oils containing one or more glycerides of unsaturated acids having long chains such as from 12 to 20 carbon atoms. Examples of these oils include:

Almond	Peanut
Beechnut	Poppy seed
Black mustard	Porpoise (body oil)
Candlenut	Pumpkin seed
Castor	Rape seed
Chaulmoogra	Safflower
Cod liver	Seal
Corn (maize)	Sesame
Cotton seed	Soja bean (soya, soy)
Lard oil	Sperm
Linseed	Sunflower
Menhaden	Tung (China wood)
Neats-foot	Walnut
Palm	Whale

The preparation of the still partially unsaturated sulfation products of these oils is well known and in fact, many are commercially available.

The copolymerization is effected in an aqueous medium in which the sulfated oil is dissolved, for example at a concentration of 5% to 15% by weight. To this solution there is added a water-soluble polymerization initiator and, optionally, a water-soluble chain-transfer agent. An aqueous solution of a chain-transfer agent, if such an agent is used, may also be dissolved directly in the monomer and this solution may then be added to the sulfated oil/catalyst solution in the flask. The sulfated oil/catalyst solution (which may also contain a chain-transfer agent) may be held at room temperature or raised to as high as 97° C. or even higher (such as to reflux) and maintained at the desired temperature while adding the acid monomer. The addition of the acid monomer results in copolymerization of such acid with the unsaturated sulfated oil yielding the product of the present invention which is highly effective as a tanning agent for leather and has the advantage of effecting tannage without imparting crackiness to the grain of the leather even without fat-liquoring the leather.

The relative proportions of the acid monomer and sulfated oil are 80 and 90% by weight of monomer to 20 to 10% by weight respectively of the oil. In other words, the amount of monomer used is about 4 to 8 times the amount of sulfated oil. The proportion of initiator is from 0.5 to 6% by weight of the monomer. Examples of initiators include hydrogen peroxide, ammonium persulfate, sodium persulfate, and potassium persulfate.

The proportion of chain transfer agent depends on the particular agent and its effectiveness in controlling the molecular weight of the copolymer. In general, the amount of chain transfer agent used is correlated with the amount of initiator so as to result in the production of a copolymer which in acid form at approximately 33% concentration in water and at 25° C. will have a viscosity in the range of about 15 to 300 poises. No chain-transfer agent is needed if the proportion of initiator used is high enough to produce a copolymer of low molecular weight in the range specified. It is estimated that the most suitable molecular weight range of the product is from about 5,000 to 50,000 number average. Examples of chain-transfer agents include hydroxylamine or salts thereof, such as hydroxylamine sulfate, mercaptoethanol, mercaptopropanol, thiodiglycol, thioglycollic acid, ascorbic and isoascorbic acid. The chain-transfer agent may be used in an amount of about 0.2 to 3.5% by weight based on the weight of the monomer.

The copolymers of the present invention are water-soluble and dilutable. They remain in solution indefinitely without signifiicant separation of oil content and are capable of tanning skins or hides without imparting crackiness to the grain.

For the purpose of tanning hides or skins, the copolymer is dissolved in water at a concentration of about 5 to 40% by weight. Of course, the copolymer need not be isolated from the aqueous solution in which it is prepared. Such solutions need only be adjusted to the desired concentration for use in tanning. A salt, such as sodium chloride or sodium sulfate, is included in the tanning solution at a concentration of 3 to 8% by weight. The tanning liquor is introduced into a suitable vessel such as the conventional tanning drum and then the skins are introduced into the drum. The weight of skins relative to the weight of liquor is generally determined to provide about 20 to 25% of active tanning agent based on the weight of wet pickled skin and about 5 to 15% of salt, when used, on the weight of skin. The tanning is effected by tumbling the skin within the drum or vessel at room temperature up to but not above 35° C. Most commonly, the temperature may extend between 28 and 32° C. The tumbling in the tanning liquor may be carried out for a number of hours such as from 4 to 24 hours.

This tannage may be followed by a mineral tanning, vegetable extract tanning, or synthetic tanning agent.

In the retanning of skins which have previously been mineral-tanned, especially chrome-tanned, or zirconium tanned or tanned by other means, the concentration of the copolymer may be from ½ to 10% by weight in the tanning liquor. Generally, there is no salt used in this tanning liquor and the amount of the tanning liquor relative to the partially tanned leather treated therewith is such as to provide about 1% to 5% of the copolymer based on the weight of the wet chrome leather. This means that to provide 3% on the leather there would be used 200% based on the weight of leather of a liquor containing 1½% of the copolymer.

The tanning composition of the present invention may be employed for the treatment of all types of skins and hides, such as horsehide, cowhide, kidskin, lambskin, goatskin, pigskin and so on. The tanned products are adapted for use in all types of leathers such as shoe, sole and upper, garment, case, upholstery and industrial leathers.

To assist those skilled in the art to practice the present invention, the following modes of operation are suggested by way of illustration, parts and percentages being by weight and the temperatures in ° C. unless otherwise specifically noted.

(1) Three solutions are prepared as follows:

Solution A:
- 312 g. aqueous sulfated castor oil (234 g. actual oil)
- 1860 ml. deionized water

Solution B:
- 1200 g. methacrylic acid (MAA)
- 168 ml. aqueous hydroxylamine solution (6.0 g. actual H.A.)

Solution C:
- 52 g. aqueous hydrogen peroxide (35%) (18 g. actual H_2O_2)
- 600 ml. deionized water

Solution A is heated in a glass reaction vessel to 90° C. Solutions B and C are added gradually simultaneously over a 50-minute period through suitable devices, such as dropping funnels, to feed the reaction vessel, holding the temperature at 89 to 93° C. The mixture is heated 1½ hours longer at 90° C. (±1° C.). It is then cooled, while agitating, to 70–75° C. There is then added 0.1% phenol (based on product) and stirring is continued another 15 minutes at 70–75° C. The 33⅓% solids copolymer solution weighs 4268 g. and has a viscosity of 33 poises at 25° C. (Brookfield LVF viscometer, No. 3 spindle at 12 r.p.m.)

(2) Tannage of pickled skin.—Thirty-eight grams of pickled calfskin is put into a bottle. To this is added a tanning solution comprised of:

- 27 grams of the 33⅓% solids tanning material (obtained in 1 above)
- 3.8 grams of NaCl
- 76 ml. of water

This bottle is sealed and is agitated in a shaking machine for 24 hours. Then 1.5 g. of sodium acetate is added and the bottle is shaken 3 hours longer; then the liquor is drained. The skin is washed thoroughly with water, fat liquored with a mixture of 0.3 g. Texol N (a commercial sulfated neats-foot oil), 0.08 g. neats-foot oil, and 57 ml. of water, shaken one hour, set out and dried; and finally sammied and staked.

An excellent piece of white leather is obtained which shows outstanding lightfastness and very good ageing characteristics.

(3) Two solutions are prepared:

Solution A:
- 105 ml. water
- 1.75 g. ammonium persulfate

Solution B:
- 50 g. methacrylic acid (MAA)
- 13 g. aqueous sulfated sperm oil (10 g. actual oil)

Solution A is heated to 90° C. Solution B is added to Solution A over a 40-minute period. The mixture is stirred 1½ hours at 90–95° C. There is then added 1.5 g. ammonium hydroxide (28% NH_3) followed by stirring 15 minutes longer at 90–95° C. The mass is agitated while cooling to approximately 70° C. The product is a 35% solids solution of copolymer. At 25° C. and 33% concentration, it has a viscosity of 70 poises.

(4) Retannage of chrome leather. — Twenty-three grams of chrome-tanned calfskin is put into a bottle. To this there is added a tanning solution comprised of:

- 2.5 grams of the tanning agent 35% solution obtained in 3 above
- 46 ml. of water

This is agitated in a shaking machine for 1½ hours. Then the liquor is drained, and the resulting leather is washed thoroughly. Finally it is set out, dried, sammied, and staked. The leather obtained shows excellent fullness and is well bleached, being much superior to chrome leather which had not been retanned. The leather also shows excellent lightfastness and ageing properties.

(5) Three solutions are prepared:

Solution A:
- 160 ml. water
- 2.0 g. hydroxylamine sulfate
- 26 g. aqueous sulfated neats-foot oil (20 g. actual oil)

Solution B:
- 100 g. methacrylic acid (MAA)

Solution C:
- 3.3 g. hydrogen peroxide (30%)
- 50 ml. water

Solution A is heated to 90° C. Solutions B and C are then added gradually and simultaneously over a 40-minute period while stirring. Then 0.7 g. H_2O_2 is added quickly. The mixture is stirred 1½ hours longer at 90–95° C. Then there is added an ammonium hydroxide solution (2 g. of 28% NH_3+4 ml. H_2O) over a 1-minute period. The mixture is stirred 20 minutes longer at 90–95° C. and then while continuing the agitation, it is cooled to approximately 70° C. The product is a 35% solids solution of the copolymer. At 25° C. and 33% concentration, it has a viscosity of 40 poises.

(6) Retannage of zirconium-tanned leather.—Forty-one grams of zirconium tanned calfskin is put into a bottle. To this there is added a tanning solution comprised of:

- 6.8 g. of the 35% solution of tanning agent of 5 above
- 82 ml. of water.

This is shaken for 3 hours. The liquor is drained and

the leather is washed thoroughly. It is then fat-liquored with 1.64 g. of Albinoil 300 W (a commercial sulfated neats-foot oil) and 0.41 g. oil in 63 ml. of water; finally set out, crusted, sammied and staked. The white leather obtained shows excellent fullness and color.

(7) Three solutions are prepared:

Solution A:
190 ml. water
30 ml. hydroxylamine solution—1.02 actual H.A.
26 g. aqueous sulfated codfish oil (20 g. actual oil)
Solution B:
90 g. methacrylic acid (MAA)
10 g. acrylic acid (AA)
Solution C:
2.9 g. hydrogen peroxide (35%)
50 ml. water

Heat Solution A to 90° C. Add Solutions B and C simultaneously over a period of 40 minutes. Add 0.5 g. H_2O_2 (35%) quickly. Stir 1½ hours longer at 89–92° C. Let agitate while cooling to approximately 70° C. The product is a 30.5% solution of acid copolymer. At 25° C. and 33% concentration, it has a viscosity of 35 poises.

(8) Pretannage of mineral tanned leather.—Forty-one grams of pickled calfskin is put into a bottle. To this there is added a tanning solution comprising:

6.9 g. of the 30.5% solution of tanning agent obtained in (7)
4.1 g. of NaCl
82 ml. of water

This is shaken for 18–20 hours. The pretanned leather is then tanned in the normal way with 9.9 g. of basic zirconium sulfate. After tannage, the skin is washed thoroughly and fat-liquored with 1.64 g. Albinoil 300 W and 0.41 g. neats-foot oil in 63 ml. water. Finally the piece is set out, crusted, sammied, and staked. The leather obtained shows excellent fullness and color.

(9) Two solution are prepared:

Solution A:
200 ml. water
13 g. aqueous sulfated soybean oil (10 g. actual oil)
0.25 g. lauroyl peroxide
Solution B:
50 g. methacrylic acid (MAA)
50 ml. water
1.5 g. mercaptoethanol

Heat Solution A to 90° C. Add Solution B over a period of 45 minutes. One hour later, add a solution of 0.8 g. ammonium persulfate in 7 ml. water. Stir 1 hour at 90° C. (±1° C.). Let agitate while cooling to 34–40° C. Vacuum strip-weight of distillate =107 g.; final copolymer solution weight is 212 g. (approximately 28% solids). At 25° C. and 33% concentration, it has a viscosity of 34 poises.

(10) Retannage of chrome-tanned calfskin with polymeric tanning agent and vegetable tanning agent.—A thirty-gram piece of chrome-tanned calfksin is put into a bottle. To this there is added a tanning solution comprising:

1.8 g. of the 28% solution of tanning agent 9 above
60 ml. of water

This is shaken for 2 hours; then the liquor is drained and the tanned piece is rinsed. Then the following solution is added:

1.2 g. of quebracho powder
60 ml. of water

This is shaken for 2½ hours and the liquor is drained; then the piece is washed thoroughly and fat-liquored with 0.60 g. of sulfated neats-foot oil in 45 ml. of water, and finally set out, dried, sammied, and staked. An excellent piece of leather is obtained showing a very light color, superior light fastness, and good fullness and roundness.

(11) Acid/sulfated oil copolymer solutions of approximately 30% concentration are obtained by repeating procedure 7 except that the sulfated codfish oil is replaced by

(a) sulfated castor oil
(b) sulfated neats-foot oil
(c) sulfated sperm oil
(d) sulfated soybean oil

Each of the resulting copolymer solutions may be used for tanning, retanning or pretanning as in any of procedures 2, 4, 6, 8 and 10.

(12)(a) Acid/sulfated oil copolymer solutions of approximately 30% concentration are obtained by repeating procedure 7 except that Solution B is replaced by a mixture of 75 g. of methacrylic acid and 25 grams of acrylic acid.

(b) Part (a) is repeated except that the sulfated codfish oil is replaced by

(a) sulfated castor oil
(b) sulfated neats-foot oil
(c) sulfated sperm oil
(d) sulfated soybean oil

Each of the resulting copolymer solutions may be used for tanning, retanning or pretanning as in any of procedures 2, 4, 6, 8, and 10.

I claim:

1. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of an acid selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof and (B) 20 to 10% by weight of an unsaturated sulfation product of an oil selected from the group consisting of animal and vegetable oils.

2. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of an acid selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof and (B) 20 to 10% by weight of an unsaturated sulfation product of an oil selected from the group consisting of animal and vegetable oils, a 33% solution in water of said copolymer in acid form at 25° C., having a viscosity of about 15 to 300 poises.

3. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of methacrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of a vegetable oil.

4. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of methacrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of an animal oil.

5. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of methacrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of castor oil.

6. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of methacrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of neats-foot oil.

7. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of methacrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of sperm oil.

8. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of methacrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of codfish oil.

9. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of methacrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of soybean oil.

10. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of a mixture of at least 75% by weight of methacrylic acid and up to 25% by weight of acrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of castor oil.

11. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of a mixture of at least

75% by weight of methacrylic acid and up to 25% by weight of acrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of neats-foot oil.

12. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of a mixture of at least 75% by weight of methacrylic acid and up to 25% by weight of acrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of sperm oil.

13. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of a mixture of at least 75% by weight of methacrylic acid and up to 25% by weight of acrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of codfish oil.

14. As a composition of matter, a copolymer of a mixture of (A) 80 to 90% by weight of a mixture of at least 75% by weight of methacrylic acid and up to 25% by weight of acrylic acid and (B) 20 to 10% by weight of an unsaturated sulfation product of soybean oil.

15. In an aqueous composition for tanning leather, the improvement wherein a copolymer of a mixture of (A) 80 to 90% by weight of an acid selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof and (B) 20 to 10% by weight of an unsaturated sulfation product of an oil selected from the group consisting of animal and vegetable oils serves as a tanning agent therein.

16. As a tanning composition, an aqueous solution containing 5 to 40% by weight, based on the total solution weight, of a copolymer of a mixture of (A) 80 to 90% by weight of an acid selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof

and (B) 20 to 10% by weight of an unsaturated sulfation product of an oil selected from the group consisting of animal and vegetable oils, a 33% solution in water of said copolymer in acid form at 25° C., having a viscosity of about 15 to 300 poises.

17. As a tanning composition, an aqueous solution containing 3 to 8% by weight, based on the total solution weight of a salt selected from the group consisting of sodium chloride and sodium sulfate, and 5 to 40% by weight, based on the total solution weight, of a copolymer of a mixture of (A) 80 to 90% by weight of an acid selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof and (B) 20 to 10% by weight of an unsaturated sulfation product of an oil selected from the group consisting of animal and vegetable oils, a 33% solution in water of said copolymer in acid form at 25° C., having a viscosity of about 15 to 300 poises.

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DONALD E. CZAJA, *Primary Examiner.*

R. W. WHITE, *Assistant Examiner.*