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TANNING AND BLEACHING LEATHER WITH A SULFOAROMATICMELAMINE-FORMALDEHYDE RESIN

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This invention relates to the treatment of skins and/or hides and more particularly, to processes for bleaching or whitening chrome tanned leather and to the leather products obtained by such processes.

It is an object of the present invention to produce white leather.

It is another object of the present invention to provide a process for bleaching chrome tanned leather.

Another object of the present invention is the provision of new and improved bleaching agents for chrome tanned leather.

A further object of the present invention is the provision of new and improved agents for tanning hides and skins to produce white leather.

The above and other objects may be attained by treating skins and/or hides or leather with a water-soluble aldehyde condensation product of a sulfonated aromatic hydrocarbon-substituted melamine or an alkali metal or ammonium salt thereof.

The invention will be described in greater detail in conjunction with the following examples in which proportions are given in parts by weight. The examples are merely illustrative, and it is not intended that the scope of the invention should be limited to the details therein set forth.

Example 1

254 parts (0.9 mol) of p-sulfophenylmelamine
360 parts (0.9 mol) of sodium hydroxide, 10% aqueous
219 parts (2.7 mols) of formaldehyde, 37% aqueous

The above ingredients are placed together in a suitable vessel equipped with means for reflux. The reaction mixture is heated and refluxed for 1–3 hours. The product is cooled and filtered.

Example 2

30.4 parts (0.1 mol) of sodium salt of p-sulfophenylmelamine
16.2 parts (0.2 mol) of formaldehyde, 37% aqueous
156 parts of water

The water and formaldehyde are mixed together in a suitable vessel equipped with means for reflux, and the sodium salt of p-sulfophenylmelamine is added. The reaction mixture is heated to reflux and maintained at that temperature for 1.5 hours. It is then cooled and filtered.

Example 3

37.4 parts (0.12 mol) of sodium salt of p-sulfophenylmelamine

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10.0 parts (0.12 mol) of formaldehyde, 37% aqueous
181 parts of water

The procedure of Example 2 is followed except that the reaction mixture is refluxed for only one hour.

Example 4

179 parts (0.5 mol) of sodium salt of p-sulfophenylmelamine, 85% purity
60.8 parts (0.75 mol) of formaldehyde, 37% aqueous
880 parts of water

The procedure of Example 2 is followed except that the reaction mixture is refluxed for only one hour and the product is clarified by passing it through a centrifuge.

Example 5

1350 parts (3.8 mols) of sodium salt of p-sulfophenylmelamine, 85% purity
452.0 parts (5.6 mols) of formaldehyde, 37% aqueous
5198 parts of water

The above ingredients are mixed together in a suitable vessel and heated at reflux for one hour. After cooling for one hour, the reaction product is clarified by passing it through a centrifuge.

Example 6

10.9 parts (0.025 mol) of the mono-sodium salt of 4,8-disulfo-alpha-naphthylmelamine
6.1 parts (0.075 mol) of formaldehyde, 37% aqueous
73.6 parts of water

An aqueous solution of the sulfonaphthylmelamine is heated with excess alkali, the excess alkali is neutralized with hydrochloric acid and the solution, with triethanolamine. Formaldehyde is then introduced and the ingredients are mixed together in a suitable vessel and heated at reflux for 1 hour. The light brown solution obtained, which is precipitated by a mixture of salt and acid, is used as a tanning and/or bleaching agent for leather.

Example 7

10.9 parts (0.025 mol) of the mono-sodium salt of 6,8-disulfo-beta-naphthylmelamine
6.1 parts (0.075 mol) of formaldehyde, 37% aqueous
73.6 parts of water

The procedure of Example 6 is followed, and the slightly hazy solution obtained is filtered

warm. The filtered solution, which is precipitated by a mixture of salt and acid, is used as a tanning and/or bleaching agent for leather.

Example 8

13.1 parts (0.025 mol based on average molecular weight) of a mixture of the mono- and diammonium salts of 3,6,8-trisulfo-alpha-naphthylmelamine
6.1 parts (0.075 mol) of formaldehyde, 37% aqueous
71.5 parts of water

The above ingredients are placed in a suitable vessel and heated. At the boiling point, the reaction mixture clears to a yellow orange solution which is refluxed for 1 hour and then cooled. The solution obtained has good bleaching properties for leather.

Example 9

Chrome tanned side leather and calfskin are washed for 15 minutes at 90° F., drained and drummed for 45 minutes at 125° F. in 200% by weight, based on the shaved weight of the stock, of water containing 5% of the resin of Example 1. They are then washed, tacked out and dried at about 20–25° C. Well bleached, blue white skins are obtained.

Example 10

100 parts of pickled kidskin are drummed with 100 parts of water containing 10 parts of sodium chloride. 23 parts of the resin of Example 1 are added, the skin is tumbled for an hour, and 10 parts of aluminum sulfate, $Al_2(SO_4)_3.18H_2O$, are added. After further tumbling for from 12–15 hours, the tanned skin has a pH of 2.4.

12.8 parts of borax are then added to the skin which is drummed for an hour. The pH of the skin is now 4.85.

The skin is washed and tacked out. Evaluated wet, it is white and well tanned.

Example 11

Pieces of chrome tanned side leather are drummed for one hour at 50° C. in 200% by weight, based on the shaved weight of the stock, of water containing 10% of the resin of Example 2, 10% of the resin of Example 3, and 5% of the resin of Example 1, respectively. They are then washed, tacked out and dried. In each case well bleached leather results.

Example 12

Pieces of chrome tanned side leather are washed for 15 minutes at about 20°–25° C. and then bleached for 40 minutes at about 50° C. in 200% by weight, based on the shaved weight of the stock, of water containing 10% and 20% of the resin of Example 4 and 10% and 20% of the resin of Example 1, respectively. They are then washed, tacked out and dried. Well bleached skins are obtained.

Example 13

Pieces of chrome tanned leather are washed in tap water for 1½ hours and then drummed for 1 hour in 150% by weight, based on the shaved weight of the stock, of water containing 10% and 20% of the resin of Example 5, respectively. They are then washed, tacked out and dried. The skins obtained are well bleached.

Example 14

Chrome tanned side leather is neutralized by drumming in a medium float of water containing 3% sodium acetate for 20 minutes at 85° F. The drum is drained to a short float, 20% of the resin of Example 5 is added, and the leather is drummed for 45 minutes at 120° F. The leather is then fat liquored and dried. A bright white leather results.

The p-sulfophenylmelamine used in Example 1 and for the preparation of its sodium salt for Examples 2–5 may be prepared as described below by sulfonation of phenylmelamine or it may be prepared directly by condensation of sulfanilic acid and ammonia with cyanuric chloride. We have found that sulfanilic acid will not condense with melamine in the same manner as it does with urea to form the corresponding sulfonated phenyl derivative.

Preparation of p-sulfophenylmelamine

10.0 parts (0.049 mol) of phenylmelamine
37 parts (0.36 mol) of 95% sulfuric acid
200 parts of water

A mixture of the first two ingredients is heated with stirring at about 100° C. After 15 minutes the solution is pink in color and contains 0.33 mol of sulfuric acid. The sulfonation is completed by stirring for an additional 30 minutes at about 100° C. The reaction product is then cooled with ice, and the water is added dropwise to the cooled sulfonation mixture. 13.5 parts of a white insoluble material is obtained after filtration, washing with water and drying at 106° C. The sulfonation thus yields 69% p-sulfophenylmelamine.

The naphthylmelamines of Examples 6–8 may be prepared by reaction of cyanuric chloride with the corresponding naphthylamine sulfonic acid. The procedure is illustrated by the following detailed preparation.

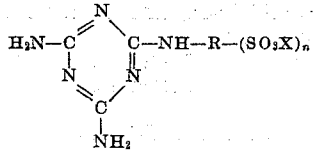
Preparation of the monosodium salt of 4,8-disulfo-alpha-naphthylmelamine

A solution of 74 parts (0.4 mol) of cyanuric chloride in 127 parts of hot acetone is poured into a mixture of 400 parts of ice and 400 parts of water. To this are added 122 parts (0.4 mol) of 1-naphthylamine-4,8-disulfonic acid as a slurry in 480 parts of water and 160 parts of 10% sodium hydroxide solution. The mixture is stirred at 15°–20° C. for 1.5 hours. 100 parts of 28% aqueous ammonia are then added and the reaction is allowed to continue for another 1.5 hours, the temperature rising to 33° C. 50 parts more of the ammonia are then added, and the reaction mixture is heated under reflux for 1.5 hours and filtered hot.

292 parts of 10% hydrochloric acid are added to the filtrate and the mixture is allowed to cool. The solution is reduced to about one fifth its volume by evaporation and then cooled and filtered. The solid is recrystallized from a small amount of water and dried at 105° C.

Other sulfonated aromatic-substituted melamines may be substituted for those of the specific examples, i. e., p-sulfophenylmelamine, 4,8-disulfo - alpha - naphthylmelamine, 6,8-disulfo-beta-naphthylmelamine and 3,6,8-trisulfoalpha-naphthylmelamine, all of which substituted melamines contain a hydrogen atom attached to an amino nitrogen atom. Furthermore, other mono-, di- and tri-alkali metal salts and ammonium salts of the melamines may be used as, for instance, the potassium salt of p-sulfophenylmelamine, the ammonium salt of p-sulfophenylmelamine, and the like. The sulfonated

aromatic hydrocarbon-substituted melamines described in the aforegoing examples and the accompanying description have the formula



where R is an aromatic hydrocarbon radical and X is selected from the group consisting of hydrogen, alkali metal and ammonium, and n is an integer from 1 to 3.

Similarly, formaldehyde-yielding materials such as paraformaldehyde and hexamethylenetetramine may be substituted for the formaldehyde of the examples as may other aldehydes including acetaldehyde, paraldehyde, furfural, and the like.

We have found that the melamine derivative or salt thereof and formaldehyde should be condensed in molar ratios of from about 1:1 to about 1:5, respectively.

The condensation of formaldehyde with the melamine derivative may be carried out at pHs varying from about 3.5 to 9.5 without effecting the bleaching ability of the product. We prefer carrying out the reaction at pHs of from about 6 to 9.

The formaldehyde and melamine derivative are preferably condensed for periods of time up to about an hour at reflux. Beyond that time little additional formaldehyde combines with the melamine derivative. At the boiling point of an aqueous solution of melamine derivative and formaldehyde the quantity of formaldehyde combining with the melamine derivative becomes constant after about one hour and even dropping the pH of the solution after this time, for example, from about 8.5 to about 4.5, does not effect the amount of combined formaldehyde.

While we have set up certain limitations on the ratio of reactants, the reaction time and the pH of reaction, the bleaching effect of the new resinous bleaching agents appears to be independent of these variables.

The water-soluble condensation products here described are acid-sensitive. In aqueous solution they may be converted to the insoluble or hydrophobe state by the addition of acid, with consequent precipitation of a solid white resin. Since the chrome salts in leather tanned therewith will generate sulfuric acid when brought into contact with water, it is possible by the process of the present invention to capitalize on the acid-sensitivity of the condensation products on the one hand and the capacity of the chrome-tanned leather to generate sulfuric acid in the presence of water on the other for the bleaching or whitening of green chrome-tanned leather.

The bleaching process of the present invention may be carried out simply by drumming chromed leather in a water solution of one of the described melamine derivative condensation products. Varying concentrations, e. g., from about 1% to about 50% by weight of solid resin based on the shaved weight of the stock, may be used in the process and our invention is in no sense limited to the use of any particular concentration. We prefer to use from about 5% to about 25% resin, on the same basis.

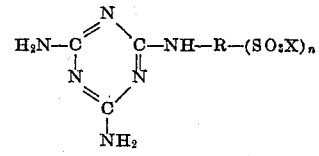
The formaldehyde-melamine derivative condensation products of the present invention may be employed alone for the whitening of chrome tanned leather, or they may be employed in combination with other bleaching agents. In such instances the leather may be first treated with a secondary bleaching agent and a condensation product of the present invention applied thereafter, the two bleaching agents may be used in conjunction with each other, or the secondary bleaching agent may be used for after-treating leather which has been bleached with the products described in the present case.

Moreover, the condensation products of the present invention may be used as tanning agents, see Example 7, either alone or in conjunction with other tanning agents, i. e., vegetable, mineral or synthetic. If the latter, our new agents may be used for the initial tannage or for the after-tannage.

The leather products obtained by the process of the present invention and having incorporated therein a formaldehyde condensation product of a sulfonated aromatic-substituted melamine offer the advantage in the manufacture of white leathers of a reduced requirement of white pigment such as titanium dioxide for covering the leather surface. Such bleached leathers may also be of advantage in obtaining brighter colors in dyeing.

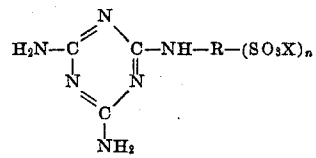
We claim:

1. A process of tanning and bleaching which comprises treating hides and skins with an aqueous solution of a water-soluble acid-sensitive condensation product of 1 mol of a sulfonated aromatic hydrocarbon substituted melamine having the formula



wherein R is an aromatic hydrocarbon radical, X is selected from the group consisting of hydrogen, alkali metal and ammonium, and n is an integer from 1 to 3 with about 1 to about 5 mols of formaldehyde.

2. A process of bleaching leather which comprises treating tanned leather with an aqueous solution of a water-soluble acid-sensitive condensation product of 1 mol of a sulfonated aromatic hydrocarbon substituted melamine having the formula

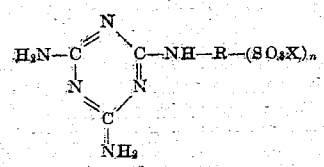


wherein R is an aromatic hydrocarbon radical, X is selected from the group consisting of hydrogen, alkali metal and ammonium, and n is an integer from 1 to 3 with about 1 to about 5 mols of formaldehyde.

3. A process according to claim 2 in which the substituted melamine is p-sulfophenylmelamine.

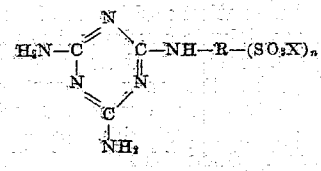
4. A process of bleaching chrome tanned leather which comprises treating chrome tanned leather with an aqueous solution of a water-soluble acid-sensitive condensation product of 1

mol of a sulfonated aromatic hydrocarbon substituted melamine having the formula



wherein R is an aromatic hydrocarbon radical, X is selected from the group consisting of hydrogen, alkali metal and ammonium, and *n* is an integer from 1 to 3 with about 1 to about 5 mols of formaldehyde.

5. A process of tanning and bleaching which comprises treating hides and skins first with an aqueous solution of a water-soluble acid-sensitive condensation product of 1 mol of a sulfonated aromatic hydrocarbon substituted melamine having the formula



wherein R is an aromatic hydrocarbon radical, X is selected from the group consisting of hydrogen, alkali metal and ammonium, and *n* is an integer from 1 to 3 with about 1 to about 5 mols of formaldehyde, and then with a different tanning agent.

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