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LEATHER TREATING AGENT

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This invention relates to a new class of leather tanning and bleaching agents, to their preparation and to their application to hides and leather. More specifically it relates to a leather tanning and bleaching agent prepared by reacting a phenol sulfonic acid, an aldehyde and a secondary aliphatic amine.

Condensation products of formaldehyde and certain sulfonated lower phenols are known and have been used in the bleaching and tanning of leather. Although some of these compounds have proven satisfactory there is a demand in the leather art for still better and more efficient synthetic tanning and bleaching agents. I have found that the reaction products of phenol sulfonic acids, including the substituted phenol sulfonic acids, with formaldehyde or other aldehydes and secondary aliphatic and heterocyclic amines are valuable in the bleaching and tanning of hides, skins and leather and particularly in the bleaching of chrome tanned leather with which they give an exceptionally light, even shade of a soft, full texture.

I prefer to prepare my new leather tanning and bleaching agents by reacting substantially equimolecular proportions of a phenol sulfonic acid, a secondary amine and formaldehyde and stopping the reaction before the product becomes water-insoluble. Ordinarily the reaction is carried out at elevated temperatures as for example 80–98° C. for 0.5–5 hours. However, the reaction will proceed to the desired stage of completion at room temperatures with a much longer reaction time. Such products prepared at low temperatures are of a lighter color but not so effective as bleaching agents. In general, it has been found that the further the material is condensed the more effective will the product be in the treatment of leather. However, this is qualified by the fact that temperatures substantially above 100° C. or an unduly prolonged reaction period will result in a product of decreased water solubility and consequently the reaction time will be governed by this consideration.

As free sulfonic acids are not readily obtainable I generally prepare them myself by carrying out the necessary sulfonation preliminary to the actual preparation of my new leather treating materials. Although oleum, concentrated H_2SO_4, SO_3, chlorsulfonic acid and other sulfonating agents may be employed I prefer to use concentrated H_2SO_4 as the sulfonating agent on account of its ease of handling and availability. A suitable phenol or substituted phenol is reacted with an excess of concentrated H_2SO_4 in the usual manner in order to sulfonate the phenol. The sulfonated mixture, containing the excess H_2SO_4 if desired, is then reacted with formaldehyde and a secondary aliphatic or heterocyclic amine. Although I may remove the excess sulfuric acid and carry out the condensation by catalyzing it with an excess of the alkaline secondary amine this procedure is of no particular advantage and requires the use of excess quantities of the amine. As the presence of sulfuric acid is not harmful to the product, since in fact bleaching of chrome tanned leather may take place in acid solutions I prefer to leave the sulfonating acid in the sulfonated phenol reaction mixture and employ it as catalyst for the condensation. I may, if desired, react the formaldehyde and secondary amine in a separate reaction vessel before reacting with the sulfonated phenol or I may add the formaldehyde and secondary amine simultaneously to the sulfonated phenol. Ordinarily, however, I add the secondary amine slowly to the sulfonated phenol while holding the mixture at about room temperature, add the formaldehyde slowly with stirring for a short time and then heat the reaction mixture until the desired stage of reaction has been reached.

The product thus obtained contains sulfuric acid remaining from the sulfonation procedure but if desired it may be sold, shipped and used without further treatment. It may however be neutralized, as with ammonia, to a desired pH, preferably not over 7.0, and made up into a solution of desired concentration.

My new leather tanning and bleaching agent may be used with, or to replace, conventionally employed chrome and vegetable tanning agents as in the case of the sulfonated phenol-formaldehyde condensation products heretofore employed for this purpose. My new product is most useful however in the bleaching of chrome tanned leather which ordinarily has a pronounced bluish cast and a stiff, hard texture. Such leathers have been bleached to a very light even color with an attendant softening of the leather. In bleaching chrome tanned leather with my new bleaching agent it is employed in an aqueous solution of 0.2–4.0% of active ingredient which may represent from 1–20% by weight of bleaching agent based on the weight of the leather. The chrome tanned leather is treated with such a solution for 0.5–1 hour at temperatures varying from room temperature to 60° C. to obtain the desired degree of bleach. Conventionally employed fat liquors may be used in the same bath.

The phenol sulfonic acids which may be re-

acted with formaldehyde and secondary aliphatic amines in accordance with my invention to yield my new class of syntans and leather bleaching agents includes all those sulfonated phenols which have at least one reactive unsubstituted ortho or para position in the aromatic nucleus. For example, if the sulfonic acid radical occupies a position in the aromatic nucleus which is para to the —OH group then one of the ortho positions and one or both of the meta positions may be substituted with a non-functional group such as an alkyl, alkylol, aryl, hydroxyl, nitro, halogen, cycloalkyl and the like. The essential requirement is simply that the phenol sulfonic acids have at least one reactive point at which formaldehyde may react.

Among the various phenol sulfonic acids which may be employed may be mentioned specifically unsubstituted phenols such as phenol sulfonic acid, α or β naphthol sulfonic acid and the hydroxy anthracene and hydroxyphenanthrene sulfonic acids. Among the substituted phenol sulfonic acids which may be used in my invention are the straight and branched chain alkyl substituted phenol sulfonic acids such as methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, amyl, hexyl, octyl, ethyl hexyl, dodecyl and octadecyl sulfonic acids including also the sulfonated commercial ortho and metacresol mixtures; the dialkyl substituted compounds such as 1.3.5 xylenol sulfonic acid; ortho or meta chlor, brom or nitro phenol sulfonic acid; hydroxy diphenyl sulfonic acid; meta dihydroxy benzene sulfonic acid, phenyl phenol sulfonic acid and the like. It will be understood that by the term "phenol sulfonic acid" as appears hereinafter and in the claims I intend to include all of the above mentioned substituted and unsubstituted phenol, naphthol, hydroxyanthracene and hydroxy phenanthracene sulfonic acids and their equivalents.

Among the various secondary aliphatic and heterocyclic amines which may be employed in my process are included the aliphatic secondary amines such as dimethyl, diethyl, di-n-propyl, diisopropyl, diallyl, methyl ethyl, methyl-n-propyl, methyl butyl, methyl dodecyl, methyl oleyl, ethyl butyl, dimethanol, diethanol, β,β'-dicyano diethyl amine and the heterocyclic secondary amines such as dicyclohexyl amine, piperazine, triethylene tetramine and morpholine.

The preparation of my compounds will now be illustrated in connection with the following specific examples which are given to illustrate some of the more specific details of the preparation but are not intended to be construed as in limitation thereof.

Example 1

196 parts by weight (2 moles) of H_2SO_4 were added slowly with stirring to 164 parts by weight (1 mole) of o-amyl phenol and the temperature of the mixture allowed to rise to 60° C. After standing 2 hours at a temperature of 60° C. 100 parts by weight of water was added and the mixture cooled to room temperature. 87 parts by weight (1 mole) of morpholine was then added and the mixture again cooled to room temperature. 1 mole of formaldehyde in the form of a 37% by weight solution was added to the reaction mixture slowly with stirring and the stirring continued for 2 hours at room temperature. The temperature of the mixture was then raised to 95–100° C. and held at this temperature for 1 hour.

One-half of the material prepared as above described was neutralized with ammonia and made up with 50% alcohol to a solution containing 50% solids. A chrome tan leather was effectively bleached with this material.

The remaining half of the reaction mixture described was heated 4 hours at 95–100° C. During this further condensation the solubility of the material decreased and on cooling a water soluble, gum-like material separated out. The resin was removed mechanically and made up to a 50% stock solution in 50% ethanol. This product, when used as a 10% water solution, was an effective syntan and bleached chrome tanned leather to a light, even shade without raising the grain.

Example 2

196 parts by weight of concentrated H_2SO_4 was added slowly over a period of 0.5 hour with stirring to 164 parts by weight of o-amyl phenol. The temperature of the reaction mixture was allowed to rise to 60° C. and was maintained at this temperature for 2 hours after the addition of sulfuric acid. 100 parts by weight of water was added with cooling to room temperature. 105 parts by weight of diethanolamine was then added dropwise to the above mixture while holding the temperature at about 25° C. 30 parts by weight of CH_2O in the form of a 37% by weight solution (81.1 parts by weight) was added dropwise with stirring and the stirring continued for ½ hour after all the formaldehyde was in. The mixture was then heated on a steam bath for 1 hour, and 200 parts by weight of water added. The material was then adjusted to a pH of 6.5–7.0 with ammonia and made up to 1200 parts by weight with water corresponding to a 30% solution of the syntan. This material also proved to be a good bleaching agent for both chrome and vegetable tanned leathers.

Example 3

1 mole of o-cresol was sulfonated with 2 moles of concentrated sulfuric acid as described in the preceding examples. 1 mole of morpholine and 1 mole of formaldehyde were condensed in a separate reaction vessel for a period of about ½ hour at a temperature of 90° C. The resulting syrup was then added to the sulfonation mixture over a period of 0.5 hour with stirring at room temperature. The temperature of the mixture was then raised to 95° C. and held at this temperature for about 1 hour. The contents of the reaction vessel were then neutralized and dissolved in water with the aid of a small amount of ethyl alcohol. If desired the condensation may be allowed to take place at room temperatures but a correspondingly longer time will be required for the reaction to reach the desired stage of completion. Such products prepared at lower temperatures are lighter in color.

An effective bleaching agent for chrome and vegetable tanned leathers was also prepared exactly as described above except that a commercial mixture of ortho and meta cresols was employed in place of the pure o-cresol. A leather bleaching agent was also prepared as above described with 1 mole of diethanolamine instead of morpholine. The products described were in general syrupy masses soluble in water and varying in color from a very light tan to dark brown and may be used either as tanning agents with

or without conventional chrome or vegetable tans to yield soft and well-filled leather, or they may be very effectively employed as bleaching agents to give light, even-colored leathers.

Example 4

1 mole of tertiary butyl phenol was sulfonated with 2 moles of sulfuric acid as described in Example 1 and diluted with 100 parts of water and cooled to room temperature. 1 mole of β,β'-dicyano-diethylamine was dissolved in 1 mole of an aqueous solution of formaldehyde with stirring and then added to the sulfonated tertiary butyl phenol-sulfuric acid mixture. The mixture was stirred 15 minutes at 60° C., refluxed 15 minutes and then cooled, neutralized with 200 parts by weight of NH_4OH and made up to a solution containing 30% by weight of the syntan based on an assumed molecular weight of 365. This material was also a very satisfactory bleach for chrome and vegetable tanned leathers.

What I claim is:

1. A process of preparing leather tanning and bleaching agents which comprises reacting in acid media at temperatures not in excess of 100° C. for not more than 5 hours a phenol sulfonic acid having at least one reactive ortho or para position in the nucleus, formaldehyde and a secondary aliphatic amine and stopping the reaction before the product becomes water-insoluble.

2. A process of preparing leather tanning and bleaching agents which comprises reacting at temperatures not in excess of 100° C. for not more than 5 hours phenol sulfonic acid, formaldehyde and a secondary aliphatic amine in the presence of sulfuric acid and stopping the reaction before the product becomes water-insoluble.

3. A process of preparing leather tanning and bleaching agents which comprises reacting at temperatures not in excess of 100° C. for not more than 5 hours an alkyl phenol sulfonic acid having at least one reactive ortho or para position in the nucleus, formaldehyde and a secondary aliphatic amine in the presence of sulfuric acid and stopping the reaction before the product becomes water-insoluble.

4. A process of preparing leather tanning and bleaching agents which comprises reacting at temperatures not in excess of 100° C. for not more than 5 hours butyl phenol sulfonic acid having at least one reactive ortho or para position in the nucleus, formaldehyde and a secondary aliphatic amine in the presence of sulfuric acid and stopping the reaction before the product becomes water-insoluble.

5. A process of preparing leather tanning and bleaching agents which comprises reacting at temperatures not in excess of 100° C. for not more than 5 hours tertiary butyl phenol sulfonic acid, formaldehyde and diethanolamine in the presence of sulfuric acid and stopping the reaction before the product becomes water-insoluble.

6. A process of preparing leather tanning and bleaching agents which comprises reacting at temperatures not in excess of 100° C. for not more than 5 hours tertiary butyl phenol sulfonic acid, formaldehyde and β,β'-dicyanodiethylamine in the presence of sulfuric acid and stopping the reaction before the product becomes water-insoluble.

7. A leather tanning and bleaching agent which comprises the water-soluble reaction product obtained by heating at temperatures not in excess of 100° C. for not more than 5 hours in acid media a phenol sulfonic acid having at least one reactive ortho or para position in the nucleus, an aldehyde and a secondary aliphatic amine.

8. A leather tanning and bleaching agent which comprises the water-soluble reaction product obtained by heating at temperatures not in excess of 100° C. for not more than 5 hours in acid media phenol sulfonic acid, formaldehyde and a secondary aliphatic amine.

9. A leather tanning and bleaching agent which comprises the water-soluble reaction product obtained by heating at temperatures not in excess of 100° C. for not more than 5 hours in acid media an alkyl phenol sulfonic acid having at least one reactive ortho or para position in the nucleus, formaldehyde and a secondary aliphatic amine.

10. A leather tanning and bleaching agent which comprises the water-soluble reaction product obtained by heating at temperatures not in excess of 100° C. for not more than 5 hours butyl phenol sulfonic acid having at least one reactive ortho or para position in the nucleus, formaldehyde and diethanolamine in the presence of sulfuric acid and stopping the reaction before the product becomes water-insoluble.

11. A leather tanning and bleaching agent which comprises the water-soluble reaction product obtained by heating at temperatures not in excess of 100° C. for not more than 5 hours butyl phenol sulfonic acid having at least one reactive ortho or para position in the nucleus, formaldehyde and β,β'-dicyanodiethylamine in the presence of sulfuric acid and stopping the reaction before the product becomes water-insoluble.

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